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Microstructural characterization of plasma-deposited SiO2-like thin films
a detailed study by means of ellipsometric porosimetry

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Microstructural characterization of plasma-deposited SiO$_2$-like thin films
A detailed study by means of ellipsometric porosimetry

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Abstract

The newly developed technique of ellipsometric porosimetry has been applied to plasma-deposited SiO$_2$ thin films. This technique allows obtaining the layer open porosity and is able to provide knowledge about the type and size of pores present in the film based on ethanol adsorption-desorption isotherms. The importance of this information is found in the application of SiO$_2$ films as diffusion barrier layer on polymer substrates: the performance of single layer barriers is controlled by different type and size of defects. The presented work is the first extensive study of ellipsometric porosimetry applied to plasma-deposited SiO$_2$ thin films. In this study ion bombardment has been applied during film growth and the effect on the microstructure has been investigated for different ion flux and energy conditions.

Varying the ion-to-growth flux ratio in the presence of ion bombardment has considerable effect on the microstructure of SiO$_2$-like films. This involves changes in the open porosity and a transition in the type and size of the pores. It was found that only at optimal ion-to-growth flux ratio the pores are quantitatively eliminated leading to complete film densification. At optimal growth flux conditions both an rf sinusoidal (rf) and a low-frequency pulse-shaped (p-s) bias were used to promote film densification for increasing ion energy. The densification process involves both a shift in pore size towards smaller pores as well as a decrease in the amount of open pores. The specific path towards pore elimination by either the rf or p-s bias depends on the difference in ion flux and energy available from each system.

Fourier transform IR spectroscopy measurements showed that the observed changes in microstructure are correlated to the chemical composition of the deposited SiO$_2$ films. It was found that the rf bias provides a more effective densification of SiO$_2$-like films than the p-s bias. Considering the distinct characteristics of the two biasing systems this led to conclude that the ion energy and ion-to-growth flux ratio are not interchangeable parameters in film densification. Provided that the ions possess enough energy, the densification process appears to be mainly driven by the flux ratio.

The ellipsometric porosimetry setup has also been utilized to experimentally determine the ethanol multilayer thickness on non-porous SiO$_2$ films as a function of relative pressure $p/p_0$. To gain more insight into the ethanol adsorption process two empirical models have been fitted to the data. This study has been performed to implement multilayer adsorption in the calculation of the pore size distribution. By comparing the obtained pore size distribution of a spin-coated silica film to a plasma-deposited SiO$_2$ film it was found that films of equal porosity can contain different type and size of open pores. This reveals that only the knowledge about the amount of pores is insufficient to fully characterize the microstructure of SiO$_2$ films.

In conclusion this work proves that the technique of ellipsometric porosimetry can considerably improve the understanding of the SiO$_2$ microstructure and has great potential to provide knowledge of the different type of defects present in barrier films.
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1 Introduction

1.1 Silicon dioxide-like films

1.1.1 Applications & technology

Thin silicon dioxide-like films\(^1\) are widely applied in industry due to their unique properties. These include hardness, transparency in the visible wavelength range, and dielectric properties, amongst others. The most well-known technological field of application for silicon dioxide (SiO\(_2\)) films is that of microelectronics. Here, the dielectric properties of SiO\(_2\) are for instance utilized to prevent electrical contact between adjacent interconnects, which are signal carrying wires in integrated circuits (IC). Originally, the functionality of the isolating film (a so-called interlayer) was less stringent due to the relatively large feature size of the IC’s. However, due to the continuing shrinkage of feature size together with increasing signal frequencies, power consumption and signal delay have become a mayor concern in device performance\(^{[1,2]}\). One way to provide a solution to both problems is by reducing the interconnect capacitance \(C\). This is possible by lowering the dielectric constant \(k\) of the interlayer, which can be understood from the following equation:

\[
C = \varepsilon_0 k G \tag{1.1}
\]

where \(\varepsilon_0\) is the permittivity of vacuum, and \(G\) is a circuit geometry factor.

According to literature the dielectric constant of a material can be decreased in two ways\(^{[3]}\): either by reducing the polarizability or by lowering the density. The polarizability of a SiO\(_2\) film can be reduced by the introduction of bonds that are less polar than Si-O, e.g., Si-C or Si-CH\(_3\). An advantage of Si-CH\(_3\) incorporation is that it simultaneously reduces the density of the film\(^{[4]}\). This is because the Si-CH\(_3\) group is chain terminating and also occupies a larger volume. Therefore, the density of SiO\(_2\) is lowered by introducing porosity into the film. The resulting film is designated a low-\(k\) dielectric as it has a dielectric constant which is below the one of thermal SiO\(_2\) (\(k = 4\)).

Another interesting application of SiO\(_2\)-like films is the use in combination with polymers. Polymers have the advantage of being lightweight, flexible, optically transparent, and impact resistant. However, one disadvantage of polymers is that they are highly permeable to vapors and gases. In the case of flexible packaging of consumables this results in the reduction of storage life and the loss of quality\(^{[4]}\). In the field of flexible electronics, such as flexible solar cells and displays, the permeation of oxygen and water vapor leads to device degradation\(^{[5]}\). In order to reduce the vapor diffusion rate a so-called barrier layer is deposited on the polymer. Dense SiO\(_2\)-like films are able to perform as such a barrier layer, while also providing the optical transparency needed in flexible electronics. However, beside the density of the film, here, defects that allow penetration of vapor and gas through the barrier control the ultimate barrier properties. Obviously, the defect density should be very low and ideally these SiO\(_2\)-like films may have a stoichiometry which differs from SiO\(_2\) due to carbon and hydrogen incorporation.
films should be free of pores. The challenge to achieve this is discussed into more detail in section 1.2.

Other possible applications for SiO\(_2\)-like films are in the field of optics (antireflective coatings, optical filters)\([6]\), glazing applications (scratch-resistant coatings on polymers)\([7,8]\), metal corrosion protection\([9]\), and biomedical applications\([10,11]\).

For each of the fields mentioned above, the SiO\(_2\)-like films need to have specific properties to meet the requirements imposed by the application. In this respect the deposition of the films by means of plasma enhanced chemical vapor deposition (PECVD) is an appealing approach. This is because PECVD has some major benefits in comparison to other deposition techniques, mainly physical vapor deposition (PVD) and non-plasma based CVD. Because of the ability to control plasma-chemical reactions and plasma-surface reactions the tuning of the film composition and microstructure is possible. Ways to do this are adjusting gas flows, changing the power fed into the plasma, biasing substrates for ion bombardment, varying the substrate temperature, and even using pulsed plasmas.

Moreover, the mechanical properties of PECVD grown films are generally better than those obtained with other techniques. Examples are enhanced film adhesion, less stress in the film, and better resistance to environmental influences.

Furthermore, due to the reactive nature of the plasma, growth species are already generated in the gas phase. This removes the necessity of high substrate temperatures to activate the precursor compounds. In this way PECVD allows the deposition on thermally sensitive substrates, like polymers.

Additionally, using an organosilicon-based plasma chemistry allows tuning and controlling the degree of organic to inorganic nature of the deposited film\([12]\). Besides Si-O bonds, here, the precursor also contains hydrocarbon groups. By controlling the combustion process of carbon containing groups in the plasma, the film chemical composition is modified from so-called silicone-like (SiC\(_x\)H\(_y\)O\(_z\)) to silica-like (SiO\(_x\)H\(_y\)).

Eventually, the PECVD process allows tailoring the physical and chemical properties of the deposited SiO\(_2\) film. Conceivable properties are density, dielectric constant, hardness, refractive index, surface energy, and scratch resistance\([6]\). However, in order to optimize the deposition process to obtain the properties, which are desired by the application, film characterization is of extreme importance.

1.1.2 Thin film characterization: previous research

In general the characterization of thin films is discussed in terms of chemical composition next to optical and structural properties. The chemical composition of SiO\(_2\)-like films deposited with the aid of the expanding thermal plasma (ETP) from organosilicon mixtures has been found highly tunable\([13]\). This mainly relates to the ultimate remote nature of the ETP configuration, where the plasma production is geometrically separated from the substrate region\([14]\). A detailed description of the ETP deposition technique is provided in the experimental part of this thesis (section 3.1). The tunability of the film chemical composition has been proven by several diagnostics. A
combination of ex situ infrared (IR) spectroscopy and in situ spectroscopic ellipsometry (SE) showed that the film chemistry changed from silicone-like to silica-like, depending on the amount of atomic oxygen present in the plasma\textsuperscript{13}. The atomic oxygen leads to the combustion of carbon-containing species in the plasma, which excludes these species from taking part in the growth process. Although the IR spectra showed no carbon-related features, the refractive index value obtained from the SE measurements was below the refractive index of thermally grown silica (1.46 at 633 nm). This indicates the presence of porosity in the silica-like film, which was confirmed by the presence of silanol (Si-OH) features in the IR spectra. These OH-containing groups are responsible for the termination of the silica chain which results in the incorporation of pores. However, due to the relative low sensitivity of the IR measurements the presence of carbon in the film could not be excluded. Therefore, further chemical analysis of the film was performed by means of X-ray photoelectron spectroscopy (XPS)\textsuperscript{12}. Not only did these measurements confirm the absence of carbon in the silica-like film, but also the layer stoichiometry. Thus, the low refractive index indeed points out the presence of porosity. In order to reduce the porosity of the silica-like film, the substrate temperature during deposition of different films was varied in the range 50-300 °C. An SE study, both in situ and ex situ, showed the increase of refractive index for increasing substrate temperature (FIG. 1-1). This indicates the decrease of porosity in the silica-film. Higher values of $n_{\text{ex}}$ compared to $n_{\text{in}}$ are due to the uptake of ambient water into the film, which also points out the presence of porosity. The fact that the two trends join at a substrate temperature of 300 °C indicates that this silica-like film is practically free of pores. The obtained refractive index of 1.46 confirms the absence of pores as this is the value of thermal silica. Moreover, also the hardness and Young’s modulus of the silica-like film at 300 °C were similar to thermal silica, as was shown by nano-indentation measurements\textsuperscript{12}.

To quantify the fraction of pores $f_{\text{pores}}$ in the film a so-called effective medium approximation (EMA) model was used, which is given by the following equation:

$$
\frac{f_{\text{pores}}}{n_{\text{pores}}^2} \frac{n_{\text{pores}}^2 - n_{\text{in}}^2}{n_{\text{pores}}^2 + 2n_{\text{in}}^2} + (1 - f_{\text{pores}}) \frac{n_{\text{in}}^2 - n_{\text{out}}^2}{n_{\text{in}}^2 + 2n_{\text{out}}^2} = 0
$$

(1.2)
where $n_{\text{pores}}$ is the refractive index of the pores, $n_{\text{in}}$ is the layer in situ refractive index, and $n_m$ represents the refractive index of the silica matrix (i.e. the silica network as deposited by ETP without taking into consideration the presence of porosity).

The value of $n_{\text{pores}}$ is equal to the refractive index of vacuum ($n=1$), as it is combined with the in situ obtained index values $n_{\text{in}}$ from the SE measurements. The refractive index of the silica matrix $n_m$ is unknown, but it was calculated by means of the Clausius-Mossotti relation\[^{[12]}\]. In general, a PECVD process may lead to different SiO$_2$ matrix density than the one of thermal or fused silica. Therefore, spectroscopic ellipsometry in the infrared region (800-4000 cm$^{-1}$) was performed as this allows the determination of the film matrix density $\rho_m$\[^{[12,15-19]}\]. Then the Clausius-Mossotti relation and equation (1.2) were used to obtain the pore fraction $f_{\text{pores}}$ as function of temperature (FIG. 1-2).

Thus, as was already reasoned, the porosity of the silica-like film decreases with increasing substrate temperature. A residual porosity of 5% for the film at 300 °C was determined.

Although the EMA method is able to provide the fraction of pores in silica-like films it has also some limitations. This is mainly related to the need of knowledge about the refractive index of the film matrix. In principle the calculation of the refractive index of the film matrix via the Clausius-Mossotti relation is only valid for carbon-free SiO$_2$ films. Also, the determination of the matrix density by means of infrared ellipsometric measurements is only possible for carbon-free SiO$_2$ films, because the matrix density is assumed to solely depend on the Si-O-Si bonding angle $\theta$. Thus, the EMA method is really restricted to carbon-free SiO$_2$ films.

Furthermore, by using the EMA method no information is obtained about the type of pores, e.g. open or closed. Additionally, the presence of pores with various sizes and their size distribution is also not unraveled. Thus, the EMA method does not provide insight into the microstructure of deposited films.

Therefore, for the work described in this thesis a new experimental setup was developed in order to characterize the microstructure of silica-like films. This setup combines spectroscopic ellipsometry (SE) with a system that accurately controls the partial
pressure of a solvent in the presence of a thin film. As will be explained later this allows not only the determination of porosity, but also the type and sizes of the pores which are present. Moreover, this does not depend on the chemical nature of the film.

The advantage of integrating SE with a solvent adsorption system is found in the monolayer sensitivity of ellipsometry. Due to the small dimensions of functional films the uptake of solvent from the gas phase induces only slight changes. For example, a silica-like film of ~100 nm thickness on a substrate of 1x1 cm$^2$ has only a volume of ~10^{-2} mm$^3$. As the volume of pores is even less, the uptake of solvent by the film will never be detected by means of a conventional volumetric or gravimetric method$^{[20,21]}$. The first method measures a change in pressure of a constant volume around a porous sample upon uptake, while the latter measures the change in mass of the porous sample. Ellipsometry, however, is capable of detecting extremely small changes in the optical properties of the film, even when the uptake of solvent is rather small. In literature the combination of ellipsometry with a solvent intrusion system for microstructural characterization is referred to as ellipsometric porosimetry (EP)$^{[3,22,23]}$.

## 1.2 Background of this research

As discussed in § 1.1.1 silicon dioxide-like layers are able to perform as vapor and gas diffusion barriers on polymeric substrates. The demands for the barrier performance depend on the specific application. In FIG. 1-3 the maximum allowable oxygen and water vapor transmission rates are visualized for several applications.

![FIG. 1-3 Maximum allowable water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) for several applications captioned in the graph.](image-url)

As can be seen the transmission rates which are allowed, differ in orders of magnitude depending on the application. In the case of flexible packaging for consumables a single inorganic barrier layer, e.g. aluminum oxide, silicon oxide or silicon nitride, is sufficient to reduce the permeation to acceptable levels. Important for the quality of a single barrier is the adhesion to the polymer and the presence of defects. In terms of adhesion plasma-deposited barriers perform better than when evaporated or sputtered. The
development of an interphase between polymer and inorganic film due to active species from the plasma (radicals, ions, and (V)UV photons) is held responsible for this enhanced adhesion. However, in spite of excellent adhesion the performance of a single barrier layer was found to be governed by defects in the deposited film. The influence of the number of defects (or defect density) is shown in FIG. 1-4\textsuperscript{[25]}. After unit conversion the graph shows that for an OTR of \(~10^{-5} \text{ cm}^3\text{m}^{-2}\text{day}^{-1}\text{atm}^{-1}\) the defect density should be less than 10 per mm\(^2\). However, the lowest OTR obtained on single barriers is around \(10^{-1}\) \text{ cm}^3\text{m}^{-2}\text{day}^{-1}\text{atm}^{-1}\), which indicates a defect density of approximately 100,000 mm\(^{-2}\). Other literature on single barrier performance has shown that the minimum WVTR is around \(0.5 \cdot 10^{-1} \text{ g}\cdot\text{m}^{-2}\text{day}^{-1}\)\textsuperscript{[26]}. Thus, the demands on barrier performance of flexible devices are certainly not achieved by a single barrier layer (FIG. 1-3).

The solution to this problem appears to be the application of a multi-layer system, consisting of alternated inorganic and organic layers. These systems are capable of reaching moisture permeation values as low as \(10^{-5} \text{ g}\cdot\text{m}^{-2}\text{day}^{-1}\)\textsuperscript{[26]}. Although the performance of multi-layer barriers is excellent, improvement is still necessary for use in flexible devices. Here, plasma deposition may even be more important due to the benefits of interphase formation, which now occurs at each organic-to-inorganic transition. Moreover, the possibility of effectively controlling the cross-over between inorganic and organic film deposition (§ 1.1.1) within a single PECVD setup may also lead to increased barrier performance. However, even in the case of multi-layer systems the performance of the barrier depends on the presence of defects. Evidently, the alternated structure of inorganic and organic layers affects the permeation process, but it does not prevent the creation of defects. Moreover, in the case of SiO\(_2\)-like barriers on polymer substrates, the microstructure of the film appears to be different compared to fused silica. Roberts et al.\textsuperscript{[27]} have pointed out that if a SiO\(_2\)-like film had a similar structure to silica glass without macroscopic defects, the transmission rates are expected to be lower by many orders of magnitude. They proposed that different types of pathways are present in a SiO\(_2\)-like film on a polymer substrate as shown in FIG. 1-5.
**Introduction**

**FIG. 1-5** A schematic showing the proposed pathways through a SiO$_2$-like barrier on polymer substrates.

The above reasoning shows that it is crucial to obtain more detailed information about the microstructure of SiO$_2$-like films on polymers. Especially, knowledge about the pore size distribution (PSD) in order to quantify the different types of defects is necessary. In this respect the aforementioned technique of ellipsometric porosimetry is expected to provide this information.

### 1.3 Goal and approach

The newly developed ellipsometric porosimetry setup is used for the first time in the combination with plasma-deposited films. In particular for the analysis of thin SiO$_2$-like films deposited in a remote plasma configuration on silica substrates. As earlier addressed, the substrate temperature is a parameter which influences the porosity of the deposited film. However, in this work the influence of ion bombardment is used to promote film densification at low substrate temperature. This is achieved by means of substrate biasing using two distinct techniques, i.e. an rf sinusoidal bias and a low-frequency pulsed-shaped bias. Also the influence of the radical growth flux arriving at the substrate is tuned in order to affect the porosity content of SiO$_2$-like films.

In detail the following research questions were addressed:

- Is ellipsometric porosimetry sensitive in detecting the porosity of thin (100 nm) plasma-deposited SiO$_2$ films on silica substrates using ethanol as probing solvent?
- Does ellipsometric porosimetry allow to obtain additional information about the microstructure of SiO$_2$-like films, compared to other (common) diagnostics, such as spectroscopic ellipsometry and Fourier transform IR spectroscopy?
- What is the influence of radical growth flux on the microstructure of SiO$_2$-like films?
- How is the microstructure of SiO$_2$-like films affected under different ion-to-growth flux and ion energy conditions? How does the densification process develop as function of these parameters?
1.4 Outline of this thesis

The thesis is structured as follows. Chapter 2 presents the theoretical basis subdivided in four main sections. The first section describes the principle of spectroscopic ellipsometry (SE) and the construction of the optical model for data analysis. The subsequent section deals with the general concepts of porosimetry with a focus on the principles of adsorption, interpretation of adsorption data, and the assessment of pore size distribution. The third section discusses the combination of SE and gas phase adsorption, i.e. ellipsometric porosimetry. In the fourth section the concepts of substrate biasing are provided, with highlights on the influence of ion bombardment on the microstructure of SiO₂ films.

In Chapter 3 the two experimental setups used in this work are described. The several components of the expanding thermal plasma (ETP) setup for the deposition of SiO₂-like films are described, in particular the two distinct substrate biasing systems. Next, the newly developed ellipsometric porosimetry (EP) setup is described in detail. Also the experimental procedure and setup calibration are discussed. The experimental chapter ends with an overview of complementary diagnostics for thin film characterization.

Chapter 4 presents the experimentally obtained results and a discussion is provided. The influence of the radical growth flux on the microstructural properties of plasma-deposited SiO₂-like films is given. Subsequently, the influence of ion bombardment on the film microstructure is discussed for series obtained using the two distinct bias systems. The second part of Chapter 4 provides a discussion about multilayer adsorption of ethanol. This results in the determination of the ethanol multilayer thickness on non-porous SiO₂-like films, both experimentally and using two empirical models. Using this information for the calculation of pore size distribution, first results are shown and discussed.

Finally, in Chapter 5 the conclusions of the work will be provided and recommendations for future work will be given.
2 Theory

2.1 Spectroscopic Ellipsometry

2.1.1 Principle

Ellipsometry measures the change of light polarization upon reflection on the surface of a sample (FIG. 2-1). The polarization state of an electromagnetic wave is determined by the orientation of the electric field. In ellipsometry the orientation of the electric field is described by components in the direction parallel and perpendicular to the plane of incidence. By convention these electric field components are then present in the $p$- and $s$-direction, respectively. The polarization state of the light beam is defined by the phase difference between the $p$- and $s$-direction and the amplitude of each term.

![Schematic representation of a light beam reflecting on a sample](image)

FIG. 2-1 A schematic representation of a light beam reflecting on a sample with an angle of incidence $\Phi_0$. The polarization change upon reflection of the p- and s-polarized light components is also indicated.

When light with a known polarization state reflects on a sample, the polarization is changed due to the interaction with the sample. The change depends on the thickness of the layers composing the sample and the dielectric function of each one of them. Thus, by measuring the change in polarization, information can be extracted on the layers dielectric function and thickness by means of an appropriate optical model. The fundamental equation of ellipsometry, which relates the total Fresnel reflection coefficients $R_p$ and $R_s$ to the ellipsometric angles $\Delta$ and $\Psi$, is given by

$$ \tilde{\rho} = \frac{R_p}{R_s} = \tan(\Psi) e^{i\Delta} $$  \hspace{1cm} (2.1)

where $\tilde{\rho}$ is the complex ellipsometric parameter expressing the polarization change.

The parameter $\Delta$ is defined as the change in phase difference that occurs upon reflection and as such it can have a value between 0 and 360°. The ratio of the magnitude of the
total reflection coefficients is defined as the tangent of $\Psi$. Therefore, the value of $\Psi$ is in the range $0$ to $180^\circ$.

Equation (2.1) shows that ellipsometry measures a ratio between properties of the incident and reflected beams and does not depend on absolute values. Therefore, ellipsometry is independent of background light and fluctuations in the light source of the ellipsometer. This makes ellipsometry very accurate and reproducible. Because $\rho$ is a complex number, phase information is also acquired and, therefore, ellipsometry is highly sensitive.

Spectroscopic ellipsometry (SE) uses a light source covering a broad spectral range, generally spacing from UV to near IR (193-1600 nm). In this way the value of $\Delta$ and $\Psi$ are determined as a function of wavelength to generate curves of $\Delta=\Delta(\lambda)$ and $\Psi=\Psi(\lambda)$. The main advantage of spectroscopic ellipsometry is that the dispersions of the dielectric properties of the sample can be determined. This allows for the analyses of complex structures such as multilayers, inhomogeneous layers, anisotropic layers, and interface roughness.

The choice of the angle of incidence $\Phi_0$ is important for the sensitivity of an ellipsometry measurement (FIG. 2-1). At the so-called Brewster angle the reflection of $p$-polarized light is close to zero. As a consequence the value of $\Delta$ drops from 180 to 0 around this angle. Also the value of $\Psi$ shows a sharp bending at the Brewster angle. Therefore the sensitivity is highest when the angle of incidence is around the Brewster angle. In this research a value close to the Brewster angle of the silicon-air interface (~76°) has been chosen, because all deposition where performed on c-Si substrates. An angle of 75° is used for ex situ measurements. The angle for in situ measurements depends on the setup and is given in the corresponding experimental section in Chapter 3.

Further information on SE can be found in literature\cite{28}.

2.1.2 Optical model

The information on the polarization change contained in $\Delta$ and $\Psi$ cannot be used to directly derive the dielectric function and thickness of a deposited layer. Therefore, an optical model of the layer stack needs to be built up. Each layer in the model is parameterized according to specific dispersion relationships used to describe a dielectric, semiconductor, or metal-like behavior. Often the dispersion relationship of the substrate is known and tabulated. Therefore, only the one related to the deposited layers needs to be determined, together with the thickness, if the layer is sufficiently transparent (i.e. both interfaces air/layer and layer/substrate are probed by the beam). By assuming some initial values for the parameters of the model an approximation of the data can be calculated. The experimental data is then compared to this calculated data and the deviation is determined by means of a mean-squared error (MSE) calculation. The calculated data is fitted to the experimental data using a Levenberg-Marquardt algorithm to minimize the MSE.

As mentioned above, crystalline silicon is used as a substrate for the deposition of SiO$_2$-like layers. Due to contact with the ambient a surface film of native oxide will be present
on the silicon. Therefore, the model will consist of a thin layer of native oxide (≈2 nm) on top of a semi-infinite (no back reflections due to unpolished backside) silicon substrate (FIG. 2-2a). The complete optical dispersions of silicon and native oxide are tabulated, so only the thickness of the native oxide is a fit parameter, in order to fully characterize the substrate. Because the c-Si tabulated dispersion relationship may not fully reproduce the silicon substrate, a point-to-point fit procedure is performed, which consists of a direct fit of each experimental data point.

The plasma-deposited SiO$_2$ film is modeled as a layer of finite thickness on top of a semi-infinite substrate (FIG. 2-2b). The dielectric function of SiO$_2$ is approximated by the Cauchy dispersion formula:

$$n(\lambda) = \sum_{i} \frac{C_i}{\lambda^i}, \quad i \in \mathbb{Z}^+$$  

(2.2)

where $n$ is the refractive index, $\lambda$ is wavelength, and $C_i$ are the Cauchy dispersion coefficients. The use of the Cauchy approximation is valid because SiO$_2$ is a transparent dielectric material with a zero extinction coefficient within the wavelength range of the ellipsometer, due to a bandgap of $\approx 8.9$ eV$^{[9]}$. The fit parameters are, therefore, the SiO$_2$ film thickness and the Cauchy coefficients $C_0$ and $C_1$. All other coefficients $C_i$ with $i > 1$ are neglected, as their use does not further improve the quality of the fit. After the fitting procedure, the film thickness and the refractive index of the deposited SiO$_2$ are extracted from the model. All refractive index values mentioned in this thesis are reported at a wavelength of 633 nm, to be able to compare with values reported in literature.

As described in § 1.1.2 of Chapter 1, ellipsometry is also employed for the layer porosity determination: the ellipsometric tool is then coupled to a vacuum chamber where adsorption and desorption studies of a solvent vapor into the pores present in the layer are performed. Details concerning the optical model employed in this latter case will be given in section 2.3. As will be explained in the next section this also allows to acquire information about the type and size of pores present in the layer.
2.2 Porosimetry

2.2.1 Adsorption in pores

In porosimetry the amount of (open) pores, pore volume, and the pore size distribution of a porous material (or adsorbent) are determined by means of adsorption and desorption studies of a so-called adsorptive (e.g. vapor/gas) within the pores of a porous solid. The process of adsorption would then correspond to an increase in concentration of the adsorptive at the interface between a solid adsorbent and the vapor phase. The reverse process is called desorption. Once the adsorption has taken place, the adsorptive is defined as the adsorbate.

The porosity in a solid is defined as the ratio between the volume of pores and the total volume occupied by the solid. As can be seen in FIG. 2-3 a porous solid can have different kinds of porosity. Open porosity consists of all the pores that are connected to the surface of the solid, i.e. in contact with environment. On the other side, all pores that are totally enclosed by solid material give rise to closed porosity. Together they contribute to the total porosity of the solid.

![FIG. 2-3 Cross-section of a hypothetical porous solid showing various types of pores: closed (C) and open (O). The pores can have different shape and size.](image)

Techniques to determine the porosity of a porous solid usually are based on a mechanism, which involves the adsorption of a vapor or gas inside the pores. This means that these techniques are only able to measure open porosity.

The adsorption in porosimetry techniques is physisorption (physical adsorption) in which the interaction of the adsorptive molecules with the surface is due to intermolecular forces, namely Van der Waals forces. Ideally, this interaction does not involve the formation of chemical bonds, as in chemisorption and, therefore, is a reversible process.

The molecular interactions consist of a balance between both attractive and repulsive forces. Independently on the nature of the adsorbent and adsorptive, close-range electronic repulsions occur, due to overlap of the electron clouds, as well as attractive dispersion interactions. The dispersion interactions originate from rapid fluctuations in electron density in one atom, which then induces an electrical moment in neighboring...
atoms\textsuperscript{[20]}. Other types of interactions are, for example, electrostatic interactions between charges, which do depend on the nature of both adsorbate and adsorptive.

A simplified representation of the total interaction experienced by the adsorbate molecules and the adsorbing surface for physisorption is given by a Lennard-Jones-like potential as shown in FIG. 2-4.

The shape of the potential shows that by interacting with the surface the adsorbate molecule is able to obtain a state of minimum energy, which is, therefore, a favorable process and results in a bound state at a distance $z_e$ from the surface. The enthalpy of adsorption typically associated with this state is in the order of 0.2 eV\textsuperscript{[30]}. From FIG. 2-4 it can also be understood that on a plane surface the molecules will usually adsorb directly on free surface sites. This is because as soon as molecules adsorb at top of each other they energetically deviate from the potential minimum. Moreover, the adsorbate-adsorbate interaction is typically less strong. Therefore, adsorption on a plane surface usually occurs via layer-by-layer coverage.

The adsorbed amount depends on the temperature $T$ of the solid adsorbent, the pressure $p$ of the adsorptive vapor, and both the nature of the solid and the gas. Therefore, when the sample is maintained at constant temperature, and in the case of a specific solid and adsorptive, the adsorbed amount is only a function of the pressure:

$$n = f \left( \frac{p}{p_0} \right)_{T, \text{gas, solid}}$$

where $n$ is the amount of vapor adsorbed (e.g. mol·gram$^{-1}$), and $p_0$ is the vapor saturation pressure of the adsorptive. Equation (2.3) is called an adsorption isotherm.

The adsorption process for increasing relative pressure $p/p_0$ can be studied at different stages depending on the nature of the pores. On the basis of their dimensions, pores can be subdivided in three classes\textsuperscript{[31]}.

- **micropores**: pore width less than 2 nm
- **mesopores**: pore width in between 2 to 50 nm
- **macropores**: pore width larger than 50 nm
Theory

However, often pores characterized by different dimensions do co-exist in the same sample and usually they are found to be intermixed. The physisorption process in the presence of porosity depends on the type of pores as will be discussed below. Thus, by studying the physisorption process on a porous solid, information may be obtained about the specific microstructure of the material.

At very low relative pressures physisorption in micropores takes place by means of volume filling, which is different from layer-by-layer coverage. The process of volume filling can be thought of as the adsorption of a first monolayer in an aperture of dimensions in the order of the molecular size. In literature\cite{32} it is shown that micropore filling might be a one-stage or two-stage process depending on the micropore size. For micropores which cannot accommodate more than two layers of adsorbed molecules, primary micropore filling occurs due to an increase in adsorption energy. This increased interaction depends on both the ratio of pore width to the adsorbate molecular diameter and the pore shape\cite{20,21}. As can be seen in FIG. 2-5 this increased adsorption energy is due to an enhanced interaction potential compared to the potential present at a freely exposed plane surface.

This is the result of an increasing overlap of the potential field from the wall on each side of the pore\cite{21}. This effect is the reason why already at very low relative pressure complete pore filling occurs in micropores of very small size.

However, micropores which are characterized by larger dimensions do not benefit from an increased interaction potential and, therefore, their filling begins to take place at slightly higher pressure. In this situation first partial monolayer adsorption takes place at the walls of the pores. As soon as some molecules come close enough to induce adsorbate-adsorbate interaction, secondary micropore filling occurs due to increased adsorption probability. The difference between primary and secondary micropore filling is shown in FIG. 2-6.
In mesopores and macropores the filling mechanism is quite different from micropore filling. At low relative pressure first monolayer adsorption at the walls of mesopores occurs. During monolayer adsorption, adsorptive molecules stick directly to the pore surface layer on available sites. When the pressure increases, more and more surface sites are occupied and eventually a complete monolayer is formed. At a certain pressure also multilayer adsorption will start. Multilayer adsorption is a process where the adsorptive molecules stick on top of already adsorbed layers, which means that adsorbate-adsorbate interactions become more dominant. However, multilayer adsorption might already begin before monolayer adsorption is completely finished. This depends on the nature of the adsorbent and adsorbate. In the case of strong adsorbent-adsorbate interaction, first all available surface sites are occupied before multilayer adsorption starts. In the reverse situation, i.e. weak adsorbent-adsorbate interaction, monolayer formation occurs only on surface sites with the highest adsorption probability. As soon as a molecule has been adsorbed, other adsorbate molecules prefer to stick on the present adsorbate sites. This leads to multilayer cluster formation and, therefore, full monolayer coverage will only occur for high relative pressures, i.e. $p/p_0 \to 1$. Of course, intermediate situations are experimentally found.

Subsequent to monolayer–multilayer adsorption, a typical pore filling mechanism for mesopores is that of capillary condensation. In capillary condensation a phase transition of the adsorptive from gas to liquid occurs at pressures below the saturation pressure. This is due to the formation of a meniscus between the adsorptive vapor and the molecules adsorbed during multilayer adsorption (FIG. 2.7). The formation occurs because molecules can reach states of lower energy the closer they are to the pore surface. Therefore, molecules adsorbed at multilayer sites have a tendency to migrate towards less occupied sites on the surface. This migration has the effect of curving the surface of the liquid, which is defined as a meniscus.
According to the Young-Laplace equation\cite{20,21} the pressure, $p^\ast$, at the concave side of the meniscus is higher than the pressure, $p^\prime$, at the convex side.

\begin{equation}
    p^\ast - p^\prime = \frac{2\gamma}{r_m}
\end{equation}

where $r_m$ is the mean radius of curvature, and $\gamma$ is the surface tension. This means that the equilibrium vapor pressure over a concave meniscus of liquid is less than the saturation vapor pressure. Therefore, condensation in pores will occur below saturation pressure. Also, equation (2.4) shows that the pressure difference is inversely proportional to the radius of curvature. This implies that the onset of capillary condensation starts in the smallest pores and evolves in larger pores for higher relative pressure. As soon as capillary condensation in a pore starts, the pore becomes filled with liquid for increasing values of relative pressure.

The above discussions show that the pores are always filled from the smallest dimensions to the largest. Therefore, studying the physisorption process as function of relative pressure allows to distinguish between the presence of different size of pores.

### 2.2.2 Classification of isotherm shape and hysteresis loops

When plotting a graph of the amount adsorbed as a function of the relative pressure $p/p_0$ an isotherm behavior will be found depending on the microstructure of the adsorbent and the interaction with the adsorbate. According to the IUPAC classification\cite{31} six characteristic shapes of physisorption isotherms can be identified (FIG. 2-8). The six types are each related to porous solids having a specific type of microstructure. Therefore, for a given porous solid, the classification can be used to obtain information about the microstructure.

The type I isotherm is characterized by a steep rise at low relative pressure associated with micropore filling. For higher pressures a plateau is reached indicating a relatively small amount of multilayer adsorption on the outer surface. If the plateau is reached at relatively low relative pressure, then only primary micropore filling occurs. Both primary and secondary micropore filling are present in the case of a plateau reached at relatively
higher pressure values. This isotherm is most common for microporous solids with a small external surface compared to the total internal pore surface\cite{31}.

At low relative pressures the isotherm of type II shows a quick rise towards an inflection point. However, no plateau is reached for further increase of pressure after this point. This isotherm shape is associated with unrestricted monolayer and multilayer adsorption on an open external surface\cite{20}. Correspondingly, this means that solids exhibiting this feature are either non-porous or macroporous. Whenever the inflection point (B) is well defined, monolayer adsorption fully develops before multilayer adsorption takes place. In the case of a less defined inflection point (B) multilayer adsorption will already start before monolayer adsorption is complete. However, in general, point B is taken to indicate the completion of the monolayer. Therefore, point B is associated with the monolayer capacity of the adsorbent.

A type IV isotherm has the same shape as a type II isotherm for low relative pressure, including the inflection point. However, at higher pressure a sudden rise occurs and finally the isotherm bends towards a plateau. A common feature of the type IV isotherm is the hysteresis loop, arising due to differences in adsorption and desorption. The reason for this difference to occur is explained in § 2.2.3. According to F. Rouquerol et al.\cite{20} this hysteresis loop is an indication for capillary condensation taking place. From § 2.2.1 it follows that porous solids showing a type IV isotherm are, therefore, mesoporous.

Both type III and V isotherms are rarely observed. They actually indicate that adsorbate-adsorbate interaction dominates over adsorbate-adsorbent\cite{20}. This leads to cluster formation and incomplete monolayer coverage as discussed in § 2.2.1. The type III isotherm is usually obtained on non-porous and macroporous materials. The hysteresis loop in the type V isotherm is associated with a difference between capillary pore filling
and emptying. Thus, a type V isotherm indicates adsorption in mesoporous solids, which sometimes also contain micropores\[^{21}\].

The shape of a type VI isotherm is due to stepwise layer-by-layer adsorption. This type is extremely rare and associated with adsorption of non-polar molecules on uniform surfaces\[^{20}\].

 Practically, experimental isotherms may exhibit features, which need to be classified according to more than one type.

As already mentioned, some isotherm types show hysteresis. The hysteresis loops exhibit various shapes and the most common are defined according to the IUPAC classification (FIG. 2-9). The four types are associated with specific pore structures. Therefore, the classification can be used to give information about the pore structure of a given adsorbent.

\[
\text{FIG. 2-9 The IUPAC classification of hysteresis loops} \ [^{31}].
\]

The type H1 loop is associated with a narrow distribution of uniform pores\[^{33}\]. This means that all pores have approximately the same pore shape and size. Therefore, the capillary condensation process starts at the same relative pressure for all pores. The amount adsorbed thus increases sharply over only a small pressure range. Hysteresis loops of type H2 represent porous solids having a complex interconnected network of pores\[^{33}\]. As a result the pores have a large range of size and shape. This also explains the more gradual increase of amount adsorbed, as the on take of capillary condensation starts at higher pressures for larger pores. Both type H1 and H2 loops are characterized by having a plateau at high relative pressure.
The type H3 and H4 hysteresis loops are both common to slit-shaped pores\[20\]. Here type H3 represents mainly adsorption in mesopores. However, the type H4 loop indicates that next to capillary condensation in mesopores, a substantial amount of adsorption takes place in micropores\[20\]. The first part of the type H4 loop indeed represents the shape of a type I isotherm (FIG. 2·8). Both isotherms do not show a plateau and the upper branch of the hysteresis loop only meets the lower branch for high relative pressure, i.e. \( p/p_0 \rightarrow 1 \).

All types of hysteresis loops may exhibit so-called low pressure hysteresis, which is indicated by the dotted lines in FIG. 2·9. This phenomenon is explained in the following section.

2.2.3 Hysteresis

The reason for the occurrence of high pressure hysteresis, as in type IV and V isotherms, is related to the process of capillary condensation. Therefore, high pressure hysteresis only occurs in mesoporous materials. This type of hysteresis may be explained by looking at the difference in capillary condensation between adsorption and desorption. As explained in § 2.2.1 the driving force behind capillary condensation is the pressure difference over the meniscus as described by equation (2.4). The mean radius of curvature \( r_m \) depends on the shape of the meniscus and is defined as:

\[
\frac{2}{r_m} = \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]  

(2.5)

where \( r_1 \) and \( r_2 \) are the principle radii of the meniscus. These radii of curvature are defined by taking two planes at right angles to each other, and each of them passes through a normal vector from a point on the meniscus \[4\]. When assuming capillary condensation taking place in a cylindrical pore the principal radii can be identified for both adsorption and desorption.

During adsorption the pores are initially empty, and the meniscus is characterized by a cylindrical shape (FIG. 2·10a). Here one plane containing the normal vector cuts the pore in a radial direction and, therefore, \( r_1 = r \). The other plane, which contains the normal vector, cuts the pore along its axis which implies that the principle radius \( r_2 = \infty \). From equation (2.5) it follows for the mean radius \( r_m \):

\[
r_m = 2r
\]  

(2.6)

FIG. 2-10 Ilustration of the meniscus in a cylindrical pore during (a) adsorption and (b) desorption.

However, during desorption, which starts when all pores are filled, the meniscus is characterized by a hemispherical shape (FIG. 2·10b). In this case two perpendicular
planes containing the normal vector cut the pore along its axis. Now, one principle radius points to the surface of the pore and the other towards the meniscus along the pore axis. This implies that \( r_1 = r_2 = r \) and using equation (2.5) the mean radius \( r_m \) becomes:

\[
 r_m = r
\]  

By recalling equation (2.4) in § 2.2.1, this leads to conclude that the pressure difference over the meniscus during desorption is larger than for desorption. This means that during desorption the condensate is stable for lower relative pressure compared to adsorption. As a result the amount adsorbed during capillary condensation is higher for desorption than for adsorption at the same relative pressure. This explains why isotherms for mesoporous materials usually exhibit high pressure hysteresis.

In some systems also low pressure hysteresis occurs, which is indicated by the dotted lines in FIG. 2-9. This kind of hysteresis may be attributed to both physical and chemical processes. Physically the adsorbate is able to locally modify the network of the adsorbent by distortion of specific chemical bonds \([31] \). This leads to the alteration of size and shape of pores and the opening of cavities previously inaccessible to adsorbate molecules. During the desorption process, the adsorbed molecules may be trapped inside the pore due to relaxation of the adsorbent structure.

Besides physical distortion also an irreversible chemical reaction between adsorbate and adsorbent might occur\([31] \). This shows that the adsorption processes in porosimetry are not always purely based on physisorption, and that also chemisorption can take place. Both effects result in an increased amount adsorbed during desorption compared to adsorption. Low pressure hysteresis may continue down to the lowest attainable pressures. To remove the residual adsorbed amount at zero relative pressure, the sample needs to be degassed at elevated temperature.

### 2.2.4 Pore Size Distribution

The pore size distribution can be determined from experimentally obtained adsorption-desorption isotherms. In the case of capillary condensation in mesopores this is usually carried out on the basis of the Kelvin equation. This equation relates the mean radius of the meniscus \( r_k \) to the relative pressure \( p/p_0 \) of the adsorptive in the following way:

\[
 \frac{2}{r_k} = -\frac{RT}{\gamma \nu L \cos(\theta)} \ln\left(\frac{p}{p_0}\right)
\]  

where \( R \) is the universal gas constant, \( T \) the absolute temperature in Kelvin, \( \gamma \) and \( \nu \) the surface tension and molar volume of the bulk liquid, and \( \theta \) the wetting angle at the condensation interface.

To be able to calculate the actual pore size the Kelvin radius \( r_k \) has to be related to the radius of the pore \( r_p \). However, this does depend on the form of the meniscus and, therefore, an assumption has to be made about the pore shape. Also, next to capillary condensation a multilayer of adsorbate is already present on the pore walls, limiting the
adsorption space for capillary condensation. In the case of desorption from cylindrical pores the meniscus has a hemispherical form (FIG. 2-11).

Then the relation between the Kelvin radius and the pore radius is given by:

\[
r_p = f \left( \frac{p}{p_0} \right) = r_k + t
\]

(2.9)

where \( t \) is the pre-adsorbed multilayer thickness depending on the relative pressure. Moreover, due to this adsorbed layer the wetting angle at the condensation interface is usually assumed to be zero and the cosine term in equation (2.8) becomes unity.

The multilayer thickness can be determined by performing adsorption experiments on a non-porous sample, which has the same properties as the porous material to be analyzed. One way to extract the thickness from the experiment is by using a modified form of the BET equation\textsuperscript{3,20} after Brunauer, Emmett and Teller. This equation relates the relative pressure \( p/p_0 \) to the multilayer thickness \( t \) as follows:

\[
t = \frac{t_0 \cdot c \cdot k \cdot \frac{P}{P_0}}{\left[ 1 - k \cdot \frac{P}{P_0} \right] \left( 1 + (c - 1) \cdot k \cdot \frac{P}{P_0} \right)}
\]

(2.10)

where \( t_0 \) is the monolayer thickness, \( c \) is the BET constant, and \( k \) is a parameter with a value less than unity. The parameter \( k \) is introduced to satisfy the requirement that the multilayer thickness has to remain finite (\( t \leq 5-6 \) monolayers) at saturation pressure\textsuperscript{21}.

Another general method to extract the multilayer thickness which is widely applied is the Frenkel-Halsey-Hill equation\textsuperscript{21}:

\[
t = t_0 \left( a \cdot \ln \left( \frac{P}{P_0} \right) \right)^{1/4}
\]

(2.11)

where \( s \) is a parameter accounting for dispersion interactions, and \( a \) is a constant for a given gas-solid system.
However, the explicit values for the parameters in equation (2.10) and (2.11) are only available for nitrogen systems and have to be regarded as empirical. Therefore, both equations are difficult to use for the determination of the multilayer thickness in case of ethanol adsorption used in this work. The unknown parameters should than be obtained by fitting the empirical models to experimental thickness data. In this research ellipsometry has been utilized in order to experimentally obtain the ethanol multilayer thickness. This approach is explained in more detail in the following section (§ 2.3.2).

A more sophisticated approach to obtain a relation between the pore radius and the Kelvin radius (or core radius) has been performed by Broekhoff and De Boer (BDB). The BDB theory provides a combined derivation of the multilayer thickness and the pore radius. In defining the theory two important concepts need to be considered. One is that during adsorption, before condensation occurs, there are two interfaces present, i.e. solid-liquid and liquid-vapor, and not only solid-liquid. Secondly, the effect on the adsorption forces of the interfacial curvature of the interface between liquid and vapor needs to be taken into account. This results in a set of two equations, which needs to be solved simultaneously to extract the pore radius $r_p$:

$$r_p - t = \frac{-2\gamma \nu_l}{RT \ln(p/p_0)} + \frac{\int_{t}^{\infty} -2(r_p - t) F(t) dt}{(r_p - t) RT \ln(p/p_0)}$$  \hspace{1cm} (2.12a)

$$r_p - t = \frac{\gamma \nu_l}{RT \ln(p/p_0)} F(t)$$  \hspace{1cm} (2.12b)

where $F(t)$ is a function accounting for the difference in chemical potential between the bulk liquid and the adsorbed multilayer. The first term on the right in equation (2.12a) is actually the Kelvin equation, and the second term is a correction due to the considerations mentioned above. However, again the explicit dependence of $F(t)$ on the multilayer thickness $t$ is known only for nitrogen adsorption. More information on the Broekhoff and De Boer method can be found in literature\textsuperscript{[34-36]}.

A limit of using the Kelvin equation is the necessary assumption on the pore shape to be able to relate the Kelvin radius to the pore radius. Usually the exact pore shape of a porous material is unknown and may even consist of a mixture of shapes. Furthermore, the Kelvin equation is based on classical thermodynamics\textsuperscript{[20,21]} and has been derived originally for macroscopic systems. So, when a liquid is confined in narrow pores, there are some effects that need to be considered.

First of all the molar volume and surface tension might deviate from that of the bulk liquid. In literature the attention is merely focused on the surface tension. The reason for this is that the surface tension explicitly depends on the radius of curvature of the meniscus\textsuperscript{[21]}. The effect of the curvature on surface tension for a hemispherical meniscus form is given by the Gibbs-Tolman-Koenig-Buff equation\textsuperscript{[36]}:

$$\gamma(r_m) = \gamma_{bulk} \cdot (1 - \frac{2\delta}{r_m})$$  \hspace{1cm} (2.13)
where $\gamma r_m / \delta$ is the surface tension on a meniscus with curvature $r_m$, and $\delta$ is the thickness of the interfacial region. The thickness $\delta$ of this interfacial layer is assumed to be about one monolayer of the adsorbate in question. For ethanol this means that the interfacial region will have a thickness of 0.35 to 0.55 nm (TABLE 3-3).

The dependence of surface tension on meniscus radius is used to correct the radius of curvature predicted by the Kelvin equation. This is achieved by replacing the bulk surface tension in equation (2.8) by the expression in equation (2.13). In FIG. 2-12 the calculated meniscus curvature for ethanol is shown, with and without the correction for surface tension.

As can be seen a substantial deviation occurs for meniscus radius below 10 nm. This is an indication that for mesopores in the lower range of 2-10 nm, the calculated pore radius is too low. Of course the above correction should be taken into account when determining the pore size distribution.

Next to the deviation from bulk properties the Kelvin equation does also fail to account for the interaction potential at the pore walls. One effect is that the curvature of the meniscus is not constant throughout the pore. This means that the radius of curvature in the vicinity of the pore wall is larger, compared to the radius in the middle of a pore where the wall effect is negligible. Another effect is contained in the derivation of the Kelvin equation from a difference in chemical potential between liquid and vapor. Normally this difference is entirely attributed to the Young-Laplace pressure drop over the meniscus. However, near the pore wall the interaction potential should also be taken into account\(^{[20]}\). Because the difference in chemical potential is constant, the contribution from capillary condensation must then be reduced. This means that capillary condensation will commence for higher relative pressure. Of course these effects become more pronounced the smaller the dimensions of the pores are.
Without the above-mentioned effects taken into account, equation (2.8) probably underestimates the meniscus radius. Moreover, the determination of pore size will become unreliable for pores below pore size of about 7 nm, as discussed in literature[^20,^36].

In micropores, having widths of only a few molecular diameters, the concepts of a meniscus and capillary condensation are meaningless. Therefore, the application of the Kelvin equation is no longer valid. Based on literature, the determination of micropore properties from vapor adsorption can be divided in three categories: adsorption potential theories, graphical methods, and computer modeling.

Several semi-empirical methods to determine the volume adsorbed during micropore filling are based on the Polanyi adsorption potential:

\[
A = RT \ln \left( \frac{p_0}{p} \right)
\]  

(2.14)

where \(A\) is defined as the differential free energy of adsorption[^21].

One of the first semi-empirical relations between the adsorption potential and the adsorbate volume is the Dubinin-Radushkevich (DR) isotherm equation:

\[
\Theta = \exp \left[ -\left( \frac{A}{\beta E_0} \right)^2 \right]
\]  

(2.15)

where \(\Theta\) is the degree of micropore filling, \(\beta\) is the affinity coefficient of the adsorptive, and \(E_0\) is the characteristic energy of adsorption.

The degree of micropore filling \(\Theta\) is defined as the ratio between the total micropore volume \(V_0\) and the volume adsorbed \(V\) at a certain relative pressure \(p/p_0\). Both the value of \(V_0\) and the factor \(\beta E_0\) can be determined by plotting the logarithm of \(V\) versus \(A^2\).

So, with the aid of equation (2.15) the total micropore volume in a microporous solid can be obtained. Furthermore, based on experimental evidence[^20], a relation exists between micropore radius \(r\) and the energy \(E_0\):

\[
r = \frac{2K}{E_0}
\]  

(2.16)

where \(K\) is an empirical constant with dimension of J·mol\(^{-1}\). However, because only \(\beta E_0\) is a known factor, the determination of absolute micropore radius using equation (2.16) is difficult. To obtain absolute values the coefficient \(\beta\) needs to be determined by a separate calibration experiment. In any case, a comparison between various samples is possible, because \(\beta\) is only dependent on the adsorptive.

A discrepancy of the DR equation is that only primary micropore filling is well described. To overcome this problem, a more general relation has to be used, known as the Dubinin-Astakhov (DA) isotherm equation:

\[
\Theta = \exp \left[ -\left( \frac{A}{\beta E_0} \right)^n \right]
\]  

(2.17)

where \(n \leq 3\) is a structural heterogeneity parameter, determining the adsorption mechanism described by the DA equation. This means that by changing the value of \(n\),
equation (2.17) is able to describe the process of primary, secondary or both types of micropore filling\(^{[37]}\).

More advanced isotherm equations can be found in literature\(^{[20,37,38]}\).

Another concept of isotherm analyses is by means of a graphical method. The several methods available all have in common that a certain reference isotherm is used to detect deviation in an isotherm under investigation. Usually, the reference isotherm is obtained at a non-porous sample, which has the same properties as the one expecting to contain pores. Moreover, these techniques are not only applicable for micropore analyses, but they are often used to detect the presence of micropores.

A technique which is valid for any adsorptive, is the construction of a so-called \(\alpha_s\)-plot. This means that the amount adsorbed \(n\) is plotted as a function of the variable \(\alpha_s\), instead of versus the relative pressure \(p/p_0\). The variable \(\alpha_s\) is defined as follows\(^{[20,21]}\):

\[
\alpha_s = n / n_s = f\left(\frac{p}{p_0}\right)
\]

(2.18)

where \(n_s\) is the reference amount adsorbed at a certain relative pressure \(p/p_0\). This amount should be chosen outside the range of both micropore filling and capillary condensation. For ethanol, used in this study, a relative pressure of ~0.3 satisfies this requirement.

An idealized \(\alpha_s\)-plot of two different microporous materials is shown in FIG. 2-13. The bending of the curves for lower values of \(\alpha_s\) is an indication for the presence of microporosity. Trend (a) is associated with primary micropore filling, whereas trend (b) is due to secondary micropore filling. The level of intersection at the adsorption axis of trend (a) shows the effect of enhanced adsorption for primary micropore filling. Conversely, the fact that trend (b) passes through the origin shows that first monolayer adsorption takes place in larger micropores.

FIG. 2-13 Showing idealized \(\alpha_s\)-plots of two different microporous materials: (a) primary micropore filling present, (b) secondary micropore filling present.

The linear trend for higher values of \(\alpha_s\) is attributed to multilayer adsorption on the external surface of the microporous material. Therefore, the effective micropore volume
The concepts explained above can provide important information about the micropore properties of a sample. However, in this work they have not been further addressed, and, therefore, should be regarded as additional information, which may be beneficial for future research.
2.3 Ellipsometric Porosimetry

Ellipsometric porosimetry is a technique in which porosimetry is combined with ellipsometry. During the porosimetry experiments a film of SiO$_2$ deposited on a silicon substrate is exposed to a solvent vapor. The ability of the film to adsorb the solvent vapor induces a change in its refractive index. This change in refractive index is monitored \textit{in situ} by spectroscopic ellipsometry. As mentioned before the solvent used in this research is ethanol, which has been mainly chosen for the practical reason that saturation pressure can be obtained near room temperature. Furthermore, ethanol induces minimal surface chemisorption and exhibits good solvent-solid interaction due to its polar nature. As ethanol is transparent in the wavelength range of the ellipsometer, the Cauchy approximation, described by equation (2.2), allows for the change in refractive index, using the same optical model as during SiO$_2$ deposition (FIG. 2-2b). However, the thickness of the SiO$_2$-like film has been found not to change during porosimetry experiments and, therefore, is kept constant\(^2\). The effective refractive index obtained in this way is indicative of a SiO$_2$ matrix admixed with pores, which are either empty or filled with ethanol. By performing measurements as a function of relative vapor pressure, isotherms are obtained which can be analyzed using the porosimetry theory. This allows characterizing the microstructure of SiO$_2$-like films in terms of the amount, type, and size of pores present.

2.3.1 Porosity

To be able to extract the porosity of the SiO$_2$ film from the experimental data, the optical properties have to be associated with the material properties of the optical system. The Lorentz-Lorenz formula describes the relation between the optical properties of a multi-component system and its material properties:

$$\sum_i N_i \alpha_i = \frac{3}{4\pi} \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{3}{4\pi} \frac{n_i^2 - 1}{n_i^2 + 2}$$

(2.20)

where $\varepsilon$ is the dielectric constant, $n$ is the refractive index, and $\alpha_i$ and $N_i$ are the mean molecular polarizability (describing the displacement of the electrons relative to the nucleus when an electric field is applied) and the number of molecules per unit volume of the various components, respectively.

For a two component system, such as a porous film containing matrix material and pores, the Lorentz-Lorenz equation reduces to:

$$N_p \alpha_p + N_m \alpha_m = \frac{3}{4\pi} \frac{n_{eff}^2 - 1}{n_{eff}^2 + 2} \equiv B_{eff}$$

(2.21)

where $B_{eff}$ is the effective volume polarizability, and subscripts $p$ and $m$ denote the properties of pores and matrix, respectively. By introducing porosity $P$ as the fraction of pores, the effective volume polarizability of the total porous film can also be expressed as:

$^2$ Experiments showed that film swelling due to adsorption and the forming of a layer of liquid ethanol on the external film surface are both negligible, i.e. only changes in thickness occur in the order of $\pm 0.1$ nm.
Theory

\[ B_{\text{eff}} = P \cdot B_p + (1 - P) \cdot B_m \]  

(2.22)

where \( B_p \) and \( B_m \) are the volume polarizability of the pores and matrix, respectively.

Now, two extreme situations are used to determine the porosity of the film:

- Zero ethanol pressure. In this case there is no ethanol present inside the pores (FIG. 2-14a).
- Saturation vapor pressure. In this case the open pores are completely filled with ethanol (FIG. 2-14b).

![FIG. 2-14 Schematic representation of the two extreme situations used to obtain porosity: (a) all pores are empty, (b) open pores are filled. Indicated are the refractive index of ethanol \( n_{\text{EtOH}} \), and the effective refractive index \( n_0 \) and \( n_{\text{sat}} \) of the porous film with and without ethanol adsorbed, respectively.](image)

In the absence of ethanol vapors, the refractive index of the pores is \( n_p = 1 \), and, therefore the volume polarizability of the pores is \( B_p = 0 \). In this situation equation (2.22), with \( B_{\text{eff}} = B_0 \) the polarizability of the film at zero ethanol pressure, reduces to:

\[ B_0 = (1 - P) \cdot B_m \]  

(2.23)

In the other extreme situation at saturated ethanol pressure, all the open pores will be filled with ethanol and equation (2.22) becomes:

\[ B_{\text{sat}} = P \cdot B_{\text{EtOH}} + (1 - P) \cdot B_m \]  

(2.24)

where \( B_{\text{sat}} \) is the effective polarizability of the film at saturated ethanol pressure, and \( B_{\text{EtOH}} \) the volume polarizability of the ethanol.

Combining equations (2.23) and (2.24) and solving for the porosity \( P \) gives:

\[ P = \frac{B_{\text{sat}} - B_0}{B_{\text{EtOH}}} \]  

(2.25)

Alternatively, using equation (2.21) for the relation between refractive index and volume polarizability, this becomes:

\[ P = \frac{n_{\text{sat}}^2 - 1}{n_0^2 + 2} \frac{n_p^2 - 1}{n_0^2 + 2} \frac{n_{\text{EtOH}}^2 - 1}{n_{\text{EtOH}}^2 + 2} \]  

(2.26)

The above equation is used to calculate the open porosity from the film effective refractive indices measured with ellipsometry prior to ethanol adsorption and after full saturation, combined with the refractive index of ethanol (1.36 at 600 nm)\(^{[22]}\).
Equation (2.26) shows that the calculation of porosity is completely independent from the properties of the film matrix. This is an advantage because in many situations the exact dielectric function of the film matrix is unknown, as was previously mentioned in § 1.1.2.

2.3.2 Multilayer thickness

In § 2.2.4 several empirical models are described which allow to calculate the adsorbed multilayer thickness as a function of relative pressure $p/p_0$. This thickness determines the actual condensation space, which is available for capillary condensation at each pressure. However, these relations contain empirical parameters which values are unknown for ethanol adsorption. To determine these values, the multilayer thickness on a non-porous sample is obtained experimentally by means of spectroscopic ellipsometry. The thickness is extracted from the experiment by changing the ellipsometry model described in § 2.1.2. Instead of modeling the penetration of the adsorptive into the pores, the adsorbate is assumed to form a multilayer on top of a flat external surface. In this case the model is composed of a semi-infinite substrate with a non-porous film of constant refractive index and thickness. An extra layer is placed on top to account for the changing adsorbate thickness (FIG. 2-15), but the refractive index is kept constant at the value for ethanol.

For increasing relative pressure the change in ellipsometry angles $\Delta$ and $\Psi$ due to adsorption are fitted according to the Cauchy approximation and the thickness is extracted. This is allowed due to the fact that ethanol is transparent within the wavelength range of the ellipsometer.

In this way the ethanol multilayer thickness is obtained as a function of relative pressure. The unknown parameter values can be determined by fitting the empirical models to the experimental data. These relations can be used to correct the pore radius calculated via the Kelvin equation for multilayer adsorption which precedes capillary condensation. Finally, this allows the determination of the pore size distribution of plasma-deposited SiO$_2$ films.
2.4 Substrate biasing

2.4.1 Principle

An external substrate bias allows for controlled ion bombardment on the surface of the substrate. This means that the ion energy is mainly controlled by the external bias voltage. The extra energy supplied at the growth region by the impinging ions may lead to enhanced surface mobility, interfacial atom mixing, re-deposition of loosely bound species, and atom displacement below the surface\[^6\]. These effects will result in the densification of the deposited film as compared to the situation without ion bombardment. In literature the effect of substrate biasing is described by the energy delivered to the growing film per deposited particle \(E_p\) which is given by

\[
E_p \approx E_i \frac{\Gamma_{\text{ions}}}{\Gamma_{\text{growth}}} \tag{2.27}
\]

where \(E_i\) is the kinetic ion energy, and \(\Gamma_{\text{ions}}\) and \(\Gamma_{\text{growth}}\) are the ion and growth fluxes, respectively. Important to notice is that the energy per deposited particle is only proportional to the ion-to-growth flux ratio and not to the separate fluxes. Under the assumption that the film is stoichiometric SiO\(_2\), the growth flux, which is the flux of depositing particles that lead to film deposition, can be related to the deposition rate \(R_d\) according to:

\[
\Gamma_{\text{growth}} = \frac{\rho_{\text{SiO}_2} \cdot N_A}{m_{\text{SiO}_2}} R_d \tag{2.28}
\]

where \(\rho_{\text{SiO}_2}\) is the density of fused silica (2.2 g-cm\(^{-3}\)), \(N_A\) is the Avogadro’s number and \(m_{\text{SiO}_2}\) is the molecular weight of SiO\(_2\).

Due to the fact that SiO\(_2\) is a dielectric, effective biasing is only obtained by applying an alternating voltage. The substrate surface is then capacitively charged, resulting in a negative mean dc voltage \(V_b\) on the substrate. Due to the negative bias the more mobile electrons ‘run’ away which cancels the quasi-neutrality of the plasma near the surface. Subsequently, the more massive and positively charged ions left behind are accelerated to the surface thereby creating the sheath region. Ions from the bulk plasma arriving at the sheath boundary are also accelerated to the surface and by doing so fewer ions stay inside the plasma. This causes the sheath thickness to grow until an equilibrium situation is obtained. The maximum energy \(E_{i,\text{max}}\) gained by the ions due to the acceleration in the sheath is given by:

\[
E_{i,\text{max}} = e \left| V_p - V_b \right| \tag{2.29}
\]

where \(e\) is the electron charge and \(V_p\) and \(V_b\) are the plasma potential and the bias potential, respectively. Usually, the plasma potential in equation (2.29) is assumed to be negligible with respect to the bias potential. Furthermore, due to collisions in the sheath the energy of the ions changes, which results in a distribution of ion energies. The shape of the ion energy distribution function (IEDF) mainly depends on the ion mean free path in the sheath, the plasma sheath transit time of the ions, and on the bias waveform applied at the substrate\[^{\text{[40]}}\].
2.4.2  Critical ion energy and distribution

Although ion bombardment is often referred to as leading to improved material quality, adverse effects may also occur if the process is not appropriately controlled. Equation (2.27) shows that the energy per deposited particle $E_p$ is controlled by both the ion energy $E_i$ and the ion-to-growth flux ratio $\Gamma_{\text{ions}}/\Gamma_{\text{growth}}$. In literature it is discussed that good-quality films are deposited under low to intermediate ion energies, combined with an appropriate ion-to-growth flux ratio to optimize the induced effect\cite{6}. This shows the advantage of an ion bombardment technique which is decoupled from the plasma chemistry. Moreover, a critical ion energy $E_{i,c}$ exists above which a transition in the microstructure of the film occurs, leading to material densification\cite{41}. However, excessive ion energies can also lead to undesirable phenomena such as high internal stress and structural damage\cite{42}.

In the case of $\text{SiO}_2$ deposition several critical values have been reported in literature. Experimental evidence for PECVD deposited $\text{SiO}_2$ shows that the critical ion energy $E_{i,c}$ and ion-to-growth flux ratio $(\Gamma_{\text{ions}}/\Gamma_{\text{growth}})_c$ are 70 eV and 0.26, respectively\cite{41}. Moreover, as deduced from changes in $\text{SiO}_2$ film properties, such as refractive index and fraction of voids\footnote{The fraction of voids were in this case obtained by means of the EMA method as explained in § 1.1.2.}, the largest influence occurs for an energy per deposited particle $E_p$ in the range from $\sim$10-100 eV\cite{43,44}. The growth of a film with ion bombardment can also be investigated by simulating the deposition process. For $\text{SiO}_2$ the transition from low- to high-density films was found to take place at a critical energy per deposited particle $E_{p,c}$ of 12-14 eV and a ion-to-growth flux ratio $(\Gamma_{\text{ions}}/\Gamma_{\text{growth}})_c$ between 0.4-0.5\cite{45}. From the simulations it was also shown that at the critical values a transition occurs from tensile to compressive stress in the film. Up to now, these studies have been performed only for dual-frequency direct plasma configurations, i.e. one frequency to generate the plasma and the other to induce (additional) ion bombardment at the substrate. In this work, however, the substrate biasing technique is applied to a remote plasma configuration, i.e. no power is coupled to the plasma in the downstream region. An issue worth to investigate, therefore, is whether the process of $\text{SiO}_2$-like film densification in a remote plasma is also governed by the above-mentioned parameters with similar ranges for the ion-to-growth flux ratio and ion energy.

The above discussion shows that control on the ion energy is crucial. This means that the shape of the IEDF is also important, because it determines the range of ion energies present. As mentioned in section 1.3 both an rf sinusoidal bias and a low-frequency pulsed shaped bias were used in this work. Due to the fact that the sheath transit time of the ions in the expanding thermal plasma is similar to the rf period (13.56 MHz)\cite{46}, the IEDF for the rf bias turns out to be bimodal (FIG. 2-16a). This means that the energy of the ions determined via equation (2.29) is an average value. Moreover, there might be ions carrying energy high enough ($E_i >> E_{i,c}$) to cause damage to the film, as well as ions too low in energy ($E_i < E_{i,c}$) to induce material densification. Because precise control of the ion energy for the rf bias is impossible, a so-called pulse-shaped bias has been applied. Here, the bias waveform consists of a negative voltage
peak combined with a short voltage spike towards floating potential, which is cycled at low frequency (~1-215 kHz). According to Wang et al.\textsuperscript{40} this waveform results in a narrow single-peaked IEDF (FIG. 2-16b) and, therefore, in a bombardment with almost monoenergetic ions. In this case the ion energy is actually tunable by changing the applied bias voltage $V_b$, which allows optimizing the bias effect for film growth.

![FIG. 2-16. An illustration of the IEDF for (a) rf sinusoidal bias and (b) low-frequency pulse-shaped bias.](image)

Also interesting to understand is whether these two distinct bias systems lead to similar film densification or whether their intrinsic differences induce different microstructural changes.

### 2.4.3 Effect on SiO$_2$ structure

The structural building block of SiO$_2$ films is the tetrahedron Si(O$_{1/2}$)$_4$ elementary unit (FIG. 2-17a). These units are connected in specific arrangements leading to a network of rings. Within the same SiO$_2$ structure the network may consist of rings having different sizes. The size $N$ of a ring is defined as the number of Si-O-Si groups constructing the ring\textsuperscript{47}, which means that an $N$-fold ring contains $2N$ Si-O bonds. A 3-fold ring is shown in FIG. 2-17b to visualize the concept.

![FIG. 2-17. Illustration of (a) the SiO$_2$ tetrahedron and (b) a 3-fold ring structure.](image)

In the amorphous form ($\alpha$-SiO$_2$) grown during plasma deposition without substrate biasing, the network may contain three –to tenfold rings\textsuperscript{47}. However, for films grown in the presence of ion bombardment, changes occur in the ring structure, thereby leaving the tetrahedron unit unchanged\textsuperscript{43}. More specifically, small rings (two, three –and
fourfold rings), which are highly strained and are associated with disorder in the SiO$_2$ network, rearrange to produce larger, more relaxed ring structures. The number of five, six—and sevenfold rings increases, confirming that they are the most probable size in a-
SiO$_2$ [47]. Finally, the number of large rings (N>9) lowers with increasing density, indicating a reduction in the number of pores. However, the pores induced by these ring structures are all in the micropore size range. Together, the structural changes due to ion bombardment lead to the densification of the grown SiO$_2$ film.
3 Experimental

This chapter discusses the details of the two experimental setups used in this work. The various components of the setup for plasma-enhanced CVD of SiO$_2$-like films are described, in particular the two distinct substrate biasing systems. Next, the ellipsometric porosimetry setup is described in detail and the experimental procedure and setup calibration are discussed. The experimental chapter ends with an overview of complementary diagnostics for thin film characterization.

3.1 Expanding Thermal Plasma technique

The Expanding Thermal Plasma (ETP) technique, a remote plasma enhanced CVD setup, has been used to deposit SiO$_2$–like films. The ETP setup consists of a high-pressure plasma source placed above a low–pressure chamber and it is defined as remote because of the geometrical separation between the location of plasma production and the deposition chamber.

3.1.1 Plasma generation and expansion: the cascaded arc

A dc cascaded arc plasma source is used to generate the plasma (FIG. 3-1).

![FIG. 3-1 A schematic showing a section of the cascaded arc plasma source. The cathodes (1), argon inlet (2), anode plate (3), nozzle with O$_2$ inlet (4), and isolated cascade plates (5) are indicated.](image)

The arc consists of a housing with three cathodes, a plasma channel, and a grounded anode plate with nozzle. The plasma channel (ø 4 mm) is build up from four copper cascade plates, separated from boron–nitride insulation rings. The plasma is ignited in argon by applying a high dc voltage pulse between the cathodes and the anode plate. Subsequently, the plasma develops from the cathode tips through the plasma channel and expands from the 4 mm nozzle into the deposition chamber. In thermal equilibrium the arc operates at a current of 75 A and a pressure of approximately 0.53 bar at an argon flow of 100 sccs. This corresponds to an electron density $n_e$ in the range of $10^{22}$ m$^{-3}$ and an electron temperature $T_e$ of $\sim$1 eV$[48]$. The power dissipated by the arc at these conditions is $\sim$4.5 kW.
To prevent the cascaded arc from melting, cooling water is supplied through small channels built around the plasma source. As a result, a temperature gradient will be present along the cylindrical direction of the plasma column. Moreover, this has the effect of confining the plasma in the middle of the channel, due to differences in conductivity. In this situation the plasma is said to be wall-stabilized.

Due to a large pressure difference, from ~$10^{-1}$ bar to ~$10^{-4}$ bar, the plasma accelerates in the source and expands supersonically into the deposition chamber. However, at a position of about 5 cm from the nozzle a stationary shock occurs, leading to a subsonic expansion below the shock front. The expansion to a low chamber pressure of 0.26–0.35 mbar reduces the electron temperature $T_e$ to 0.1–0.3 eV and the electron density $n_e$ to $10^{17}$–$10^{19}$ m$^{-3}$, depending on the presence of gases affecting the plasma reactivity\cite{49}. Due to a directed velocity of ~600 m/s in the downstream region of the expansion, the transport of plasma species towards the substrate is convective\cite{50}. More information about plasma generation in the cascaded arc and the expansion can be found in literature and references therein\cite{50,52}.

### 3.1.2 Deposition setup

The ETP experimental setup is shown in FIG. 3-2. The main part of the setup is a vertically-positioned stainless steel cylindrical vessel. At the top of the vessel the plasma source is placed at a distance of 60 cm from the substrate holder. In FIG. 3-2 the *in situ* ellipsometry configuration used to monitor the deposition process is also shown, as mounted at an angle of incidence of 68°. During processing the setup is pumped by two mechanical booster pumps (Edward EH2600, 2600 m$^3$h$^{-1}$; Edward EH500, 500 m$^3$h$^{-1}$) and one rotary piston pump (Edwards, 240 m$^3$h$^{-1}$). Overnight, a turbo molecular pump (Leybold Turbovac 1500, 90 m$^3$h$^{-1}$) in line with a rotary pump (Edwards, 40 m$^3$h$^{-1}$) is used in order to maintain a base pressure of ~$10^{-6}$ mbar.

For the deposition of SiO$_2$-like layers, O$_2$ and hexamethyldisiloxane (HMDSO; [CH$_3$)$_3$SiOSi(CH$_3$)$_3$) are admixed downstream in the expanding argon plasma. Oxygen is directly injected in the nozzle through slits. HMDSO is an organosilicon precursor with a boiling point of 101 °C and a vapor pressure of 44 mbar at 20 °C. Therefore, liquid HMDSO is evaporated using a Bronkhorst controlled evaporation module (CEM W202) in combination with a Bronkhorst liquid flow controller (L2C2). Together with an argon carrier gas, the HMDSO vapor is then transported through a gas line and injected into the deposition chamber via a punctured ring placed 5 cm of distance from the nozzle. To prevent condensation of HMDSO inside the gas line, a heating ribbon is used to keep the gas line at a temperature of approximately 70 °C.

Recently, the mass flow controller system has been upgraded with the option of setting a gradual increase or decrease of O$_2$ and HMDSO flow rates. This function is used to develop SiO$_2$-like films with graded optical and chemical properties along the growth direction.
FIG. 3-2 Schematic drawing of the ETP experimental setup with in situ ellipsometry light source (1) and detector (2).

Due to the highly reactive argon plasma environment (argon ions and electrons), the injected molecules are chemically activated. However, the low electron temperature in the subsonic part of the expansion makes electron–impact dissociation an unlikely process to occur. Recent investigations have shown that both HMDSO and $O_2$ molecules are activated by charge exchange reactions with argon ions. This process is followed by dissociative recombination with low energy electrons. The description of the dissociation paths of HMDSO and $O_2$ leading to the growth of a carbon-free $SiO_2$ film is given in Frame 3.1.

Single side polished phosphor-doped n–type crystalline silicon $\langle 100 \rangle$-wafers, which have a thickness of 500–550 µm and a resistivity of 10–20 $\Omega$·cm, are used as substrate material. The wafers are cut in samples of ~2x2 cm², cleaned in an ethanol ultrasonic bath, and dried with a nitrogen flow. Up to three samples are clamped on an aluminum substrate holder, which is placed on a copper yoke inside the deposition chamber. This is achieved with the aid of a loadlock system to circumvent the necessity to pressurize the complete system. Due to the heat load from the plasma the temperature of the substrate will increase. Therefore, the copper yoke is actively cooled by a circulation of process water. To control the temperature of the substrate holder, a flow of liquid nitrogen is switched on each time the value set at 25 °C is exceeded. However, measurements performed with temperature sensor stickers (Thermax, range 40–182 °C) attached on top of several samples have shown that the actual substrate temperature does exceed the temperature set. For the plasma conditions used in this research, see TABLE 3.1 in § 3.1.4, the substrate temperature was found to be in the range 120–182 °C after 67 seconds of plasma exposure.
Frame 3.1: Dissociation pathways of HMDSO and O₂ in an argon expanding thermal plasma.

In the plasma source argon ions and electrons as well as argon meta-stables are generated due to high-energy electron-impact dissociation, according to:

\[ Ar + e^- \rightarrow Ar^+ + e^- \]  
\[ Ar + e^- \rightarrow Ar^+ + 2e^- \]

The ionization process is accompanied by an efficiency of about 10 to 15% at an arc current of 75 A.

In the expansion below the shock front the electron temperature is reduced to about 0.1-0.3 eV. Therefore, as mentioned before, the chemical activation of HMDSO and O₂ molecules injected into the plasma expansion is very unlikely to occur via electron-impact dissociation.

Instead, the dissociation of both HMDSO and O₂ molecules begins via charge exchange reactions with argon ions. The following reactions show these primary processes, where the \( M \) symbol indicates a CH₃ (methyl) group: a,b

\[ M_3Si-O-Si-M_3 + Ar^+ \rightarrow M_3Si-O-Si^-+ M_2 + Ar \quad (\kappa_{CE} = 4 \cdot 10^{-16} \text{m}^3\cdot\text{s}^{-1}) \]  
\[ M_3Si-O-Si^-+ CH_2 + 2e^- \rightarrow M_3Si-O-Si^-+ M + O \quad (\kappa_{CE} = 6 \cdot 10^{-17} \text{m}^3\cdot\text{s}^{-1}) \]

Note that the charge exchange reaction with HMDSO is of dissociative nature, also creating smaller ions, compared to the HMDSO parent ion, and radicals. These products might again react with other HMDSO molecules leading to polymerization and further decomposition of HMDSO. However, under the present experimental conditions (\( \Phi_{HMDSO}<\Phi_{Ar,a} \)) these secondary reactions appear to be negligible compared to recombination reactions with electrons. Thus, the dissociative recombination with low energy electrons present in the expansion is the main secondary reaction path for the ions formed in reaction III. a,b

\[ M_3Si-O-Si^-+ M_2 + e^- \rightarrow M_3Si-O^-+ M_2-Si \]  
\[ M_3Si-O-Si^-+ M_2 = CH_2 + e^- \rightarrow M_3Si-O^-+ O-Si=CH_2 \]  
\[ M_3Si-O^-+ e^- \rightarrow M_2-Si^-+ M \]  
\[ O_2^+ + e^- \rightarrow O + O^- \quad (\kappa_{DR} = 1 \cdot 10^{-13} \text{m}^3\cdot\text{s}^{-1}) \]

From the above reactions IIIa-c the most probable precursor species indentified are SiM₂, SiM₃ and OSiCH₂. a Moreover, the O radicals produced via reaction (IIId) are also expected to dissociate HMDSO molecules. This leads to the production of several radical species, as indicated by the following reaction:

\[ M_3Si-O-Si-M_3 + O \rightarrow M_3Si-O-Si-M_2-O^-+ M \]  
\[ \rightarrow M_3Si-O-M_2-Si^-+ M-O^- \]  
\[ \rightarrow M_3Si-O^-+ O-Si-M_2 \]

The most probable precursor species from this reaction are the Si₂O₃M₂ and SiOM₂ radicals from the second and third dissociation pathways. These, however, are speculations since no experimental observation has been carried out.

The precursor species will attach to the silicon surface via either a Si-O or a Si-C bond. This will lead to the incorporation of both oxygen and carbon atoms in the growing film. However, in an O₂-rich environment, the O radicals and O₂ molecules will initiate combustion reactions in the plasma phase leading to the elimination of CH₂ groups in the form of CO, CO₂ and H₂O, therefore, resulting in carbon-free SiO₂-like films, with a variable degree of porosity.

\[ a \text{ M. Creatore et al. [14]} \quad b \text{ M.F.A.M. van Hest et al. [53]} \quad c \text{ M.F.A.M. van Hest et al. [54]} \]
To shield the substrate from the plasma during ignition and precursor flow rate stabilization, a stainless steel shutter is placed ~1 cm above substrate level. The shutter also prevents deposition to occur and, therefore, is used to control the plasma exposure time. The shutter has two modes of operation, i.e. the open–closed period is either time controlled or manually handled.

The experimental setup is automated with PLCs and controlled by means of a graphical user interface. More details about the experimental setup can be found in literature\cite{12,55,56}.

3.1.3 External substrate bias systems

As a consequence of the low electron temperature, which results in a small self–bias voltage (< 2V) present at the substrate, ion bombardment towards the substrate can be neglected. Therefore, an external bias system needs to be connected to the substrate holder, whenever the effect of ion bombardment on film growth needs to be investigated. However, an external system allows for maximum control over the process. Thus, the influence of substrate biasing can be studied without affecting other plasma properties. The experimental details of external substrate biasing are explained in this section.

Two distinct external methods are used to apply a bias to the substrate holder. One is a sinusoidal radiofrequency bias of 13.56 MHz generated by an rf power source (RFPP, RF5S) (FIG. 3-3a). The signal is coupled to the substrate holder through an L–type impedance matching network to maximize the power transfer. In principle this means that the impedance of the plasma \(Z_L\) is matched to the impedance of the source \(Z_S\). A schematic of the rf bias circuitry is shown in FIG. 3-3b.

![FIG. 3-3. The rf bias system: (a) representation of the bias potential, (b) electrical circuit, showing the power source with impedance, matching network, and variable plasma impedance.](image)

The matching network consists of a variable capacitor \(C_1\) and inductor \(L_1\) in series and a variable capacitor \(C_2\) placed parallel to the plasma impedance \(Z_L\). The total impedance of the network and the plasma is matched to the impedance of the rf source \(R_S\) (50 Ω) by changing the value of the variable capacitors \(C_1\) and \(C_2\).

The signal coupled to the substrate holder is measured with an active voltage probe (Fluke) which is connected to a digital real–time oscilloscope (Tektronix TDS210). On the
Experimenta Experimenta Experimenta Experimenta

oscilloscope the dc component $V_{dc}$ of the signal is determined and its value is read from the screen. After the system is approximately matched, the ion flux $\Gamma_{ions}$ from the plasma is determined from the coupled rf power $P_{rf}$ and the dc voltage $V_{dc}$ by

$$\Gamma_{ions} = \frac{I_{rf}}{e \cdot A_{eff}} \approx \frac{P_{rf}}{e \cdot |V_{dc}| \cdot A_{eff}}$$

(3.1)

where $I_{rf}$ is the ion current, $e$ is the electron charge, $A_{eff}$ is the effective ion collection area, and $|V_{dc}|$ is the absolute value of the dc voltage. Although this relation is only strictly valid in case that all the rf power is completely utilized to accelerate the ions. In FIG. 3-4 the measured dc bias voltage is shown as a function of rf power coupled to the substrate holder.

As can be seen a deviation in the linear relationship exist for rf powers above $\sim$10 W. This means that not all energy is used to accelerate ions within the plasma sheath, but part of the rf power is consumed to create additional plasma. However, the deviation is not very distinct. Therefore, the assumption was made that the ion flux calculated using equation (3.1) is correct for the whole range of applied rf powers. Moreover, no other means to determine the ion flux from the plasma was available while performing this research.

As explained in section 1.3 and § 2.4.2 also a low-frequency pulse-shaped bias system has been used to induce ion bombardment. The system is a homebuilt device named “Sloper” and consists of an external control unit and an amplifier built in the yoke of the deposition setup. To minimize parasitic capacitance to ground an assembly of glass cylinders shields the yoke. A pulse-shaped signal is generated by the control unit with tunable frequency in the range $\sim$1–215 kHz. The control unit allows for either a square or sloped waveform or a dc signal. For both waveforms the time for which the signal is at floating potential can be set at 2.5, 25 or 250 $\mu$s. The signal from the control unit is sent to a power amplifier, which generates an output bias voltage variable between 0 and $-$300 V. The output bias voltage is directly coupled to the substrate holder by means of dedicated electronics in the yoke. In FIG. 3-5b the circuit diagram of the pulse-shaped bias system is shown.
In this bias system, no matching network is employed between the power amplifier and the substrate holder, in contrast to the rf bias system. The generated waveform consists of many frequency components, while conventional matching networks are only optimized for a single frequency.

The ion flux \( I_{\text{ions}} \) from the plasma for the pulse-shaped bias is determined by the following equation:

\[
I_{\text{ions}} = \frac{I_{\text{ions}}}{e \cdot A_{\text{eff}}}
\]

where \( I_{\text{ions}} \) is the ion current, \( e \) is the electron charge, and \( A_{\text{eff}} \) is the effective ion collection area.

To determine the ion current \( I_{\text{ions}} \), preliminary experiments have to be performed using the same conditions as during deposition. The total integrated current present in the circuit is shown by the control unit. Therefore, at each processing frequency, both the self–induced current without plasma \( (I_{\text{induced}}) \) and the current with plasma present \( (I_{\text{plasma}}) \) need to be measured (FIG. 3-6a). Afterwards, the self–induced current is subtracted from the plasma current to obtain only the contribution from the ions. Furthermore, a correction needs to be made for the duty cycle \( D \) of the waveform, which is defined as the ratio between the duration of the negative part \( \tau_{\text{neg}} \) and the total period \( T \) of the signal:

\[
D = \frac{\tau_{\text{neg}}}{T} = \frac{\tau_{\text{neg}}}{\tau_{\text{neg}} + \tau_{\text{zero}}}
\]

where \( \tau_{\text{zero}} \) is the time for which the signal is at floating potential.

Taking the corrections above into account the ion current \( I_{\text{ions}} \) is determined by

\[
I_{\text{ions}} = \frac{(I_{\text{plasma}} - I_{\text{induced}})}{D}
\]

Using equation (3.4) to calculate the ion current for measurements performed as a function of applied bias voltage \( V_{\text{bias}} \) gives typically a graph as shown in FIG. 3-6b.
As can be seen the ion current from the plasma linearly increases for increasing bias voltage. Although in principle a constant current is expected, the increase might be explained by the following effects:

- Extra plasma is generated locally around the substrate holder, which will increase the amount of ions.
- The self-induced current changes due to the presence of the plasma, which will influence the contribution to the ion current.

The first explanation is less probable due to the low frequency used in the pulse-shaped bias. Moreover, the effect of local plasma generation should not be present at low bias voltage and only initiate above a certain threshold voltage. This would lead to a transient in ion current from constant to linearly increasing for higher bias voltage, which is not observed experimentally.

Therefore, the second option is more probable, also because the self-induced current is linearly proportional to the bias voltage. This means that the actual ion current from the plasma is the value, which is obtained by extrapolating the ion current data to zero bias voltage. Then, this value should be used to calculate the ion flux $\Gamma_{\text{ions}}$ from the plasma via equation (3.2), under the assumption that no plasma generation occurs. However, this approach is not experimentally supported and care should be taken on interpreting the results. Moreover, the current shown by the control unit does not result from a dedicated measurement, which means that a deviation may exist between the observed ion current and the actual ion current.

Important for the operation of the pulse-shaped bias is the maximum ion current of 200 mA which can be handled by the amplifier. Therefore, the bias signal from the control unit can only be fed to the amplifier after reduction of the ion flux towards the substrate, i.e. by the injection of process gasses.
3.1.4 Experimental conditions

The experimental conditions used during the deposition of the SiO$_2$ films in this research are summarized in TABLE 3-1. The first column indicates the specific series of experiments for which the conditions are as specified, e.g. variation of the HMDSO flow rate and the application of substrate biasing. The result section in which the properties of the deposited films from each series are discussed is denoted in the second column.

**TABLE 3-1: Experimental conditions for the different types of depositions performed.**

Φ$_{Ar}$, Φ$_{O_2}$, and Φ$_{HMDSO}$ are the flow rates of argon, oxygen, and HMDSO, respectively. $I_{arc}$ is the arc current, $p_{arc}$ is the pressure in the arc, and $p_{vessel}$ is the pressure in the deposition vessel. $|V_{bias}|$ is the magnitude of the applied bias voltage.

| experiment series               | result section | $\Phi_{Ar}$ (sccs) | $\Phi_{O_2}$ (sccs) | $\Phi_{HMDSO}$ (sccs) | $I_{arc}$ (A) | $p_{arc}$ (mbar) | $p_{vessel}$ (mbar) | $|V_{bias}|$ (V) |
|--------------------------------|----------------|-------------------|--------------------|-----------------------|---------------|-----------------|-------------------|--------------|
| HMDSO variation (no bias)      | 4.1            | 100               | 5.0                | 0.16-0.46             | 75            | 620             | -                 | -            |
| HMDSO variation (p-s bias)     |                |                   |                    |                       |               |                 |                   |              |
| Substrate biasing (rf bias)    | 4.2            | 100               | 5.0                | 0.16                  | 75            | 620             | 0.35              | 0-46         |
| Substrate biasing (p-s bias)   |                |                   |                    |                       |               |                 |                   |              |

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3.2 Ellipsometric Porosimetry technique

As outlined in Chapter 2 the ellipsometric porosimetry technique has been used to determine the open porosity as well as adsorption–desorption isotherms on SiO$_2$–like deposited films. During the porosimetry experiments a film of SiO$_2$ deposited on a silicon substrate is exposed to ethanol vapors using a newly developed setup, designed and built up in cooperation with the Chemistry department. The adsorption–desorption process at constant temperature and at different ethanol partial pressure values is monitored by means of in situ spectroscopic ellipsometry.

3.2.1 Experimental details

- Porosimetry setup

The ellipsometric porosimetry experimental setup consists of two main parts, i.e. a process chamber and the ellipsometry system (FIG. 3-7). The ellipsometry light source and detector are mounted on the chamber at an angle of incidence of 71°. In order to allow for in situ ellipsometry measurements, the ellipsometry system is separated from the process chamber by means of two quartz windows. The vacuum system and the flow lines are connected to the process chamber through automatic gate valves. The chamber has a volume of approximately 400 cm$^3$.

![FIG. 3-7. Schematic drawing of the ellipsometric porosimetry experimental setup.](image)

The substrate holder is temperature controlled in the range of 14–350 °C: this is achieved by a combination of a continuous cold nitrogen gas flow (-40 °C) and a resistance heater implemented in the holder. The substrate holder temperature is measured with a thermocouple (type K$^\dagger$). A temperature controller (West P6100) is used.

$^\dagger$ type K: thermocouple consisting of a chromel-alumel junction which is capable of measuring a temperature in the range -200 to +1200 °C.
to adjust the substrate temperature to the desired value by changing the frequency of current pulses (4 A) applied to the heating wire at constant voltage (9 V).

- **Experimental procedure**

Due to contact with the ambient right after the deposition, the porous SiO$_2$ films adsorb water, which needs to be removed before the ethanol adsorption studies are carried out. After sample introduction, therefore, the process chamber is sealed and evacuated by means of a vacuum system. Subsequently, the sample is degassed at elevated temperature in the range 215–350 °C, depending on the type of porosity and ageing of the film. During degassing the thermal contact between the substrate holder and the sample is increased by applying a small flow of helium through holes in the holder. A dynamic ellipsometry scan (10 revs/meas) is performed to monitor the degassing process in time (FIG. 3-8).

![Graph](image_url)

**FIG. 3-8.** The typical change in the Ψ-signal during degassing of the sample at elevated temperature. In this specific case the temperature is raised from room temperature to 280 °C.

When the ellipsometric angles show a constant value, an accurate spectroscopic ellipsometry scan (100 revs/meas) is taken to obtain the refractive index of the degassed sample. This value is compared to the value measured *in situ* after deposition of the SiO$_2$–like film. If both values are equal within the error (±0.01) the degassing can be considered complete, otherwise the degassing procedure is carried out at higher temperature.

After degassing, the valve between the chamber and the vacuum system is closed and the pumps are switched off. Next, the substrate temperature is lowered to 14 °C. The Antoine equation provides the saturation vapor pressure $p_{sat}$ of ethanol in mmHg at this temperature according to:

$$\ln(p_{sat}) = A - \frac{B}{(T + C)}$$

(3.5)
where $T$ is temperature in Kelvin and $A$, $B$, and $C$ are substance specific coefficients which can be found in literature\cite{57}. For ethanol at a temperature of 14 °C, equation (3.5) gives a saturation vapor pressure of ~40.2 mbar.

Also during the cooling procedure a small amount of helium is applied to increase the thermal contact. Again, the cooling process is monitored by means of a dynamic ellipsometry scan (10 revs/meas).

As soon as the temperature is stable, the process chamber is filled with helium until a continuous flow develops at a constant pressure of 1040 mbar, which is imposed by a backpressure valve. Under these conditions the adsorption process is carried out by introducing a specific vapor mixture of helium and ethanol. Helium is a carrier gas for ethanol and allows obtaining a partial pressure of ethanol between 0 and 40 mbar. During the adsorption process the relative ethanol pressure, which is the ratio between its partial pressure and saturation pressure values, is increased from 0 to 1 by changing the composition of the vapor mixture. The calibration of the mixture composition and relative ethanol pressure is reported in § 3.2.2.

After each change of mixture composition a dynamic ellipsometry scan (10 revs/meas) is performed to monitor whether the SiO$_2$–like film has reached equilibrium with the vapor mixture (FIG. 3-9).

![FIG. 3-9. The typical change in the $\Psi$-signal after a change in mixture composition.](image)

At each relative pressure the change in refractive index due to the adsorption of ethanol in the SiO$_2$–like film is determined by means of a spectroscopic ellipsometry scan (100 revs/meas) at the equilibrium condition.

When saturation pressure is reached the desorption process is started by decreasing the relative ethanol pressure. This is achieved by introducing the same mixture compositions as during adsorption in the reverse order. Again, spectroscopic ellipsometry scans (100 revs/meas) are taken at each composition when equilibrium has been reached.
The obtained ellipsometry data are used to built up an adsorption–desorption isotherm as reported in § 2.2.2.

- **Process handling system**
  In FIG. 3-10 the configuration of flow lines and control valves is schematically shown. The vacuum system consists of a combination of a rotary membrane pump (VacuuBrand MV2, ~2 m$^3$h$^{-1}$) and a turbo molecular pump (Varian V70LP, ~180 m$^3$h$^{-1}$) reaching a base pressure of ~10$^{-5}$ mbar. A pressure gauge (Varian, CT-100) monitors the pressure between the two pumps.

![FIG. 3-10. Flow lines and valve manifold of the ellipsometric porosimetry set up. The pump configuration with pressure gauge and a Cryostat bath are also indicated.](image)

Ethanol (Merck, pro analysis, 99.9%) is provided using two Bronkhorst liquid flow controllers in line for small flow (L01V02, 2.5–500 mg·h$^{-1}$) and large flow rates (L13V02, 500–10000 mg·h$^{-1}$), respectively. Ethanol is mixed with helium (Hoek Loos, purity 4.6), delivered via a Bronkhorst gas flow controller (F201CV, 4.4–2200 ml·min$^{-1}$), by means of a mixing valve. Subsequently, the mixture is evaporated using a Bronkhorst controlled evaporation module (CEM, W102A). To prevent condensation of the ethanol from the mixture outside the process chamber, all delivery lines behind the CEM unit are kept at ~70 °C by means of a heating sock. To be able to obtain small concentrations of ethanol in the mixture, the amount of mixture created is larger than needed inside the process chamber. Therefore, an extra Bronkhorst gas flow controller (F201CV, max. 80% ethanol) is used to deliver a constant flow of 150 ml·min$^{-1}$ to the chamber. Excess mixture is condensed by means of a Cryostat bath (Lauda Ecoline RE205) with heat exchanger and
retained in a container (FIG. 3-10). Moreover, this also provides a means to stabilize the mixture before introducing it to the reactor. Also the nitrogen gas used for substrate cooling is passed through the Cryostat before entering the substrate holder. A Bronkhorst backpressure valve (P–702C) at the mixture outlet line maintains the pressure in the chamber at 1040 mbar (FIG. 3-10). This valve is also set at a flow rate of 150 ml·min\(^{-1}\) to ensure a constant partial ethanol pressure in the chamber. At this flow rate the flush time of the chamber is approximately 2.5 minutes.

To prevent that condensation of ethanol occurs, but on the sample, the process chamber and the quartz windows are maintained at ~30 °C by means of convective heating. This is achieved by blowing warm air through a plastic housing placed around the process chamber and the quartz windows.

• **Setup control**

As mentioned in the previous section several valves need to be opened or closed and precise control on the flow rates is essential. Therefore the setup was automated using National Instruments compact Fieldpoint programmable automation controllers (PACs) and National Instruments LabVIEW software on a standard computer. The interface also allows for operation of the vacuum system and control on the temperature of the chamber housing and substrate.

During all experiments performed for the present study the setup was controlled by manually setting the values at the interface. Very recently, “procedures” have been developed within the same software, which allow performing automatically several steps of the porosimetry experiment.

Several safety procedures are also implemented to prevent damage to the setup. For example, the vacuum system cannot be connected to the chamber if a vapor mixture is present.

A second computer is used to control the spectroscopic ellipsometry setup via an I/O interface and Woollam WVASE32 software. This software is also used to process the experimental data to obtain the refractive index, via the method explained in section §2.1.2.

### 3.2.2 Calibration

As mentioned in §3.2.1 the composition of the vapor mixture is generated by means of automated flow controllers and an evaporation system. To obtain the desired composition in the process chamber the flow system has been calibrated. Moreover, also the relative ethanol pressure at each mixture composition needs to be determined, because this is the variable of interest. The helium flow controller has been calibrated by passing the flow through a cylinder containing an exact quantity of water. At each helium flow the time necessary to expel all the water from the cylinder is measured. These data are used to determine the actual flow rate in relation to the set flow rate.

To calibrate the mixture composition a calibrated flow of helium together with a certain flow of ethanol is injected in a gas chromatograph and the area of the resulting peak is determined. This area is compared to the peak area obtained from a helium-ethanol mixture with an exactly known concentration. By comparing the two peak areas the
*actual flow rate of ethanol* can be calculated and the corresponding mixture composition in terms of % concentration. In this way each required composition is determined. Together with the fixed backpressure of 1040 mbar this allows the calculation of the partial pressure of ethanol at each mixture composition. Subsequently, the relative ethanol pressures are obtained by dividing the partial pressure values to the saturation pressure of ethanol (~40.2 mbar).

In TABLE 3-2 the calibration results, necessary to perform the porosimetry experiments, are shown.

<table>
<thead>
<tr>
<th>He (s.p.) (ml/min)</th>
<th>EtOH (s.p.) (g/h)</th>
<th>pressure (mbar)</th>
<th>relative pressure</th>
<th>He (s.p.) (ml/min)</th>
<th>EtOH (s.p.) (g/h)</th>
<th>pressure (mbar)</th>
<th>relative pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>25</td>
<td>0.09</td>
<td>0.00225</td>
<td>1040</td>
<td>1000</td>
<td>6.89</td>
<td>0.17199</td>
</tr>
<tr>
<td>2000</td>
<td>50</td>
<td>0.19</td>
<td>0.00474</td>
<td>1400</td>
<td>1500</td>
<td>7.87</td>
<td>0.19646</td>
</tr>
<tr>
<td>2000</td>
<td>75</td>
<td>0.28</td>
<td>0.00699</td>
<td>1160</td>
<td>1500</td>
<td>9.34</td>
<td>0.23315</td>
</tr>
<tr>
<td>2000</td>
<td>100</td>
<td>0.38</td>
<td>0.00949</td>
<td>1230</td>
<td>2000</td>
<td>11.78</td>
<td>0.29406</td>
</tr>
<tr>
<td>2000</td>
<td>125</td>
<td>0.47</td>
<td>0.01173</td>
<td>1280</td>
<td>2500</td>
<td>14.16</td>
<td>0.35347</td>
</tr>
<tr>
<td>2000</td>
<td>150</td>
<td>0.57</td>
<td>0.01423</td>
<td>1400</td>
<td>3000</td>
<td>15.62</td>
<td>0.38992</td>
</tr>
<tr>
<td>2000</td>
<td>175</td>
<td>0.66</td>
<td>0.01648</td>
<td>1310</td>
<td>3000</td>
<td>16.59</td>
<td>0.41413</td>
</tr>
<tr>
<td>2000</td>
<td>200</td>
<td>0.76</td>
<td>0.01897</td>
<td>1425</td>
<td>3500</td>
<td>17.88</td>
<td>0.44633</td>
</tr>
<tr>
<td>2000</td>
<td>250</td>
<td>0.95</td>
<td>0.02371</td>
<td>1335</td>
<td>3500</td>
<td>18.97</td>
<td>0.47354</td>
</tr>
<tr>
<td>2000</td>
<td>300</td>
<td>1.13</td>
<td>0.02821</td>
<td>1355</td>
<td>4000</td>
<td>21.34</td>
<td>0.53270</td>
</tr>
<tr>
<td>2000</td>
<td>350</td>
<td>1.32</td>
<td>0.03295</td>
<td>1370</td>
<td>4500</td>
<td>23.70</td>
<td>0.59161</td>
</tr>
<tr>
<td>2000</td>
<td>400</td>
<td>1.51</td>
<td>0.03769</td>
<td>1380</td>
<td>5000</td>
<td>26.10</td>
<td>0.65152</td>
</tr>
<tr>
<td>1800</td>
<td>400</td>
<td>1.67</td>
<td>0.04169</td>
<td>1390</td>
<td>5500</td>
<td>28.45</td>
<td>0.71018</td>
</tr>
<tr>
<td>1500</td>
<td>400</td>
<td>1.98</td>
<td>0.04943</td>
<td>1400</td>
<td>6000</td>
<td>30.76</td>
<td>0.76785</td>
</tr>
<tr>
<td>1050</td>
<td>500</td>
<td>3.43</td>
<td>0.09562</td>
<td>1405</td>
<td>6500</td>
<td>33.13</td>
<td>0.82701</td>
</tr>
<tr>
<td>1400</td>
<td>1000</td>
<td>5.26</td>
<td>0.13130</td>
<td>1410</td>
<td>7000</td>
<td>35.47</td>
<td>0.88542</td>
</tr>
<tr>
<td>1250</td>
<td>1000</td>
<td>5.84</td>
<td>0.14578</td>
<td>1325</td>
<td>7500</td>
<td>40.06</td>
<td>1.00000</td>
</tr>
</tbody>
</table>

Due to the fact that the thermocouple used to control the substrate holder temperature is implemented in the holder, the actual temperature of the sample will be different. Therefore, experiments have been performed to determine the *actual* temperature as a function of the temperature set at the user interface. A separate thermocouple (type K) was connected at the top of a test sample (1 cm² silicon) by means of a heat conducting glue. In order to measure under experimental conditions the wires were lead through one of the ellipsometry ports. The signal was converted to a temperature by means of a handheld digital thermologger (Conrad, K204). During the experiments the process chamber was evacuated. The influence of the helium thermal contact on the actual sample temperature has been investigated by measuring with and without helium. The results are shown in the graph reported in FIG. 3-11.
The actual sample temperature is always lower for all temperatures set above 50 °C. This results in a maximum obtainable sample temperature of ~285 °C. The graph also shows the influence of the helium thermal contact, which gets more pronounced for increasing temperature. Therefore, the degassing and cooling procedures should be carried out with a small flow of helium present.

Also for the case of a vapor mixture present in the process chamber with a substrate temperature set at 14 °C, the actual sample temperature has been measured. During the flushing of the sample with pure helium gas a sample temperature of (14±1) °C was found. This means that the sample temperature during the adsorption–desorption process is fairly stable. However, the influence on the ethanol vapor saturation pressure results in a pressure varying in the range 37.7–42.8 mbar. This gives a maximum error of 6% with respect to the intended 40.2 mbar.

### 3.2.3 Ethanol properties

In this work ethanol has been used as the adsorptive for the porosimetry measurements. Therefore, various properties of ethanol are listed in TABLE 3-3.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular dimension (nm)</td>
<td>0.35 (short axis) 0.55 (long axis)</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.7935 (liquid @ 15 °C) 0.00202 (gas)</td>
</tr>
<tr>
<td>Mean polarizability (Å/molec.)</td>
<td>5.110</td>
</tr>
<tr>
<td>Saturation pressure (mbar)</td>
<td>40.2 (@ 14 °C)</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.36 (@ 600nm)</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C₂H₅OH</td>
</tr>
<tr>
<td>Structure</td>
<td></td>
</tr>
</tbody>
</table>
3.3 Complementary Diagnostics

In this section several diagnostics are briefly introduced since they were used to obtain complementary information besides the data obtained during film deposition and from the porosimetry experiments.

3.3.1 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a non–intrusive optical technique, which provides information about the chemical composition of a deposited film. The basic component of a Fourier transform infrared (FTIR) spectrometer is a Michelson interferometer. A Michelson interferometer consists of two mirrors located at a right angle to each other and oriented perpendicularly with a beam splitter placed at the vertex of the right angle and oriented at a 45° angle relative to the two mirrors (FIG. 3-12). An infrared beam incident on the beam splitter is divided into two parts, each of which propagates down one of the two arms and is reflected on the mirrors. The two beams then interfere at the beam splitter and the light transmitted is directed to the detector.

![Schematic diagram of a Michelson interferometer showing the path of the light beam from light source to the detector. One of the reflecting mirrors is movable to allow for an interference pattern to be recorded.](image)

In a FTIR spectrometer one of the reflecting mirrors is movable, to allow for an interference pattern to be recorded. The light intensity \( I(x) \) received at the detector at each position \( x \) of the movable mirror is called an interferogram. By Fourier transforming the interferogram, the spectral intensity distribution \( S(\nu) \) as function of frequency \( \nu \) is obtained. Usually, the frequency \( \nu \) is expressed in units of inverse centimeters (cm\(^{-1}\)), or wavenumbers.

When a sample (either a silicon substrate or a Si/SiO\(_2\) sample) is placed between the infrared source and the beam splitter, absorption occurs. This causes a change in the spectral intensity distribution. Therefore, in order to gather information on the deposited film, the transmittance \( T \) of a SiO\(_2\)–like film is measured:
\[ T(\nu) = \frac{S_{\text{substrate+film}}(\nu)}{S_{\text{substrate}}(\nu)} \] (3.6)

where \( S_{\text{substrate}} \) and \( S_{\text{substrate+film}} \) are the spectral intensity distribution of the silicon substrate with and without SiO\(_2\) film deposited, respectively.

In this research a Bruker Tensor 27 was used to perform measurements in a range of 400–8000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). All spectra are composed of 50 times averaged signals. The sample compartment is continuously purged with \( \text{N}_2 \) to minimize absorption by CO\(_2\) and H\(_2\)O from the atmosphere adsorbed on the film and present in the gas phase. The IR peak positions in SiO\(_2\) films as found in literature are listed in TABLE 3-4.

**TABLE 3-4: Infrared adsorption peak positions of SiO\(_2\) films.**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Mode</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O</td>
<td>1076</td>
<td>asymmetric stretch (in phase)</td>
<td>[58]</td>
</tr>
<tr>
<td>Si-O</td>
<td>1200</td>
<td>asymmetric stretch (180° out of phase)</td>
<td>[58]</td>
</tr>
<tr>
<td>Si-O</td>
<td>810</td>
<td>symmetric stretch</td>
<td>[58]</td>
</tr>
<tr>
<td>Si-O</td>
<td>457</td>
<td>rocking mode</td>
<td>[58]</td>
</tr>
<tr>
<td>C-H</td>
<td>2970</td>
<td>stretching mode</td>
<td>[42]</td>
</tr>
<tr>
<td>Si-CH(_3)_x</td>
<td>1260</td>
<td>bending mode</td>
<td>[59]</td>
</tr>
<tr>
<td>Si-(CH(_3))(_x)_x</td>
<td>840</td>
<td>stretching mode</td>
<td>[60]</td>
</tr>
<tr>
<td>Si-(CH(_3))(_x)_x</td>
<td>885</td>
<td>stretching mode</td>
<td>[60]</td>
</tr>
<tr>
<td>Si-H</td>
<td>2170</td>
<td>stretching mode</td>
<td>[61]</td>
</tr>
<tr>
<td>Si-OH</td>
<td>3450</td>
<td>stretching mode (hydrogen bonded)</td>
<td>[61,62]</td>
</tr>
<tr>
<td>Si-OH</td>
<td>3650</td>
<td>stretching mode (non-hydrogen bonded)</td>
<td>[61]</td>
</tr>
<tr>
<td>SiO-H</td>
<td>930</td>
<td>bending mode</td>
<td>[61,62]</td>
</tr>
</tbody>
</table>

3.3.2 Atomic force microscopy

Atomic force microscopy (AFM) is a powerful surface analysis technique with a resolution in the range from nano– to micrometers. This allows the imaging of surface structure and roughness towards the atomic scale (FIG. 3-13).

The AFM consists of a micro scale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever. In our case the deflection is measured using a laser beam reflected from the top of the cantilever on to a photodiode array. To be able to scan the surface the sample is mounted on a holder which is precisely displaced in \( x \) and \( y \) directions by means of piezoelectric elements. Another piezoelectric element in combination with a feedback mechanism is used to adjust the tip–to–sample distance to maintain a constant force between the tip and the sample.

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All AFM measurements in this research were performed in semi–contact dynamic mode. In dynamic mode the cantilever is externally oscillated at or close to its resonance frequency. The oscillation amplitude, phase and resonance frequency are modified by tip–sample interaction forces. These changes in oscillation with respect to the external reference oscillation provide information about the sample’s characteristics. Here, a user–defined amplitude of the oscillation is used as the feedback signal. Specially designed software (Nova, version 1.0.26) converts the obtained information into a topography image of the surface.

The AFM microscope used is a Solver Pro Scanning Probe Microscope from NT–MDT with NSG–11 tips (resonance frequency 120–325 kHz, tip curvature 10 nm). During a measurement an area of 2x2 µm² is scanned. In order to make statistical calculations several scans on different spots of the sample have to be taken.
4 Results & Discussion

In this chapter the results of various measurements performed in order to characterize the deposited SiO$_2$-like films are shown and discussed.

In section 4.1 the microstructural changes in SiO$_2$-like films are discussed as caused by tuning specific deposition conditions. The data interpretation is achieved by analyzing the SiO$_2$ film properties, such as the chemical composition determined from Fourier transform infrared (FTIR) measurements and the optical properties acquired with spectroscopic ellipsometry (SE). Furthermore, the porosity extracted from ellipsometric porosimetry (EP) measurements, as well as the type of pores present deduced from the shape of the isotherms are discussed. In § 4.1.1 the influence of radical growth flux is investigated by tuning the HMDSO flow rate. This is done for films deposited in the presence and absence of high-energy ion bombardment. Subsequently, in § 4.1.2 the influence of a variable ion energy at constant growth flux is discussed for sinusoidal radiofrequency (13.56 MHz) and pulse-shaped low-frequency (54 kHz) biasing conditions.

In section 4.2 the multilayer adsorption of ethanol on several dense SiO$_2$-like films is investigated. First, in § 4.2.1 the adsorption isotherms obtained on these dense films are compared and a reasoning is provided to identify films which can be truly defined as non-porous. For the non-porous films the ethanol multilayer thickness is determined from the SE analysis, after which observed differences are discussed. Subsequently, in § 4.2.2 two empirical models are used to model the experimental multilayer thickness, namely, the BET and FHH equation. From the obtained fit results the validity of the two equations is discussed with reference to literature. Finally, in § 4.2.3 the pore size distribution for two films containing mesopores is determined from the Kelvin equation. The influence of the ethanol multilayer on the Kelvin equation is discussed.

4.1 Microstructural characterization of SiO$_2$-like films

As explained in the Introduction chapter (section 1.2) the knowledge on the microstructure of SiO$_2$-like films is essential with respect to their application as diffusion barriers on polymers. In previous research the tunability of the chemical composition of ETP deposited films has been shown, i.e. from silicone-like to silica-like, depending on the plasma chemistry\textsuperscript{[13]}. The obtained silica-like films were found to be porous when deposited at room temperature. Further studies showed that both substrate temperature and ion bombardment are an effective tool to improve the density of the deposited films depending on the radical growth flux provided\textsuperscript{[12,42,63]}. Although changes in porosity were observed, no knowledge has been previously obtained about the type and size of the pores present during different stages of film densification or under the influence of varying growth rate. This section reports about the potential of ellipsometric porosimetry, combined with other diagnostics, in order to shed light on these research issues.
4.1.1 Influence of the radical growth flux

The influence of the radical growth flux on the microstructure of SiO\textsubscript{2}-like films has been investigated by varying the flow rate of HMDSO in the range 0.16–0.46 sccs. To get insight into the effect of high-energy ion bombardment, all depositions were performed in the absence and presence of pulse-shaped substrate biasing (-240 V). In particular this will provide insight into the influence of the ion-to-growth flux on the film densification process in a remote plasma. The other plasma parameters were kept constant at the conditions specified in TABLE 3-1.

- Optical analyses of the deposited films

In FIG. 4-1 the in situ refractive index ($n_{in}$) values, measured at the end of film deposition, are shown as a function of the HMDSO flow rate ($\Phi_{HMDSO}$). The error in the determination of the refractive index of ±0.001 is also included. This value is equal to the standard deviation determined from time dependent measurements. In the absence as well as presence of a substrate biasing it can be observed that the refractive index $n_{in}$ decreases linearly with increasing HMDSO flow rate. The difference in slope is due to a less efficient ion bombardment with increasing flow rate as discussed here below.

![FIG. 4-1 in situ refractive index values as a function of the HMDSO flow rate without applied bias (closed symbols) and with applied pulse-shaped bias (open symbols). The fits through the data points serve as a guide to the eye.](image)

For the SiO\textsubscript{2} films deposited in absence of biasing the decrease in $n_{in}$ is caused by the increase in radical growth flux ($3.8–8.4 \times 10^{19} \text{ m}^{-2}\text{s}^{-1}$) to the substrate for increasing HMDSO flow rate: the higher the growth flux, the more disordered is the deposited layer. This is most probably because of reduced surface diffusion processes during film growth. The substantial porosity of these films is supported by the fact that all in situ values are below the refractive index of fused silica (1.457 at 633nm).

In the case of films grown in the presence of a high pulse-shaped (p-s) bias voltage (-240 V) the decrease in refractive index is more pronounced, although all refractive index
values are higher than in the absence of ion bombardment, due to film densification. Moreover, the ion-assisted SiO\textsubscript{2} film deposited at the lowest HMDSO flow rate (0.16 sccs) has a refractive index equal to that of fused silica. This is an indication that the film contains almost no pores. Furthermore, the difference between refractive index obtained with and without ion bombardment becomes smaller for higher HMDSO flow rate. This shows that, besides the influence of an increasing flow rate, the ion-to-growth flux ratio definitely plays a role in the film densification process.

To see whether the changes in refractive index due to different HMDSO flow rates are only related to changes in porosity and not in chemical composition, the FTIR spectra of the SiO\textsubscript{2}-like films deposited both in the absence and presence of ion bombardment have been measured. These are shown in FIG. 4-2 with the position of known infrared adsorption bands for SiO\textsubscript{2}-like films (TABLE 3-3) indicated in the graph. Clearly, no carbon-related peaks are present in the IR spectra for all HMDSO flow rates. This means that the developed plasma chemistry causes a complete combustion of the hydrocarbon radicals (see Frame 3.1). Thus, the changes observed in the refractive index at different HMDSO flow rate are not due to incorporation of carbon in the SiO\textsubscript{2}-like films. This is consistent with results previously obtained for SiO\textsubscript{2}-like films deposited under similar conditions\cite{42}. The other characteristic features which are visible in the spectra are discussed later to be able to place them in a broader context (page 65).

**Porosity content of the deposited films**

The trends in FIG. 4-1 provide no quantitative information on the porosity content of the films. Therefore, ellipsometric porosimetry measurements were performed for the films under examination. As explained in § 2.3.1 the porosity \(P\) of a film can be extracted from the measurement using its refractive index obtained before adsorption of ethanol \(n_0\) and at saturation pressure \(n_{sat}\). The measured values for the analyzed films are shown in TABLE 4-1 together with the porosity values calculated via equation (2.26).

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FIG. 4-2 ex situ FTIR spectra of SiO\textsubscript{2}-like films deposited at different HMDSO flow rates (a) without applied bias, (b) with applied pulse-shaped bias.
When comparing the refractive index values $n_0$ before adsorption with the in situ refractive indices reported in FIG. 4-1, most $n_0$ values are found to be higher than the $n_{in}$. 

**TABLE 4-1:** Porosimetry results for SiO$_2$ films deposited at different HMDSO flow rates, both with and without applied substrate bias. The refractive index before adsorption $n_0$ and at saturation pressure $n_{sat}$ are reported for every $\Phi_{\text{HMDSO}}$ together with the calculated porosity $P$.

<table>
<thead>
<tr>
<th>$\Phi_{\text{HMDSO}}$ (sccs)</th>
<th>without bias $n_0$</th>
<th>$n_{sat}$</th>
<th>P (%)</th>
<th>with bias $n_0$</th>
<th>$n_{sat}$</th>
<th>P (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.16</td>
<td>1.405</td>
<td>1.462</td>
<td>13.4</td>
<td>1.456</td>
<td>1.463</td>
<td>0</td>
</tr>
<tr>
<td>0.30</td>
<td>1.386</td>
<td>1.449</td>
<td>15.1</td>
<td>1.418</td>
<td>1.464</td>
<td>11.0</td>
</tr>
<tr>
<td>0.46</td>
<td>1.376</td>
<td>1.451</td>
<td>18.0</td>
<td>1.388</td>
<td>1.463</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Due to exposure to air, the films have undergone an irreversible ageing, i.e. in terms of oxidation through O$_2$ and H$_2$O vapor. The values of $n_0$ therefore, correspond to the films from which only physisorbed H$_2$O present in the porous structure can be removed by means of pumping and annealing, according to the procedure described in § 3.2.1.

The calculated porosity values are shown in FIG. 4-3 as a function of the HMDSO flow rate. An increase of porosity is observed for increasing flow rate for both the situation with and without external substrate bias applied.

![FIG. 4-3. Calculated porosity values as a function of HMDSO flow rate without bias applied (closed symbols) and with pulse-shaped bias applied (open symbols). The fits through the data points serve as a guide to the eye.](image)

In the absence of ion bombardment the increase in porosity is linear with HMDSO flow rate. This is in agreement with the decrease in refractive index discussed above. However, when a high pulse-shaped bias voltage of -240 V is applied, the increase in porosity as function of HMDSO flow rate is non-linear. This shows that in the presence of ion-bombardment the porosity trend gives complementary information to the refractive index.
The influence of the high bias voltage promotes a quantitative porosity removal from 13.4% to 0% for the lowest HMDSO flow rate (0.16 sccs). Also at an intermediate flow rate of 0.30 sccs the ion bombardment still reduces the porosity, although the change is less pronounced: 15.1% without and 11% with applied bias. This shows that although the energy of the ions is high, as can be deduced from equation (2.29) in § 2.4.2, the amount of ions is not sufficient to induce full densification. Finally, at the highest HMDSO flow rate (0.46 sccs) the porosity is not affected within the error (±1%) by the presence of ion bombardment, although there is a difference in refractive index (FIG. 4·1). Clearly, the refractive index of a film does not provide a complete picture about film density in terms of accessibility to environmental species. A possible reason for this will be discussed later on (page 63).

To see whether the obtained porosity values are realistic for SiO$_2$-like films, a comparison is made with previous evaluations of film porosity. This is done for a carbon-free SiO$_2$-like film deposited at a HMDSO flow rate of 0.4 sccs in the absence of ion bombardment$^{[13]}$. For this film Creatore et al.$^{[13]}$ obtained a porosity of 23% by means of the EMA method as explained in § 1.1.2. Using ellipsometric porosimetry the SiO$_2$-like film deposited at a HMDSO flow rate of 0.46 sccs has a porosity of 18% in the absence of substrate biasing (TABLE 4·1). Thus, different values of porosity are obtained for films deposited at similar conditions. Moreover, both films have an in situ refractive index of approximately 1.35. Baklanov et al.$^{[23]}$ also observed this difference for a spin-on low $k$ silica film with a measured refractive index of 1.35. By means of the EMA method a porosity of 25% was found, while ellipsometric porosimetry measurements using toluene as the solvent showed a value of 15.2%. The difference was attributed to problems with the liquid penetration into fine micropores.

This leads to consider that the EMA method provides the total porosity$^{[12]}$, whereas ellipsometric porosimetry probes only the open porosity. Either due to the physical presence of the probe molecule (steric and isotropic effects$^{[22]}$) or because the pores are not connected to the external surface. Thus, the porosity values calculated from ellipsometric porosimetry are most probably in agreement with previous results, taking into account the difference between open porosity and total porosity. Besides, with respect to the application of diffusion barrier, knowledge about the open porosity is of most interest.

As discussed above the substrate biasing technique appears to be mostly effective at lower growth fluxes. To prove that this is indeed attributable to the amount of available ions, the ion-to-growth flux ratio is determined as a function of HMDSO flow rate. At each HMDSO flow rate the growth flux $\Gamma_{growth}$ is obtained from equation (2.28) in § 2.4.2 corresponding to the deposition rate $R_d$ listed in TABLE 4·2. The ion flux $\Gamma_{ions}$ for the pulse-shaped bias is calculated via equation (3.2) with the appropriate ion current $I_{ions}$ obtained according to equation (3.4) from § 3.1.3. The ion-to-growth flux ratio $\Gamma_{ions}/\Gamma_{growth}$ determined for each HMDSO flow rate at a bias voltage of -240 V is shown in TABLE 4·2.
A decreasing ion-to-growth flux ratio is observed for increasing HMDSO flow rate, which means less effective biasing for higher flow rate due to insufficient ions. The trend in porosity with applied bias approaches the one without bias for increasing HMDSO flow rate (FIG. 4-3), indicating that substrate biasing becomes effective for flow rates below 0.46 sccs. According to TABLE 4-2 this corresponds to an ion-to-growth flux ratio larger than ~0.11. Furthermore, at a HMDSO flow rate of 0.16 sccs the refractive index \( n_{in} \) of 1.458 together with the zero porosity indicate an optimum in the flux ratio within the range 0.21-0.66. Due to lack of data in the full range, the ion-to-growth flux ratio of 0.66 is taken as the critical ratio defined in § 2.4.2. This value is slightly higher than the ratio of 0.4-0.5 found by Lefèvre et al.[45]. However, considering the different plasma generation (rf-induced) and chemistry (silane-based) in this reference, the agreement is good. Moreover, from previous research using a pulse-shaped substrate bias in combination with the ETP plasma, a critical ion-to-growth flux ratio of 0.61 was determined[63]. In conclusion this discussion confirms that the densification is controlled by the ion flux per depositing particle.

- **Microstructural analyses of the deposited films**

Besides the information on the film porosity, the isotherm studies allow to obtain details about the microstructure, i.e. type and size of the pores, by analyzing the shape of adsorption-desorption isotherms and the possible presence of hysteresis, as discussed in § 2.2.2. The adsorption-desorption isotherms corresponding to the HMDSO flow rate series are discussed below.

**Isotherms at a flow rate of 0.16 sccs**

In FIG. 4-4 the obtained isotherms at a HMDSO flow rate of 0.16 sccs are shown, both in the absence and presence of substrate biasing. Due to the high-energy ion bombardment in combination with an ion-to-growth flux ratio of 0.66, the isotherm shape changes from a type I to a type II isotherm. This indicates a change from a microporous to a non-porous SiO\(_2\) film. The type II isotherm (non-porous) for the ion-assisted grown film has a well defined inflection point, meaning that monolayer adsorption is mostly complete before multilayer adsorption begins. This also indicates that ethanol interacts strongly with the SiO\(_2\) surface, while the interaction between the solvent molecules is less pronounced. Thus, the ethanol molecules prefer to physisorp at available surface sites, thereby covering the complete surface, instead of forming small clusters at the most active sites. In literature

\[ \text{In § 4.1.2 the densification process is investigated as function of ion energy at constant growth flux, which allows properly the determination of the critical ion-to-growth flux ratio.} \]
this is attributed to the fact that the hydroxyl (-OH) group of ethanol induces hydrogen bonding with SiO₂ surface groups.

The type I isotherm (microporous) for the film deposited without substrate biasing has a steep rise for extremely small relative pressures \( \frac{p}{p_0} \ll 0.1 \). This is due to the process of primary micropore filling, which takes place in pores of about twice the molecular diameter (§ 2.2.1). For ethanol this diameter is between 0.35 and 0.55 nm depending on the configuration of the molecule (TABLE 3-3). So, in the case of ethanol, primary micropore filling occurs in pores of approximately 0.7-1.1 nm. This is in agreement with literature, which reports primary micropore filling for pores of such dimensions occurring for relative pressure \( \frac{p}{p_0} \) in the range 0.016-0.022 \[^{[65]}\]. Moreover, this allows concluding that the smallest micropores probed by ethanol in SiO₂-like films have a diameter of approximately 0.7 nm.

For relative pressures above 0.022 secondary micropore filling occurs, which can be observed from the more gradual increase of the refractive index. Normally, this process will continue until a plateau is reached for higher pressure. However, in our case a linear increase occurs for a relative pressure between 0.2 and 0.4, indicating the simultaneous occurrence of a second process. This process may be adsorption in small mesopores (\( \leq 2 \) nm), supported by the fact that the slope of the linear section is the same as in the obtained type IV isotherms (FIG. 4-5 and FIG. 4-6). Moreover, adsorption in mesopores is not always accompanied by a hysteresis loop \[^{[20,66]}\]. This means that the mesopores are too small for capillary condensation to take place. Finally, for relative pressures above \( \sim 0.55 \) a plateau is reached which slightly rises, indicating the occurrence of multilayer adsorption on the outer film surface.

This discussion leads us to conclude that at an HMDSO flow rate of 0.16 sccs without ion bombardment the deposited SiO₂ film contains a wide range of micropores, most likely
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Extending into the lower mesopore range. In the presence of effective ion bombardment the micropores are all affected, which results in a non-porous film.

Isotherms at a flow rate of 0.30 sccs
For a HMDSO flow rate of 0.30 sccs the shape of both isotherms change compared to those at 0.16 sccs (FIG. 4-5). In the absence of biasing a type IV isotherm is recorded, indicating the incorporation of more and larger mesopores. However, an ideal type IV isotherm should resemble a type II (non-porous) isotherm for relative pressures up to the hysteresis loop (§ 2.2.2). Thus, looking at the inset in FIG. 4-4 the uptake for $p/p_0 < 0.1$ should only lead to a very small change in refractive index. In our case the ethanol uptake is much higher, promoting a large variation in refractive index and, therefore, indicating also the presence of micropores. This means that for the lower relative pressures the isotherm shape corresponds more to a type I. Moreover, the shape of the hysteresis loop resembles more a type H4, which is also an indication that next to mesopores also a substantial amount of adsorption occurs in micropores (§ 2.2.2). Again, the steep rise and subsequent more gradual increase of refractive index show that both primary and secondary micropore filling occurs. The onset of capillary condensation over a large range of pressures ($p/p_0\sim0.35-0.65$) indicates that the mesopores have a rather large distribution in size. However, the small increase of the refractive index for both the adsorption and desorption branch in the capillary condensation regime, indicates the presence of a small amount of mesopores relative to the number of micropores.

![Graph showing refractive index as a function of relative ethanol pressure](image)

FIG. 4-5 Isotherms showing refractive index $n$ as a function of relative ethanol pressure $p/p_0$ during adsorption (closed symbols) and desorption (open symbols): ●/○ – without bias; ♦/◊ – with bias.

When high-energy ion bombardment is applied, the increase of HMDSO flow rate from 0.16 to 0.30 sccs is accompanied by a change in the isotherm shape from a type II to a type I. Thus, microporosity appears in the SiO$_2$ film due to the less effective biasing at higher flow rate. Both primary and secondary micropore filling occurs, which means that a wide range of micropores is present. Also, the isotherm is a true type I, without the pronounced linear increase observed for the type IV isotherms, which indicates the
Results & Discussion

absence of mesopores. Thus, ion bombardment still induces densification in the mesoporous size range, whereas micropores are marginally affected.

Isotherms at a flow rate of 0.46 sccs
From FIG. 4-6 it can be concluded that at a HMDSO flow rate of 0.46 sccs both isotherm shapes are of type IV.
The SiO₂ film deposited without bias has a slightly more pronounced hysteresis loop compared to the isotherm obtained at a HMDSO flow rate of 0.30 sccs (FIG. 4-5). Also a larger increase of both the adsorption and desorption branch leading towards the plateau is observed for \( p/p₀ > 0.35 \). This indicates that more mesopores are incorporated in the film, although, the amount of mesopores is still small compared to the number of micropores. When looking at the low pressure range (\( p/p₀ < 0.35 \)) the change in refractive index from empty pores until the onset of capillary condensation is noticeably larger when compared to the isotherm obtained at a flow rate of 0.30 sccs. Therefore, a HMDSO flow rate of 0.46 sccs also results in the incorporation of more micropores during SiO₂ film growth.

When a substrate bias is applied at a HMDSO flow rate of 0.46 sccs, the obtained type IV isotherm shows that ion bombardment is no longer effective in removing the mesopores, due to the low ion-to-growth flux ratio, as reported in TABLE 4-2. Since the isotherm is barely affected as compared to the situation without ion bombardment, similar considerations can be drawn in terms of refractive index change.

Although both isotherms at a HMDSO flow rate of 0.46 sccs are of type IV, the one obtained with high-energy ion bombardment is completely shifted to higher refractive index values. As was observed in FIG. 4-1 also the in situ refractive index values show the same trend. However, the calculated porosity is nearly the same in both situations.
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(TABLE 4-1). The most probable explanation is that the SiO₂ film deposited without ion bombardment contains more closed porosity. As ethanol is not able to probe closed pores, the measured changes in the refractive index during adsorption do only arise from filling of the open pores. However, ellipsometry measures an effective refractive index which contains a contribution from the film matrix, open pores, and closed pores (FIG. 2·14). Thus, the absolute value of refractive index will be different, depending on the amount of closed pores present in the film. The open porosity, however, is determined by the difference in refractive index at saturation pressure and before adsorption, which is independent of absolute value. Therefore, the obtained open porosity can be the same, while the different values of in situ refractive index as well as the shift in isotherm level correspond to a difference in closed porosity. Following this reasoning, the conclusion can be drawn that under these experimental conditions the ion bombardment affects only the closed porosity.

A general observation is that for all type IV isotherms the onset of capillary condensation occurs at a relative pressure of 0.353. In literature this point is shown to be only dependent on the adsorptive and the operational temperature

TABLE 4-3 for the HMDSO flow rate series.

Thus, the absolute value of refractive index will be different, depending on the amount of closed pores present in the film. The open porosity, however, is determined by the difference in refractive index at saturation pressure and before adsorption, which is independent of absolute value. Therefore, the obtained open porosity can be the same, while the different values of in situ refractive index as well as the shift in isotherm level correspond to a difference in closed porosity. Following this reasoning, the conclusion can be drawn that under these experimental conditions the ion bombardment affects only the closed porosity.

The amount of micropores and mesopores to the open porosity can be calculated, as reported in TABLE 4-3 for the HMDSO flow rate series.

TABLE 4-3: The open porosity of micropores \( P_{\text{micro}} \) and mesopores \( P_{\text{meso}} \) reported for every \( \Phi_{\text{HMDSO}} \)-The ratio \( \rho \) between micro–and mesopore contribution is also indicated.

| \( \Phi_{\text{HMDSO}} \) (sccs) | without bias | with bias (-240 V) |
|-------------------------------|-------------|----------------|----------------|----------------|
|                               | \( P_{\text{micro}} \) | \( P_{\text{meso}} \) | \( P_{\text{micro}} \) | \( P_{\text{meso}} \) |
| 0.16                          | 11.0        | 2.4            | 0.22           | 0              | 0              | -              |
| 0.30                          | 11.2        | 3.9            | 0.35           | 8.9            | 2.1            | 0.24           |
| 0.46                          | 13.2        | 4.8            | 0.36           | 13.4           | 4.4            | 0.33           |

The amount of micro–and mesopores increases with increasing HMDSO flow rate, both in the absence and presence of ion bombardment. However, the presence of micropores is always larger compared to the amount of mesopores, as was already indicated by the isotherms. The ratio \( \rho \) between micro–and mesopore contribution for the situation without substrate biasing, shows that an increase of the HMDSO flow rate from 0.16 to 0.30 sccs leads mostly to the incorporation of mesopores in the deposited film. For further increase of flow rate to 0.46 sccs the ratio \( \rho \) remains constant, which means that the amount of micro–and mesopores is equally affected.
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At a flow rate of 0.30 sccs the presence of ion bombardment not only decreases the amount of both micro– and mesopores, but also decreases the ratio $\rho$ from 0.35 to 0.24. Thus, the mesopores are mostly affected when compared to the micropores. At a HMDSO flow rate of 0.46 sccs the ion bombardment has no effect, as the differences in porosity are within the experimental error ($\pm 1\%$). The information from TABLE 4–3 supports the above discussion of the isotherms.

- Chemical analysis of the deposited films

The influence of radical growth flux on the microstructure of plasma-deposited SiO$_2$ films is evident from the above discussion. To see whether the observed changes in microstructure are related to changes in chemical composition, the FTIR spectra shown in FIG. 4–2 are further analyzed as they may provide complementary information. For this reason the FTIR spectra in the frequency range of the symmetric and asymmetric Si–O–Si stretching and the Si–OH stretching modes are shown in detail for the different HMDSO flow rates (FIG. 4–7).

![FTIR spectra of SiO$_2$-like films deposited at different HMDSO flow rates without substrate bias applied: (a) frequency region containing the Si–OH stretching (S) modes, (b) frequency region containing the Si–O–Si stretching (S) modes and the SiO–H bending (B) mode. Here, AS and SS indicate asymmetric and symmetric stretching, respectively.](image)

As can be seen from the Si–OH stretch peaks (FIG. 4–7a) the films contain a substantial amount of −OH (hydroxyl) groups for all HMDSO flow rates. At flow rates of 0.16 and 0.30 sccs the peak areas are the same within the error. However, at a HMDSO flow rate of 0.46 sccs the intensity of the stretching peaks is higher and the overall band broadens and shifts towards lower wavenumber values. This means that the S1 stretching peak is more pronounced than the S2 peak. The S1 peak is known to be associated with silanol (Si–OH) groups which are hydrogen bonded to neighboring −OH groups, while the S2 peak results from isolated or ‘free’ silanol groups. Thus, the more pronounced S1 peak at a HMDSO flow rate of 0.46 sccs indicates that the concentration of −OH groups is high enough to induce hydrogen bonding.
In FIG. 4-7b the AS1 and AS2 asymmetric stretching peaks of Si-O-Si are shown, together with the SS symmetric stretching peak. For increasing HMDSO flow rate the AS1 and SS peak areas decrease. The AS2 peak appears to be unaffected for flow rates of 0.16 and 0.30 sccs, however, at a flow rate of 0.46 sccs the shape clearly changes. In literature this shape of the Si-O-Si asymmetric stretching band is related to larger amounts of terminal groups, like –OH\[42\]. Furthermore, a small SiO-H bending feature appears at ~920 cm\(^{-1}\) for increasing HMDSO flow rate.

All trends in FIG. 4-7 indicate a reduction of Si-O-Si bonds with increasing HMDSO flow rate while the number of Si-OH bonds increases. From literature –OH groups are known to be chain terminating\[42,68\], which means that the growth of a continuous Si-O-Si chain is ended by the incorporation of an –OH group at the silicon bond. This introduces porosity in the SiO\(_2\) structure. Thus, the more –OH groups are present the more porous the film becomes. So, the presence of the Si-OH stretching band for all HMDSO flow rates indicates that the films contain substantial porosity, as was already pointed out by the porosimetry measurements. However, an increase of the Si-OH peak intensity is only observed for 0.46 sccs of HMDSO. Moreover, this increase seems to be mainly associated with the S1 contribution. As can be observed in TABLE 4-3, the change in silanol concentration coincides with the further increase in the amount of micropores. This leads to hypothesize that the S1 peak is correlated to the process of secondary micropore filling, i.e. the close proximity of silanol groups at the surface of large micropores induces hydrogen bonding in between them. Accordingly, the more pronounced S1 peak at a flow rate of 0.46 sccs explains the increase in the amount of micropores. In general this indicates that Si-OH groups are most likely related to the presence of mesopores and large micropores.

By analyzing the shape of the main Si-O-Si adsorption band, additional information on changes in the SiO\(_2\)-like film microstructure may be assessed. From literature it is known that peaks at higher wavenumber values refer to larger bonding angles\[45\]. Moreover, the AS2 stretching peak is associated with disorder in the network structure and the presence of defects in the film\[42\]. Therefore, the AS1-to-AS2 peak area ratio is a measure for structural changes in the SiO\(_2\) film.

The area ratios, as obtained from the deconvolution of the adsorption band, are shown in FIG. 4-8a as a function of HMDSO flow rate. For an HMDSO flow rate of 0.46 sccs four Gaussian peaks were needed to correctly deconvolute the experimental data (FIG. 4-8b), whereas for the other flow rates two peaks were sufficient. However, the areas of the two peaks around the position of the AS1 peak (~1076 cm\(^{-1}\)) can be combined into a total peak area ‘representing’ the AS1 stretch. In the same way this is done for the two peaks around the AS2 peak position (~1200 cm\(^{-1}\)). Thus, the AS1-to-AS2 ratio can also be calculated for a HMDSO flow rate of 0.46 sccs.
The AS1-to-AS2 peak area ratio decreases linearly for increasing HMDSO flow rate. This means that at higher flow rate the AS2 peak becomes more important. Thus, increasing the HMDSO flow rate leads to larger bonding angles, which means that, relatively, the amount of larger rings becomes more pronounced. Furthermore, this shows that besides an increasing amount of porosity, the film matrix density also decreases\[^{12}\].

The presence of ion bombardment increases the AS1-to-AS2 area ratio at each HMDSO flow rate. Thus, ion bombardment leads to densification and reduction of porosity, as was indeed previously observed\[^{42}\]. Furthermore, the decrease of the AS1/AS2 ratio is larger than in the absence of ion bombardment. This reflects in the trends observed in the refractive index as a function of HMDSO flow rate which was shown in FIG. 4-1. Thus, the infrared data confirms the efficiency of ion bombardment at low HMDSO flow rate.

Moreover, the higher AS1-to-AS2 ratio at a flow rate of 0.46 sccs in the presence of ion bombardment further explains the difference in refractive index at equal open porosity.
In conclusion, the data presented in this section show that the SiO$_2$ microstructure can be unraveled by means of ellipsometric porosimetry. The technique provides information on the *open* porosity, while the simple determination of the refractive index does not allow discerning between *open* and *closed* porosity. Examination of the isotherm shape allows determining the amount and type of *open* pores present in the film. In particular the ellipsometric porosimetry measurements lead to the following considerations:

- Relatively small changes in the radical growth flux ($3.8\cdot8.4\cdot10^{19}$ m$^{2}$s$^{-1}$) have considerable effects on the microstructure of the deposited SiO$_2$-like films. The induced changes in porosity involve a transition in type and size of the pores. However, the minimum pore size probed by ethanol is ~0.7 nm.

- In the absence of ion bombardment the increase in growth flux induces an increase in both the amount of micro –and mesopores. However, the amount of micropores always dominates over that of the mesopores, i.e. the microporosity increases from 11 to 13.2%, while the mesoporosity only ranges from 2.4 to 4.8%.

- Changing the growth flux in the presence of ion bombardment influences the film densification at constant and high ion energy (240 eV). Only under an optimal ion-to-growth flux ratio (~0.66) both micro –and mesopores are quantitatively eliminated leading to complete film densification. When the flux ratio is not optimal, the mesopores are mainly affected in comparison to the micropores.

The presence of a critical ion-to-growth flux ratio (~0.66) in controlling the efficiency of film densification is thus confirmed. Even while using ions of a constant high energy, the ion-to-growth flux ratio is a parameter that can be used to tune the densification process, i.e. the type and size of pores present in the deposited SiO$_2$ film.

Complementing the ellipsometric porosimetry data with the performed FTIR analysis gives the following additional information:

- A correlation appears to exist between the concentration of Si-OH groups and the presence of mesopores and large micropores in SiO$_2$-like films. Hydrogen-bonded -OH groups appear to be mainly associated with micropores close to the mesopore regime.

- The difference in refractive index for films with equal *open* porosity is related to the specific arrangement of the SiO$_2$ ring network, i.e. the matrix density or *closed* porosity is different. Thus, determination of the refractive index only is insufficient to obtain a complete picture about film density in terms of accessibility to environmental species.
4.1.2 Influence of the ion energy: a comparison of two biasing techniques

In the previous section the influence of the ion-to-growth flux ratio on the SiO\textsubscript{2}-like film densification has been addressed under conditions of high ion energy. To investigate the influence of ion energy on the densification process, depositions have been performed as function of applied bias voltage at constant growth flux. The substrate biasing has been achieved by means of the sinusoidal radiofrequency and low-frequency pulse-shaped bias in order to compare the induced microstructural changes. The other plasma parameters were kept constant at the conditions specified in TABLE 3-1.

- Optical analyses of the deposited films

In FIG. 4-9 the measured \textit{in situ} refractive index ($n_{\text{in}}$) as a function of the applied bias voltage is shown for SiO\textsubscript{2} films deposited at a constant HMDSO flow rate of 0.16 sccs under radiofrequency (rf) and pulse-shaped (p-s) low-frequency biasing. In both cases $n_{\text{in}}$ increases exponentially for increasing bias voltage: from the fits it can be deduced that for the used deposition conditions the refractive index saturates at a value of 1.488 for the rf bias and a value of 1.479 for the p-s bias. Both these values of $n_{\text{in}}$ are higher than the one of thermal silica (1.465) showing that ion bombardment eventually leads to dense films.

When looking at FIG. 4-9 into more detail the overall refractive index values of the SiO\textsubscript{2} films obtained using the rf bias are higher compared to those of the p-s bias. This suggests that the rf bias provides a more effective film densification than in the case of the p-s bias. However, the discussion here below brings to the conclusion that this can be attributed to a change in downstream pressure due to the different argon flow rate values: 100 and 80 sccs for the rf and p-s bias series, respectively. In fact, when the p-s experiments are performed at an argon flow rate of 100 sccs, similar refractive index values are obtained as for the rf bias series (see inset of FIG. 4-9b).
At constant HMDSO and O\textsubscript{2} flow rates the pressure in the chamber will decrease with decreasing argon flow rate at constant pumping speed. This will lead to an increase of the width of the expanding plasma beam, resulting in a lower flux of depositing particles per unit of area. As shown in FIG. 4-10 this causes an increase in the deposition rate for increasing argon flow rate, accompanied by an increase in the refractive index. Furthermore, previous research has shown that for an argon flow rate ≥40 sccs, the flux of Ar\textsuperscript{+} emanating from the source is constant at an arc current of 75 A\textsuperscript{[52]}. So, in principle the dissociation process of HMDSO and O\textsubscript{2} is the same for both an argon flow rate of 100 and 80 sccs, as can be reasoned from the reaction mechanisms shown in Frame 3.1 in § 3.1.2.

Then, the changes in refractive index in FIG. 4-10b lead to conclude, that the overall lower refractive index values obtained with the p-s bias (at 80 sccs) compared to the rf bias (FIG. 4-9) are mainly caused by the difference in argon flow rate.

A last remark concerns with the refractive index value for the SiO\textsubscript{2}-like film deposited in the absence of ion bombardment in FIG. 4-9b. According to the trend in FIG. 4-10b this value should approximately be 1.375 at an argon flow rate of 80 sccs. The lower value obtained for this film is most likely due to a deviation in the actual HMDSO flow rate during deposition.

In case of the p-s bias, porosimetry measurements have been only performed for the films deposited at an argon flow rate of 80 sccs. However, to investigate the influence of the ion energy on the densification process this makes no difference. In the following, therefore, only the p-s bias series at 80 sccs will be further discussed, together with the rf bias series. A remarkable difference between the rf and p-s bias is found in the range of bias voltages necessary to achieve film densification: in the case of the p-s bias the ion energy needed to densify the SiO\textsubscript{2}-like film is much larger. Two hypotheses are here taken into consideration:

The difference may be related to the fact that $V_{dc}$, in the case of the rf bias, is only an average voltage. This means that ions of above-average energy may contribute to a better
Results & Discussion

In our deposition plasma the ion sheath transit time is in the order of ~100 ns, which has been determined by means of the Child-Langmuir law assuming an electron temperature in the plasma beam of 0.3 eV (§ 3.1.1). This is comparable to the rf waveform period (~74 ns) and, therefore, the ions experience a varying sheath potential. So, when applying the rf bias the ions are accelerated by an electric field that corresponds to the potential drop across the sheath at the moment the ions arrive at the plasma sheath boundary. This is the reason for the occurrence of the bimodal ion energy distribution (IED) as discussed in § 2.4.2. According to literature the low and high-energy peaks of the IED are roughly located at the average energy, plus or minus the amplitude of the rf potential, respectively. From voltage probe measurements the highest potential drop across the sheath in this study is found to be approximately -78 V. Thus, even the highest energy obtained with the rf bias is never above one third of the maximum energy value of the p-s bias. This means that, independently of the bimodal energy distribution, the energy of the ions in case of the p-s bias is always higher than in the case of the rf bias.

Another explanation in case of rf biasing may be the capacitive coupling of rf power, which will lead to the generation of an additional local plasma. This is supported by the presence of a glow observed around the substrate holder. Due to this local plasma, additional ions are present which are also accelerated towards the substrate and cause ion bombardment. This means that even though the ion energy is less than for the p-s bias, the increased amount of ions in the case of the rf bias contributes to better film densification. To quantify this hypothesis the critical parameters concerning the ion bombardment are calculated, using the refractive index of thermal silica (1.465) as reference for a dense SiO$_2$ film. This corresponds to a required applied bias voltage of approximately -42 and -280 V in case of the rf and p-s bias (FIG. 4-9), respectively. Then, the critical parameters are calculated according to the principles described in § 2.4.1 and § 3.1.3. In TABLE 4-4 the critical values of the ion-to-growth flux ratio $\Gamma_{\text{ions}}/\Gamma_{\text{growth}}$, ion energy $E_i$, and energy per deposited particle $E_p$ are shown for both biasing techniques.

<table>
<thead>
<tr>
<th>parameter</th>
<th>rf bias</th>
<th>p-s bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left(\Gamma_{\text{ions}}/\Gamma_{\text{growth}}\right)_c$</td>
<td>2.74</td>
<td>0.37</td>
</tr>
<tr>
<td>$E_{i,c}$</td>
<td>42</td>
<td>280</td>
</tr>
<tr>
<td>$E_{p,c}$</td>
<td>115</td>
<td>104</td>
</tr>
</tbody>
</table>

The ion-to-growth flux ratio of the p-s bias is in the same order as the 0.4·0.5 found by Lefèvre et al., however, the ratio of the rf bias is roughly 7.5 times larger. Thus, this indeed supports the hypothesis of additional plasma generation around the substrate holder when using rf biasing. In terms of ion energy the situation is opposite, i.e. low energy for the rf bias compared to the p-s bias. Although the ion-to-growth flux ratio and ion energy are totally different between the rf and p-s bias, combination of the two parameters gives comparable results for the energy per deposited particle in both cases. So, this could give an explanation for the equal densification at different ranges of densification than via p-s biasing.
applied bias voltage observed in FIG. 4-9. However, the calculations of the different parameters depend on various assumptions as explained in § 3.1.3. Therefore, dedicated experiments should be performed to determine the actual biasing parameters for both systems in order to validate the above statements.

The trend in refractive index shows that increasing ion energy leads to film densification for both bias systems. However, no insight has been provided into the development of the densification process in terms of porosity content and pore size distribution. This means that the microstructural changes may evolve differently depending on the bias system used to promote the film densification.

- **Porosity content of the deposited films**

To further investigate the influence of ion energy on the microstructure of SiO$_2$-like films, porosimetry measurements have been performed for films deposited at various bias voltages. In TABLE 4-5 the obtained results are shown and the calculated porosity $P$ is plotted as a function of applied bias voltage in FIG. 4-11 for both the rf and p-s bias series.

<table>
<thead>
<tr>
<th>bias voltage</th>
<th>rf bias</th>
<th>p-s bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>V_{dc}</td>
<td>$ (V)</td>
</tr>
<tr>
<td>2.8</td>
<td>1.419</td>
<td>1.466</td>
</tr>
<tr>
<td>12</td>
<td>1.444</td>
<td>1.471</td>
</tr>
<tr>
<td>16</td>
<td>1.455</td>
<td>1.468</td>
</tr>
<tr>
<td>21</td>
<td>1.459</td>
<td>1.470</td>
</tr>
<tr>
<td>30</td>
<td>1.457</td>
<td>1.465</td>
</tr>
<tr>
<td>46</td>
<td>1.472</td>
<td>1.477</td>
</tr>
</tbody>
</table>

As already observed in the case of the samples deposited at different HMDSO flow rates in § 4.1.1, the obtained $n_0$ values are higher than the $n_{sat}$ values (FIG. 4-9). Again this is most likely due to irreversible ageing due to oxidation or small changes in the microstructure caused by the heating procedure.

As can be observed in FIG. 4-11 the porosity $P$ decreases linearly with increasing bias voltage for both the rf and p-s bias. In the case of the p-s bias a single slope is observed for the whole range of the applied bias voltages. The rf bias first shows a relative steep decrease for a bias voltage up to $|V_{dc}| = 16$ V and then decreases slower for higher bias voltages. Consequently, already ~70% of the pores disappear, when the applied bias voltage is only a third of the highest value applied. In comparison, the p-s bias only reaches this amount when the applied bias voltage is more than two thirds of the investigated voltage range.
Moreover, the trends in porosity $P$ do not reflect the exponential trends in the \textit{in situ} refractive index for increasing bias voltage (FIG. 4·9). As previously reported when commenting on the HMDSO flow rate series, the difference is related to the probing nature of the porosimetry measurements. This shows again that the refractive index of a film does not provide a complete picture about film density in terms of accessibility to environmental species. Thus, the porosimetry measurements can give complementary information about the microstructure of the SiO$_2$-like films under the influence of ion bombardment. For a detailed interpretation of the trends in FIG. 4·11, the corresponding adsorption isotherms are discussed first.

- **Microstructural analyses of the deposited films**

The isotherms are shown in FIG. 4·12 for each bias voltage in the case of rf and p·s bias. Due to the absence of hysteresis for all the isotherms obtained, the desorption branches are omitted as they do not contain additional information. The obtained refractive indices as function of the relative pressure have been scaled to the $n_0$ value of each film to highlight the influence of the ion bombardment, according to:

$$\text{Adsorption} = \left( \frac{n_x^2 - 1}{n_x^2 + 2} \right) - \left( \frac{n_0^2 - 1}{n_0^2 + 2} \right)$$

(4.1)

where $n_x$ is the obtained refractive index at a certain relative pressure $x$.

First the results of the films deposited with the rf·bias shown in FIG. 4·11a and FIG. 4·12a are discussed. In the absence of bias the isotherm shape is characterized by a combination of type I and type IV, as witnessed by the presence of an inflection point but the absence of hysteresis. This behavior indicates that the SiO$_2$ film contains both micropores and mesopores. However, the absence of hysteresis suggests that the mesopores are small and, therefore, are in the micropore-mesopore boundary region ($\leq$2 nm). The steep rise for low relative pressure values and the subsequent gradual increase implies the occurrence of both primary and secondary micropore filling. Thus, a large
Results & Discussion

The distribution of micropore size towards the mesopore range is present which results in a porosity of 11.1%. By applying a bias voltage of ~12 V the isotherm shape becomes a true type I, which indicates that only micropores are present in the deposited SiO$_2$ film. Thus, already at this low bias voltage all mesopores are completely removed from the film. The overall lower level of the isotherm compared to the one obtained without ion bombardment implies that also the amount of micropores is considerably reduced. However, the ongoing rise of the isotherm up to large relative pressure values shows that the film still contains a large pore size distribution. In this case the film has, relatively, an extremely small external surface, which means that almost no multilayer adsorption takes place. The complete removal of mesopores combined with the reduction of the amount of micropores, leads to a residual porosity of 6.2%.

Increasing the applied bias voltage to ~16 V results in an isotherm shape which is still predominately type I. However, a partial type II behavior is indicated by the upwards bending for relative pressures above ~0.5, as a typical type I isotherm would lead to a straight plateau. Again the amount of micropores is considerably reduced, as indicated by the lower level of the isotherm. The upwards bending for $p/p_0 > 0.5$ is due to relatively more multilayer adsorption on the external film surface. This implies that the total inner micropore surface starts to become equal to the external surface.

Further increase of the applied bias voltage above ~16 V leads to a transition in isotherm shape from mostly type I towards completely type II at ~46 V. This indicates that the amount of micropores decreases and eventually a non-porous film is obtained, in terms of ethanol adsorption. Thus, the remaining pores are at least smaller in size than ~0.7 nm, as previously reasoned in § 4.1.1.

In the case of the SiO$_2$ films deposited in the presence of the p-s bias the change in isotherm shape with increasing bias voltage is different (FIG. 4-12b), as already indicated by the porosity trend (FIG. 4-11b). In the absence of external biasing the
isotherm shape is characterized by a combination of type I and type IV, also in agreement with the data in the rf series. Thus, a porosity of 11.9% is obtained due to a large distribution of micropore size and some small mesopores. When a bias voltage of -60 V is applied the overall isotherm shape is at lower level, but still exhibits the characteristics of both a type I and type IV. Although less pronounced, the type IV shape still indicates that some mesopores are present. However, the amount of both micro- and mesopores present in the SiO$_2$-like film is reduced. This leads to a decrease in the calculated porosity to 9.3%.

Increasing the applied bias voltage to -140 V, leads to an isotherm shape which is truly a type I. Thus, at this voltage the deposited SiO$_2$ film is completely free of mesopores. Again, the overall isotherm level is lower which means that the amount of micropores is also decreased. However, the ongoing rise of the isotherm indicates a large distribution of micropore size and only a small external surface for multilayer adsorption. Although all mesopores have been removed, the calculated porosity is still 5.2%. This indicates the presence of a consistent amount of micropores of various sizes.

Further increase of applied bias voltage to -180 V leads to an isotherm shape of both type I and II. Thus, the SiO$_2$-like film still contains some micropores. However, the pronounced type II behavior at relative pressures above ~0.5 indicates that the external film surface is larger than the inner micropore surface. Moreover, the size distribution of micropores is small as indicated by the shallow rise of the isotherm above a relative pressure of ~0.1.

Finally, at an applied bias voltage of -240 V the isotherm shape shows only a type II behavior. Thus, the deposited SiO$_2$ film is non-porous and only multilayer adsorption on the external surface occurs. Therefore, the porosity of this film is zero in terms of ethanol adsorption. Again, the possible micropores left will be of size smaller than ~0.7 nm.

A more extensive discussion about non-porous SiO$_2$-like films and their use in determining the multilayer thickness of ethanol is given in section 4.2. This will allow the calculation of the pore size distribution of mesoporous films.

The above discussion shows that the rf bias first affects the pores in the micropore-mesopore boundary region for bias voltages up to ~16 V. Only for higher bias voltages the amount of smaller micropores decreases and eventually a non-porous SiO$_2$-like film is obtained. In the case of the p-s bias both the micro- and mesopores are parallel affected for all bias voltages applied. Still, the removal of the smallest micropores leading to a non-porous film needs much energy ($\Delta V=60V \leftrightarrow \Delta P=2\%$) using the p-s bias. Thus, in general, more and more energy is needed to affect micropores of reducing size. The specific route towards pore elimination by either the rf or p-s bias, leads to the different trends in porosity as function of applied bias voltage (FIG. 4-11).

A plausible reasoning for this difference between the two biasing methods is the difference in ion flux and energy. The rf bias provides a relatively small range of average energies. Moreover, the ions have a bimodal energy distribution (FIG. 2-16a), which means that a considerable fraction of the ions even have energies lower than on average. So, for bias voltages below ~16 V the energy of the ions is just too low to affect small
micropores, independently of the extra ion generation. However, apparently these low energy ions are very effective in the removal of mesopores and larger micropores. This indicates that due to the generation of additional ions the rf bias is more effective in the removal of mesopores. Thus, the ion flux may also be responsible for the observed differences. Then, the reduction of porosity is limited by the ions available possessing high enough energy.

In the case of the p-s bias the energy of the ions has a narrow ion energy distribution, potentially accompanied by some broadening due to collisions in the sheath (FIG. 2-16b). Combined with the applied high voltages, this means that the energy of the ions is high enough to affect pores of all dimensions in the whole voltage range. This reasoning is supported by the single-slope behavior of decreasing porosity with increasing bias voltage in case of the p-s bias (FIG. 4-11b). Although, relatively, a smaller reduction of mesopores is observed for the lowest bias voltages compared to the rf bias.

Furthermore, in case of the rf bias the observed porosity trend cannot be attributed to additional radical species originating from the local plasma generation. Since the depletion of HMDSO is already quantitative, dissociation of precursor molecules by the additionally created ions will not occur. This is supported by the observed trend in deposition rate as shown in FIG. 4-13 for both bias systems. In case of the generation of extra growth species an increase in deposition rate would have been expected which is not observed.

Finally, a consideration concerning the kind of SiO$_2$ structures which are associated with the different type of pores. A relation between the two may be obtained from the fact that the minimum pore size accessible by ethanol molecules is ~0.7 nm. As explained in § 2.4.3 amorphous SiO$_2$ films consist of a network of rings which have different sizes. To obtain an estimation of the diameter of the rings, they are approximated as regular planar structures. In this way the diameter can be calculated from the circumference of the ring, which is determined by multiplying the Si-O bond-length (1.62 Å$^{[47]}$) by the ring

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**Results & Discussion**

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**FIG. 4-13.** Deposition rate calculated from deposition time and film thickness measured by spectroscopic ellipsometry as function of applied bias voltage for (a) radiofrequency bias, (b) pulse-shaped low-frequency bias

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Finally, a consideration concerning the kind of SiO$_2$ structures which are associated with the different type of pores. A relation between the two may be obtained from the fact that the minimum pore size accessible by ethanol molecules is ~0.7 nm. As explained in § 2.4.3 amorphous SiO$_2$ films consist of a network of rings which have different sizes. To obtain an estimation of the diameter of the rings, they are approximated as regular planar structures. In this way the diameter can be calculated from the circumference of the ring, which is determined by multiplying the Si-O bond-length (1.62 Å$^{[47]}$) by the ring
size \( N \). This allows to obtain the diameter of the ring as a function of the ring size, as shown in Fig. 4-14.

![Graph showing calculated diameter of SiO\(_2\) rings as a function of the ring size \( N \).](image)

**Fig. 4-14.** Calculated diameter of SiO\(_2\) rings as a function of the ring size \( N \).

The graph shows that the minimum ring size \( N \) probed during the porosimetry measurements using ethanol as adsorbent is approximately seven. Thus, the porosity observed in the adsorption isotherms only originates from sevenfold rings and higher. However, this does not mean that smaller rings are not present in the films, but that they are not probed from ethanol molecules. On the contrary, literature shows that the largest ring present in amorphous SiO\(_2\) films is of size ten, provided that chain terminating groups are absent\(^{[47]}\). Therefore, the presence of mesopores indicates that there exist voids in SiO\(_2\)-like films which are larger in size than a single tenfold ring.

- **Chemical analysis of the deposited films**
  
  The influence of the ion energy on the microstructure of the SiO\(_2\)-like films is evident from the preceding discussion. To see whether the observed changes in microstructure are related to changes in chemical composition, infrared absorbance measurements have been also performed.

As in the case of the SiO\(_2\) films deposited at different growth flux in § 4.1.1, the AS1-to-AS2 peak area ratio of the Si-O-Si stretch mode has been calculated. The ratio is plotted as function of the applied bias voltage in Fig. 4-15 for both the rf and p-s bias. In case of the rf bias, a steady linear increase in the AS1-to-AS2 ratio is observed for increasing bias voltage. Thus, higher bias voltages lead to smaller bonding angles and less disorder in the network structure of the SiO\(_2\)-like films\(^{[42, 45]}\). Important to notice is the ongoing increase of the AS1/AS2 ratio for the whole range of applied bias voltages. The porosity trend in Fig. 4-11a, however, shows only a small decrease in porosity for \(|V_{dc}| > 16 \) V. Moreover, a non-porous film in terms of ethanol adsorption is already obtained for an applied bias voltage of \(\sim 46 \) V as observed from the isotherms in Fig. 4-12a. This leads to
conclude that the rearrangement of the SiO$_2$ network continues for ring sizes below the probing limit of ethanol (N<7) in case of the rf bias.

![Graphs showing AS1/AS2 ratio vs. applied bias voltage for rf and p-s bias]

**FIG. 4-15.** Calculated AS1-to-AS2 peak area ratio as function of applied bias voltage for (a) radiofrequency bias, (b) pulse-shaped low-frequency bias

The fits through the data points serve as a guide to the eye.

In case of the p-s bias, the SiO$_2$ ring network reaches a constant arrangement for bias voltages above ~140 V. However, as discussed, the obtained isotherms for the p-s bias series point out the transition from mesoporous to non-porous films (FIG. 4-12b). This indicates that the p-s bias provides a less or not effective rearrangement of sevenfold ring structures and smaller. Only, the energy of the ions at each applied bias voltage is expected to be high enough to affect every type of ring arrangement. As shown earlier, however, the p-s bias has an ion flux which is approximately a factor 7 smaller compared to the rf bias. Therefore, from the trends in FIG. 4-15 it can be concluded that the flux of ions is essential for the modification of the SiO$_2$ ring network. Moreover, this leads to hypothesize that the AS1-to-AS2 ratio provides only information about changes in ring arrangement. The fact that the trends in porosity (FIG. 4-11) do not reflect the trends in FIG. 4-15 for either the rf or p-s bias supports this reasoning.

Additional information about the film chemical composition is obtained from the integrated area ratio of the Si-OH stretching peaks at 3450 and 3650 cm$^{-1}$ and the Si-O-Si stretching peaks at 1076 (AS1) and 1200 cm$^{-1}$ (AS2). This ratio, shown in FIG. 4-16 for both rf and p-s bias as a function of applied bias voltage, is a measurement of the relative concentration of Si-OH groups compared to the concentration of Si-O-Si bonds. In the case of the rf bias an exponential decrease in the relative concentration of Si-OH groups is observed. The sharp drop for low bias voltages reflects the observed trend of porosity in FIG. 4-11a. However, while the porosity keeps decreasing for $|V_{dc}|>16$ V, the SiOH/SiOSi ratio remains constant. In the case of the p-s bias a linear decrease in the relative Si-OH group concentration is observed for increasing bias voltage. Again, this trend correlates with the porosity results as observed in FIG. 4-11b.
Thus, apparently the reduction of porosity for both rf and p-s bias is largely due to the condensation of Si-OH groups. This confirms that the densification process involves both the rearrangement of the SiO₂ ring structure and the condensation of Si-OH groups, as found in previous research\(^{42}\). According to the isotherm analysis the densification associated with the condensation of Si-OH groups is related to the removal of mesopores and large micropores. Since, in the case of the rf bias, only the AS₁-to-AS₂ ratio shows an continuing trend, it can be concluded that the condensation of Si-OH groups saturates as soon as the largest pores are eliminated. Then, the small decrease in porosity above \(|V_{dc}| = 16\) V is caused by the disappearance of the largest ring structures, which corresponds to the smallest micropores. This also supports the hypothesis that the AS₁/AS₂ ratio is only related to the ring structure. In case of the p-s bias the condensation process of Si-OH groups does not reach saturation within the range of applied bias voltages. This shows that the p-s bias is also less effective in the removal of the larger pores, although a pronounced reduction of the porosity does occur. The fact that for the rf bias the Si-OH condensation does reach saturation and the network rearrangement continues for increasing applied bias voltage, shows that the rf bias provides a very effective densification of SiO₂-like films.

The above comparison between the two biasing methods shows that the rf bias provides a more effective densification of plasma-deposited SiO₂ films than the p-s bias. Thus, the influence of the p-s bias is actually limited by the amount of available ions, even though the ion energy is considerably larger. In fact this means that the ion energy and the ion-to-growth flux ratio are not interchangeable parameters in film densification. This leads to hypothesize that the energy per deposited particle, which is the product of ion energy and ion-to-growth flux ratio, is most certainly not a universal parameter describing the efficiency of ion bombardment during film growth. In conclusion, provided that the ions possess enough energy, the densification process is controlled by the ion-to-growth flux ratio.
In conclusion, the data presented in this section show that SiO$_2$ films deposited in the presence of ion bombardment exhibit a general trend of increasing density for increasing ion energy. The accompanying changes in the SiO$_2$ microstructure, as monitored by means of ellipsometric porosimetry, lead to the following considerations:

- Increasing the ion energy promotes the reduction of open porosity, eventually leading to a non-porous film in terms of ethanol adsorption. This involves both a shift in pore size towards smaller pores as well as a decrease in the amount of pores. The actual transition in the SiO$_2$ microstructure, however, depends on the used bias system.

- In case of the rf bias, the mesopores and large micropores are first affected leading to a quantitative decrease of porosity from 11.1% to 3% at an ion energy of only 16 eV. Further increase of the ion energy reduces the amount of smaller micropores leading to a non-porous film at 46 eV.

- When utilizing the p-s bias, the micro- and mesopores are simultaneously affected over the whole range of available ion energy. This leads to a steady decrease in porosity down from 11.9% until a non-porous film is obtained at the highest ion energy of 240 eV.

The specific path towards pore elimination by either the rf or p-s bias depends on the difference in ion flux and energy available from each system. A considerable higher ion flux (~7x) for the rf bias compared to the p-s bias is ascribed to additional ion generation. Complementing the ellipsometric porosimetry data with the performed FTIR analysis leads the following additional considerations:

- A correlation between the concentration of Si-OH groups and the presence of mesopores and large micropores is confirmed. Condensation of these Si-OH groups for increasing ion energy leads to most of the reduction in porosity.

- The disappearance of the largest SiO$_2$ ring structures (N$\geq$7) is associated with the removal of the smallest micropores probed from ethanol. This leads to the reduction of residual porosity, i.e. not associated with Si-OH.

- In case of the rf bias, rearrangement of the SiO$_2$ ring structure appears to occur even below the probe limit of ethanol (N$<$7), while for the p-s bias this process is missing.

The rf bias provides a more effective densification of plasma-deposited SiO$_2$ films than the p-s bias. This leads to conclude that the ion energy and ion-to-growth flux ratio are not interchangeable parameters in film densification. Provided that the ions possess enough energy, the densification process appears to be mainly driven by the ion-to-growth flux ratio.
4.2 Determination of the ethanol multilayer thickness

As explained in Chapter 2 of this report, the process of capillary condensation in mesopores is preceded by multilayer adsorption on the pore surface. When utilizing the Kelvin equation to calculate the pore size distribution of mesopores, the thickness of the multilayer has to be taken into account. Important to understand is that for increasing pore size the onset of capillary condensation occurs at higher relative pressure. This means that the thickness of the pre-adsorbed multilayer present at the onset of capillary condensation depends on the pore size. To our knowledge, the ethanol multilayer thickness as a function of the relative pressure has not been studied before in literature. This section, therefore, reports on the determination of the ethanol multilayer thickness by studying the adsorption process on non-porous SiO$_2$-like films.

4.2.1 When a “dense film” is really dense?

In section 4.1 the microstructure of several deposited SiO$_2$ films has been associated to a type II isotherm. According to the porosimetry theory (section 2.2), this kind of isotherm is typical of non-porous layers. However, still, clear differences can be observed when these nominally “dense films” are compared. This means that the ethanol multilayer thickness determined from the adsorption isotherms will be different depending on the sample. This section discusses which isotherms can be truly associated with non-porous films and as such should be chosen to obtain the multilayer ethanol thickness, necessary for the determination of the pore size distribution of mesoporous films (§ 2.2.4). Several properties of the “dense” SiO$_2$-like films are shown in TABLE 4-6.

TABLE 4-6: Properties of the “dense” SiO$_2$-like films with a type II adsorption isotherm. Indicated are the porosity $P$, in _situ_ refractive index $n_{in}$, degassing temperature $T_{deg}$, and water contact angle $\theta$.

<table>
<thead>
<tr>
<th>Label</th>
<th>$P$ (%)</th>
<th>$n_{in}$</th>
<th>$T_{deg}$ (°C)</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.9</td>
<td>1.469</td>
<td>172</td>
<td>49 ± 0.8</td>
</tr>
<tr>
<td>B</td>
<td>1.0</td>
<td>1.469</td>
<td>184</td>
<td>52 ± 0.3</td>
</tr>
<tr>
<td>C</td>
<td>1.2</td>
<td>1.465</td>
<td>218</td>
<td>52 ± 1.1</td>
</tr>
<tr>
<td>D</td>
<td>1.7</td>
<td>1.458</td>
<td>216</td>
<td>47 ± 1.3</td>
</tr>
<tr>
<td>E</td>
<td>1.8</td>
<td>1.452</td>
<td>232</td>
<td>49 ± 0.3</td>
</tr>
</tbody>
</table>

In FIG. 4-17 the adsorption isotherms are shown as scaled to the $n_0$ refractive index value of each SiO$_2$-like film, according to equation (4.1), with the purpose of highlighting the differences between the isotherms. It is worth to mention that the optical model used to obtain these isotherms is physically incorrect, due to the assumption that the refractive index of SiO$_2$ changes as a result of ethanol adsorption in the layer. However, in the case of a non-porous SiO$_2$ film ethanol does not penetrate the layer, but is instead adsorbed on the external surface. Thus, the optical model of SiO$_2$ has to be changed according to the procedure described in § 2.3.2 of Chapter 2. From this model the multilayer thickness of ethanol is obtained at each relative pressure $p/p_0$ on a SiO$_2$ film of constant refractive index and thickness. However, for the purpose of explaining differences clearly present among the isotherm data, FIG. 4-17 is discussed first before adopting the correct model.
Results & Discussion

Two sets of isotherms are observed due to differences in adsorption at relative pressures $p/p_0$ below ~0.1. This means that the SiO$_2$-like films in each set have the same amount of initial adsorption.

![Type II adsorption isotherms showing the normalized adsorption as a function of relative ethanol pressure $p/p_0$ for the indicated porosity values $P$.](image)

The higher initial adsorption for the samples D and E indicates that still some micropores are present. However, the typical type II behavior for higher relative pressures shows that only primary micropore filling occurs. The lower *in situ* refractive index of films D and E in TABLE 4-6, support the presence of some micropores.

In case of the films in the lower branch (A to C) the initial absorption cannot be explained by the presence of pores, as their *in situ* refractive indices are close to the value for thermal silica. Combined with the typical type II shape of the isotherms, this means that the SiO$_2$-like films are really non-porous. However, the lower branch splits up for higher relative pressures, which could indicate a difference in multilayer adsorption for these films. To further discuss this difference, however, the appropriate optical model is applied to extract the multilayer thickness of ethanol. The results are shown in FIG. 4-18 as a function of relative pressure $p/p_0$. As from here the SiO$_2$-like films in the lower set will be only reported as film A, B and C, according to the labels shown in TABLE 4-6.

As expected, the shape of the curves reflects the type II isotherm behavior. The curves of films A and B are now equal within the experimental error of the thickness determination ($\pm 0.05$ nm). However, film C shows a larger multilayer thickness, taking into account the uncertainty. Thus, this indicates that a difference exist in the multilayer adsorption on the external surface of this film. The presence of specific surface groups may be responsible for this observed difference.

In general the concentration of silanol groups (Si-OH) at the surface of SiO$_2$ films has been found to influence the adsorption layer thickness of ethanol$^{[50,71]}$. The reason is that
Results & Discussion

the silanol groups of SiO$_2$ induce hydrogen-bonding interactions between the SiO$_2$ surface and the hydroxyl (–OH) group of ethanol. This specific kind of dipole–dipole effect leads to additional adsorption of ethanol, which is especially important at non-porous surfaces. However, the question remains whether film C indeed contains more silanol groups.

![Graph showing ethanol multilayer thickness](image.png)

FIG. 4-18. Ethanol multilayer thickness obtained by spectroscopic ellipsometry as function of relative pressure $p/p_0$ for the SiO$_2$-like films characterized by a type II adsorption isotherm.

In TABLE 4-6 the actual degassing temperatures $T_{heat}$ of the SiO$_2$-like films are reported. A substantial higher degassing temperature was needed for film C compared to the other two SiO$_2$-like films. This means that the removal of water from this film required more energy. Furthermore, an observation which was made during the porosimetry experiments is that the smaller are the pores present in porous films, the higher is the degassing temperature needed to remove all the water. But, film C is clearly non-porous in terms of ethanol adsorption. A water molecule, however, is smaller compared to the ethanol molecule, which allows hypothesizing on the presence of ‘ultramicro pores’ in film C. Although not accessible by ethanol molecules, water molecules are able to enter the film through these ‘ultramicro pores’. This would also mean that film C initially contains more water compared to films A and B, accounting for the higher degassing temperature. Furthermore, thermal desorption studies in literature using infrared absorption spectroscopy (FTIR) have shown that heating of SiO$_2$, which contains physisorbed water, leads to the production of free –OH groups at the surface$^{[47]}$. Increasing the temperature causes the H$_2$O content to decrease in favor of an increasing concentration of free –OH groups for degassing temperatures lower than 300°C. Thus, the higher initial amount of water in film C will lead to a higher concentration of silanol groups at the film surface. This would explain the larger ethanol multilayer thickness obtained for film C as shown in FIG. 4-18.

To obtain an indication about the presence of silanol groups at the surface, contact angle measurements of water were performed on the SiO$_2$ films under examination$^{[30]}$. A small droplet (200 µl) of water is placed on the surface of the film and the angle $\phi$ at the solid-
liquid interface is determined (FIG. 4-19b). The obtained contact angles for the SiO$_2$-like films with a type II adsorption isotherm are listed in TABLE 4-6 and a typical snapshot of the water droplet placed at the surface is shown in FIG. 4-19a. The angles are close to each other with an average value of about 50°. However, to relate the obtained contact angles to the relative presence of -OH groups at the surface, the shape of a droplet of water on a sheet of polyethylene naphthalate (PEN) is shown in FIG. 4-19b. The polymer sheet has been made hydrophilic by exposure to an O$_2$ plasma, which results in the formation of a substantial amount of -OH groups at the polymer surface. The obtained contact angle for the hydrophilic polymer sheet is approximately 36°.

![FIG. 4-19. Obtained snapshots from a water droplet (200 µl) placed at the surface of (a) the dense SiO$_2$ films discussed in this section, and (b) a sheet of hydrophilic polyethylene naphthalate (PEN).](image)

This shows that the average contact angle of ~50° is too high to define the deposited films as hydrophilic. Moreover, no trend is observed in the contact angles of each SiO$_2$ film, which could indicate different concentration of silanol surface groups. However, the contact angle measurements have been performed in air, which contains hydrophobic species, e.g. nitrogen and oxygen. These species are known to cause a process at the surface of films known as “hydrophobic recovery”. This process leads to the rearrangement of polar surface groups towards the bulk of the film, in order to minimize their contact area with the hydrophobic species in air. As silanol groups are polar, the contact with air will lead to a decrease of surface -OH groups. This means that even though the contact angle of the SiO$_2$ film is relatively high, reactivation of the surface due to degassing in a vacuum chamber may increase the amount of -OH surface groups. Thus, the relative effect of hydrogen bonding may still be responsible for the increased multilayer thickness of film C observed in FIG. 4-18. Moreover, the FTIR analyses in § 4.1.2 have shown the presence of a residual amount of Si-OH content even for the most dense films deposited at high bias voltages (FIG. 4-16). Thus, it can be expected that silanol groups play a role in the adsorption of ethanol. Therefore, the above hypothesis is likely to explain the difference in multilayer thickness.

To exclude influence of surface roughness also AFM scans have been performed for the SiO$_2$-like films A to C. The obtained images are shown in FIG. 4-20, together with the determined RMS roughness of each film.
Results & Discussion

FIG. 4-20. AFM images (2 µm x 2 µm) of the SiO$_2$-like films characterized by a type II adsorption isotherm. The films have an RMS roughness (nm) of (a) 0.185 ± 0.01, (b) 0.803 ± 0.05, (c) 0.182 ± 0.02.

As can be seen, the surface morphology of films A and C looks very smooth. Essentially no difference exists between the two films, which is supported by the extremely low RMS roughness values. The surface roughness of film B is more pronounced, as also indicated by the higher RMS roughness. However, this does not explain the higher adsorption of film C. In principle the largest adsorption is expected for the most pronounced surface roughness.

The above discussion shows that the three SiO$_2$-like films in FIG. 4-18 are truly non-porous in terms of ethanol adsorption. This means that the experimentally obtained ethanol thickness on these films is most similar to the pre-adsorbed multilayer present in mesopores. The presence of silanol surface groups leads to enhanced adsorption due to hydrogen bonding. Therefore, a higher concentration of silanol surface groups could explain the increased multilayer thickness of film C. In order to obtain more knowledge about the ethanol adsorption process on non-porous films, two different empirical models, introduced in § 2.2.4, will be fitted to the experimental data. Moreover, this will provide analytical expressions which allow to calculate the ethanol multilayer thickness at arbitrary relative pressure.

4.2.2 Modeling the experimental data: BET versus FHH

In § 2.2.4 several empirical models have been shown which provide the multilayer thickness of a certain solvent on a non-porous solid film as a function of the relative pressure $p/p_0$. However, as already mentioned in § 2.3.2, these relations contain empirical parameters, which are unknown for the ethanol adsorption on SiO$_2$. The experimentally obtained multilayer thickness for the films in FIG. 4-18 allows determining these parameters. This is achieved by modeling the theoretical relations to the experimental data using the empirical parameters as fit variables. The regression analysis is performed according to the Levenberg-Marquardt algorithm in order to minimize the mean squared error.
Results & Discussion

To simulate the data both the Brunauer-Emmett-Teller (BET) and Frenkel-Halsey-Hill (FHH) equation are used, which are defined by equation (2.10) and equation (2.11) in § 2.2.4, respectively. The unknown parameters for the BET equation are the monolayer thickness \(t_0\), the BET constant \(c\), and infinity parameter \(k\). In case of the FHH equation the fit parameters are the monolayer thickness \(t_0\), the dispersion exponent \(s\), and parameter \(a\) which is constant for a specific gas-solid system. The parameters obtained from the fits to the SiO\(_2\)-like films A to C are reported in TABLE 4-7. The variable \(t_{\text{sat}}\) is the ethanol multilayer thickness at saturation pressure, i.e. at \(p/p_0=1\). They are simultaneously discussed with the graphs below.

TABLE 4-7: Obtained parameters for the BET and FHH equation from the non-porous SiO\(_2\) films A to C.

<table>
<thead>
<tr>
<th>Film</th>
<th>BET</th>
<th>FHH</th>
<th>The thickness values are presented in nanometers (nm).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(t_0)</td>
<td>(c)</td>
<td>(k)</td>
</tr>
<tr>
<td>A</td>
<td>0.319</td>
<td>253.4</td>
<td>0.687</td>
</tr>
<tr>
<td>B</td>
<td>0.303</td>
<td>286.5</td>
<td>0.683</td>
</tr>
<tr>
<td>C</td>
<td>0.384</td>
<td>144.8</td>
<td>0.710</td>
</tr>
</tbody>
</table>

In FIG. 4-21a the experimental data of film A is shown together with the obtained fits of the BET and FHH equation. As can be seen both equations fit well the experimental data, producing almost equal curves in the range \(0.1<p/p_0<0.8\). This is excellent as within this range capillary condensation occurs in mesoporous films. To obtain the pore size distribution of the mesopores, the Kelvin equation (§ 2.2.4) is applied to describe this process. The ethanol multilayer thickness obtained from the non-porous films under examination is used hereby to correct for a decrease in condensation space.

For relative pressures outside this intermediate region deviations occur from the experimental data and also between the two equations. At pressures \(p/p_0<0.1\) the FHH equation does not fit the experimental curve. However, this is not surprising because the mathematical nature of the equation does not allow generating such a sharp bending. This also means that the value of the obtained ethanol monolayer thickness \(t_0\) of \(\approx 0.35\) nm from the FHH equation should be interpreted with care. Probably, the value is overestimated due to the fact that the initial sharp bending of the experimental curve determines the monolayer capacity. A more extensive discussion about the monolayer thickness is given at the end of this section.

In the low-pressure region the BET equation fits the sharp bending in the experimental data more accurately. The obtained monolayer thickness \(t_0\) from the BET equation is \(\approx 0.32\) nm, which is somewhat lower than the FHH result. However, the value from the BET equation is probably correct as this equation is derived to describe also the initial adsorption. Moreover, extensive use of the BET equation to determine the monolayer capacity of non-porous films has shown that in case of a sharp bending a good agreement exist with the actual monolayer capacity\(^{[20,21]}\). The high value of the BET constant \(c\) of \(\approx 253\) shows that in our case the bending is really sharp \((c>100)^{[21]}\). Thus, the monolayer thickness from the BET equation is taken as the correct value. Furthermore, the high \(c\) value also means that the monolayer formation is already complete for quite low-pressure values.
Results & Discussion

When looking at the high-pressure region ($p/p_0 > 0.8$) the two equations start to deviate from each other. However, in this case the FHH equation is expected to give the correct result as it is derived especially for the high pressure multilayer region\[^{20}\]. On the contrary the BET equation is known to fail to describe the multilayer thickness for these high relative pressures. Again, this is solely attributable to the mathematical nature of the BET equation, as it is basically built up from two hyperbolae\[^{21}\].

Using the obtained parameters allows theoretically generating thickness curves over the complete pressure range. In FIG. 4-21b these curves are shown for both the BET and FHH equation. For relative pressures up to $\sim 0.9$ no new information is present as this is also the range of the experimental data. However, for higher pressures the already observed deviation between the BET and FHH model becomes increasingly evident. This results in a multilayer thickness at saturation pressure ($p/p_0 = 1$) of $\sim 1.0$ nm from the BET model and $\sim 2.7$ nm from the FHH equation. The multilayer formation at saturation pressure is actually due to the condensation of ethanol on a solid surface. This can also be seen as the direct adsorption of ethanol molecules from the liquid phase onto the solid. On the contrary, for pressures below saturation pressure the adsorption occurs from the gas phase. In literature the multilayer thickness of ethanol from the liquid phase is known to be in the range 2-4 nm for adsorption on SiO$_2$ surfaces depending on the chemical nature of the surface\[^{20}\]. Thus, the obtained ethanol thickness of $\sim 2.7$ nm from the FHH model is reasonable. Moreover, the upward sweep of the FHH model really shows the transition towards condensation. As already expected the BET equation is not capable of modeling the multilayer thickness in this range around saturation pressure.

In FIG. 4-22a the experimental data of film B is shown together with the obtained fits of both the BET and FHH equation. Again the curves from the two equations overlap in the range $0.1 < p/p_0 < 0.8$ where they both perfectly fit the experimental data. For relative pressures outside this range deviations occur due to the same reasons as discussed above.

FIG. 4.21. Ethanol multilayer thickness of non-porous film A as a function of the relative pressure $p/p_0$. (a) the experimental data with the obtained curves from the BET and FHH equation; (b) the fit results employed in the BET and FHH equation to model the complete pressure range.
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FIG. 4-22. Ethanol multilayer thickness of non-porous film B as a function of the relative pressure $p/p_0$.
(a) the experimental data with the obtained curves from the BET and FHH equation; (b) the fit results employed in the BET and FHH equation to model the complete pressure range.

The obtained monolayer thickness from the FHH equation is ~0.35 nm, which is the same as for film A. The BET equation gives a slightly lower value of ~0.30 nm, but the change is in order of the experimental error. Moreover, the high value of the BET constant ($c \approx 286$) shows that the result is most probably correct for this film. At the high pressure side ($p/p_0 > 0.8$) the expected deviation occurs between the two equations.

The thickness curves generated by substituting the obtained fit parameters in the FHH and BET equation are shown in FIG. 4-22b. When looking at the region above relative pressures of ~0.9 the increasing deviation between the two equations is again observed. At saturation pressure the BET model gives an ethanol multilayer thickness of ~1.0 nm. From the FHH model a value of ~2.6 nm is obtained, which is comparable to the result of film A considering the experimental error. Also, the multilayer thickness of ~2.6 nm is in the range of 2-4 nm found in literature as mentioned above.

In FIG. 4-23a the experimental data of film C is shown together with the obtained fits of both the BET and FHH equation. Once more both fits are excellent in the range $0.1 < p/p_0 < 0.8$ and outside this region deviations occur.

For this film the ethanol monolayer thickness acquired is ~0.38 nm for both equations. In comparison with film A and B this value is rather high (TABLE 4-7). A first explanation may be the increased adsorption which was observed for film C (FIG. 4-18) due to higher concentration of silanol surface groups (§ 4.2.1). However, in principle the thickness of a monolayer of ethanol should remain constant as long as the molecules are arranged in the same way. Only the multilayer adsorption is influenced, as the potential field associated with hydrogen bonding ranges considerably further from the surface compared to the other Van der Waals forces\textsuperscript{70,72}. Thus, this means that either the arrangement of the molecules is different or the fit parameters are correlated.
Results & Discussion

When looking at TABLE 4-7 and comparing the fit parameters from the three films also the other parameters for film C are noticeably different, except for the parameter \( k \) from the BET equation. However, the parameter \( k \) has no physical meaning and only provides a mathematical solution to obtain better agreement between the BET equation and the experimental data in the high-pressure region. The value of \( k \) should be positive and smaller than unity (fraction), which is indeed the case.

The BET constant \( c \) is related to the energy of adsorption in the first layer. In literature it is shown that the higher the value of \( c \) the higher the energy of adsorption\(^{20}\). Moreover, in the distribution of adsorption energy for silica surfaces the contribution of hydrogen bonding due to silanol groups is found at the lowest energies\(^{72}\). Thus, the lower value of the BET constant for film C is related to the more pronounced contribution of -OH groups to the adsorption process. But this also means that the surface ‘heterogeneity’ increases in terms of energy. The BET theory, however, assumes all the surface sites to be energetically identical\(^{21}\). This might explain the higher value of the monolayer thickness obtained (~0.38 nm) as the BET equation is less adequate to describe the adsorption process.

In case of the FHH equation the parameter \( a \) should be constant for a specific gas-solid system\(^{20,21}\), which is not observed. When keeping this parameter constant at the value of film A or B during the fit procedure, only the obtained monolayer thickness \( t_0 \) increases but the dispersion parameter \( s \) remains the same. Moreover, the resulting curves for all films are completely identical in terms of the 3-parameter fits. This shows again that the FHH equation is incapable of modeling the monolayer formation. Because the value of \( a \) can be fixed without influencing the shape of the FHH curve, the dispersion parameter \( s \) appears to be more relevant. In literature the value of \( s \) is found to be in the range 2-3\(^{20,21,36}\), which matches well with the obtained values for all films. The parameter \( s \) is related to the degree of energetic surface ‘heterogeneity’ of the film. Here, a higher heterogeneity causes a reduction in the value of \( s \)\(^{20}\). Again, this corresponds to the lower value of \( s \) obtained for film C compared to the ones of film A and B. Moreover, in literature a value of 2.75 has been found for hydroxylated silicas\(^{21}\), which is exactly the

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**FIG. 4-23.** Ethanol multilayer thickness of non-porous film C as a function of relative pressure \( p/p_0 \). (a) the experimental data with the obtained curves from the BET and FHH equation; (b) the fit results employed in the BET and FHH equation to model the complete pressure range.
value found for film C. Thus, once more this relates the increased adsorption of film C (FIG. 4·18) to the concentration of -OH groups at the surface of SiO₂ films. The above discussion about the fit parameters shows that the obtained monolayer thickness of ethanol for film C is probably overestimated by both equations.

The monolayer thickness of ethanol depends on the way the molecules arrange on the SiO₂ surface. Both an experimental study and a simulation have shown that ethanol molecules arrange parallel to the surface of SiO₂ films due to the presence of Si-OH groups[70,71]. Hereby, the hydroxyl group (-OH) of ethanol interacts with the silanol group at the SiO₂ surface via hydrogen bonding. The alkyl group (-C₂H₅) of ethanol is then arranged parallel to the surface as shown in FIG. 4·24. Thus, it is expected that the monolayer thickness of ethanol is equal to the short axis dimension of the molecule (~0.35 nm). However, in literature a value of ~0.25 nm has been found[70], which indicates the distortion of the molecule shape on adsorption. In any case the obtained values for the monolayer thickness of ethanol on films A and B are within the range 0.25-0.35 nm for both the BET and FHH equation. For film C the values are above this range and probably too large, but still reasonable considering the experimental error (~0.05 nm). Thus, this shows that the arrangement of ethanol molecules adsorbed on our plasma-deposited SiO₂ films is most likely as depicted in FIG. 4·24.

FIG. 4·24. Arrangement of an ethanol molecule on the surface of a plasma-deposited SiO₂ film.

Using the obtained fit parameters from film C in the BET and FHH equation leads to the multilayer curves shown in FIG. 4·23b. The multilayer thickness at saturation pressure (p/p₀=1) for the BET equation is ~1.3 nm. The FHH equation gives a value of ~3.9 nm which is again in the range 2-4 nm found in literature[70]. Moreover, the higher value compared to film A and B reflects in the higher concentration of silanol groups.

The obtained parameters from the modeling are found to be in fair agreement with literature. Especially, the monolayer thickness t₀ of ethanol corresponds to a molecule arrangement, which is indeed observed for ethanol adsorption on SiO₂ surfaces. Furthermore, the extrapolation of the FHH model towards saturation pressure gives typical values of ethanol multilayer thickness found in other studies. This means that the obtained ethanol thickness as function of relative pressure p/p₀ originates from pure multilayer adsorption. Additionally, the fit parameter study shows that hydrogen bonding is indeed important for the adsorption process on non-porous SiO₂ films.
4.2.3 Pore size distribution: Multilayer influence on the Kelvin equation

As explained in § 2.2.4 the pore size distribution (PSD) of solid films containing mesopores can be determined by means of the Kelvin equation defined by equation (2.8). However, due to the presence of a pre-adsorbed multilayer of ethanol at the onset of capillary condensation the pore size is underestimated. The models described in the previous section are used to provide the multilayer thickness in order to correct the Kelvin radius $r_k$ according to equation (2.9). As the relative pressures over which capillary condensation occurs is within the range $0.1 < p/p_0 < 0.8$ both the BET and FHH model are equivalent.

As a ‘proof of principle’ the concept is demonstrated with the adsorption data obtained from a truly mesoporous silica film. This film has been deposited by means of a wet chemistry process (spin coating), which allows tuning the porosity of the film. The obtained adsorption-desorption isotherm is shown in FIG. 4-25a. The shape is that of a typical type IV isotherm with a distinct hysteresis loop. Together with the pronounced increase in adsorption this shows that the silica film contains indeed a considerable amount of mesopores. In addition the calculated porosity of 19.6% confirms that the film is rather porous. However, the initial adsorption at low relative pressure ($p/p_0 < 0.1$) indicates that also micropores contribute to this value. As the PSD calculation is independent of these pores this is not further discussed.

![FIG. 4-25. Showing (a) a type IV isotherm obtained on a truly mesoporous SiO$_2$ film, and (b) the corresponding pore size distribution determined via the Kelvin equation.]

The Kelvin equation allows converting each relative pressure into a radius, which represents the available condensation space. The radii are corrected for multilayer adsorption by using the FHH model to provide the multilayer thickness at each relative pressure. This gives the refractive index as a function of pore radius. By differentiating the refractive index with respect to the pore radius the PSD is calculated. The obtained PSD for the mesoporous silica film is shown in FIG. 4-25b. To emphasize the influence of the multilayer thickness on the calculated PSD, also the result without multilayer correction is shown.
When calculating the PSD directly from the Kelvin radius a peak is observed at 1.2 nm. In the case of a correction for the multilayer the peak shifts towards 1.7 nm. This means that Kelvin equation underestimates the average pore radius by approximately 30%. In literature the average pore radius extracted from the ethanol desorption isotherm of a spin-on low $k$ silica (Honeywell nanoglass E) was found to be 1.8 nm\cite{66}. This shows that the average pore radius of 1.7 nm is realistic for silica films. The presence of some broadening indicates that the silica film contains mesopores of various sizes. Besides the different position of the two peaks also a decrease in peak height is observed. However, this is a direct result of the multilayer correction as it leads to a decrease in the gradient between refractive index and pore radius. Thus, the peak area is a measure for the amount of mesopores present in the film. The integrated peak area of the mesoporous silica is ~0.055. Due to the fact that refractive index is used as the adsorption parameter this value does not represent a physical quantity. However, because this film is defined as mesoporous the value can serve as a reference.

In § 4.1.1 several type IV isotherms were shown which are obtained from plasma-deposited SiO$_2$ films. The most pronounced hysteresis loop was found for the film deposited with a HMDSO flow rate of 0.46 sccs in the absence of ion bombardment. The porosity of this film was calculated to be 18%. Thus, the film is expected to contain a relevant amount of mesopores. The obtained adsorption-desorption isotherm is shown in FIG. 4-26a. In contrast to the pronounced hysteresis loop in FIG. 4-25a, the hysteresis from the SiO$_2$-like film is less evident. Nevertheless, some hysteresis is present which justifies the application of the Kelvin equation to determine the PSD for this film. The result is shown in FIG. 4-26b with and without multilayer correction.

The peaks are observed at a position of ~1.1 nm by direct use of the Kelvin radius and at ~1.5 nm when the multilayer correction is implemented. When comparing with the results of the mesoporous silica in FIG. 4-25b both peaks are at lower pore size. This suggests that the plasma-deposited film contains slightly smaller mesopores. A more pronounced difference is the considerable lower peak height of the plasma-deposited SiO$_2$
Results & Discussion

The calculated peak area for this film is ~0.026. This means that the mesoporous silica contains almost twice the amount of mesopores compared to the SiO$_2$-like film. As the porosity of the mesoporous silica is only 1.6% higher this is quite remarkable. The only explanation is that the amount of micropores is substantially higher in the case of the plasma-deposited SiO$_2$ film. This is indeed indicated by the larger initial adsorption for this film. Thus, equal porosity does not imply that the same type and size of pores are present in a film. Furthermore, the range of refractive indices contributing to the isotherm for the SiO$_2$-like film is at higher values compared to the mesoporous silica. As reasoned in § 4.1.1 this means that the amount of closed pores present in the SiO$_2$-like film is smaller than of the mesoporous silica. Moreover, this is again evidence that the refractive index does not provide complete insight into whether a film is accessible to environmental species or not.

The above discussion shows that the pore size distribution of silica films can be derived from ethanol adsorption-desorption isotherms by using the Kelvin equation. However, the pore size is underestimated considerably, when multilayer adsorption is not taken into account. Of course this is related to the fact that the mesopore size of the analyzed films is in same order as the ethanol multilayer thickness. Comparison of a spin-coated silica film to the plasma-deposited SiO$_2$ film shows that films of equal porosity can contain different type and size of open pores. This means that only the knowledge about the amount of pores is insufficient to fully characterize the microstructure of SiO$_2$ films.
5 General conclusion

5.1 Conclusions

The expanding thermal plasma (ETP) technique has been employed for the deposition of thin carbon-free SiO$_2$ films by means of organosilicon/O$_2$ plasma mixtures. When deposited at low substrate temperature these films are porous. In this work, therefore, the use of ion bombardment has been investigated for the densification of SiO$_2$ films during deposition at room temperature. The remote nature of the ETP technique and low self-biasing allows for controlled ion bombardment using external substrate biasing. This has been achieved using two distinct biasing techniques, i.e. an rf sinusoidal and a low-frequency pulsed-shaped substrate bias. The new technique of ellipsometric porosimetry has been used in order to characterize the densification process of the plasma-deposited SiO$_2$ films. This technique allows to obtain the open porosity and is able to provide knowledge about the type and size of pores present in the film based on ethanol adsorption-desorption isotherms. Complemented with two established diagnostic tools, i.e. spectroscopic ellipsometry and Fourier transform IR spectroscopy, the technique of ellipsometric porosimetry has been found to provide detailed understanding of the SiO$_2$ microstructure. The presented work is the first extensive study of ellipsometric porosimetry applied to plasma-deposited SiO$_2$ thin films. In this study the effect of ion bombardment on the microstructure has been investigated for different ion flux and energy conditions. The main conclusions of this work are presented here below.

The ellipsometric porosimetry setup has been utilized to experimentally determine the ethanol multilayer thickness on non-porous SiO$_2$-like films as a function of relative pressure $p/p_0$. To gain more insight in the ethanol adsorption process two empirical models have been fitted to the data. This study has been performed to implement multilayer adsorption in the calculation of the mesopore size distribution.

- The presence of silanol groups at the surface of non-porous SiO$_2$-like films induce enhanced adsorption of ethanol due to hydrogen bonding. An increasing concentration of surface silanol groups leads to an increasing ethanol multilayer thickness.

- Ethanol molecules arrange parallel to the surface of SiO$_2$-like films, i.e. the alkyl group is arranged parallel while the hydroxyl group accounts for the interaction with the surface via hydrogen bonding. A monolayer thickness of ethanol in the range (0.30-0.38)±0.05 nm confirms the parallel arrangement as this is comparable to the short axis dimension of the ethanol molecule (~0.35 nm).

- The Kelvin equation allows for the determination of the pore size distribution of mesoporous SiO$_2$ films from ethanol adsorption-desorption isotherms. When multilayer adsorption is not taken into account the average pore size is underestimated considerably. For SiO$_2$ films deposited on silicon substrates the average mesopore size is near the micropore-mesopore boundary region, i.e. in the range 1.5-1.7 nm.
Comparing the pore size distribution of a spin-coated silica film to a plasma-deposited SiO$_2$ film shows that films of equal porosity can contain different type and size of open pores. This reveals that only the knowledge about the amount of pores is insufficient to fully characterize the microstructure of SiO$_2$ films.

The microstructure of SiO$_2$ films deposited in absence and presence of high-energy ion bombardment has been characterized for radical growth fluxes in the range 3.8-8.4·10$^{19}$ m$^{-2}$s$^{-1}$. Two important issues have been investigated by means of this series: the microstructural changes induced by the radical growth flux and the influence of ion bombardment at different ion-to-growth flux ratios.

- The relatively small changes in radical growth flux have considerable effects on the microstructure of SiO$_2$-like films, both in the presence and absence of ion bombardment. This involves changes in the amount of open porosity and a transition in the type and size of the pores.

- In the absence of ion bombardment the deposited films are porous at each growth flux. Increasing the growth flux in the investigated range induces an increase in both the amount of micro- and mesopores. The amount of micropores is always larger in comparison with mesopores. Quantitatively, the microporosity increases from 11 to 13.2%, while the mesoporosity only ranges from 2.4 to 4.8%.

- Changing the growth flux in the presence of ion bombardment influences the film densification at constant and high ion energy (240 eV). Only under an optimal ion-to-growth flux ratio (~0.66) both micro- and mesopores are quantitatively eliminated leading to complete film densification. When the flux ratio is not optimal, the mesopores are mainly affected in comparison to the micropores.

The rf and p·s bias have both been used to promote film densification during the deposition of SiO$_2$-like films at optimal growth flux conditions. In this series the influence of ion energy on the SiO$_2$ microstructure has been investigated by varying the applied bias voltage. The generated range of ion energies depend on the bias system, i.e. a range of 0-52 eV for the rf bias and 0-240 eV in case of the p·s bias.

- Increasing the ion energy promotes the reduction of open porosity, eventually leading to a non-porous film in terms of ethanol adsorption. This involves both a shift in pore size towards smaller pores as well as a decrease in the amount of open pores. The actual transition in the SiO$_2$ microstructure, however, depends on the used bias system.

- In case of the rf bias, the mesopores and large micropores are first affected leading to a quantitative decrease of porosity from 11.1% to 3% at an ion energy of only 16 eV. Further increase of the ion energy reduces the amount of smaller micropores leading to a non-porous film at 46 eV.
General conclusions

- When utilizing the p-s bias, the micro–and mesopores are simultaneously affected over the whole range of available ion energy. This leads to a steady decrease in porosity down from 11.9% until a non-porous film is obtained at the highest ion energy of 240 eV.

- The specific path towards pore elimination by either the rf or p-s bias depends on the difference in ion flux and energy available from each system. A considerable higher ion flux (~7x) for the rf bias compared to the p-s bias is ascribed to additional ion generation.

Fourier transform IR spectroscopy measurements have been performed complementary to the microstructural characterization. In this study the chemical composition of the deposited SiO$_2$ films has been correlated to the observed changes in microstructure.

- A correlation between the concentration of Si-OH groups and the presence of mesopores and large micropores is confirmed. Hydrogen-bonded -OH groups appear to be mainly associated with micropores close to the mesopore regime. Condensation of these Si-OH groups for increasing ion energy leads to most of the reduction in porosity.

- The disappearance of the largest SiO$_2$ ring structures (N≥7) is associated with the removal of the smallest micropores probed from ethanol. This leads to the reduction of residual porosity, i.e. not associated with Si-OH.

- In case of the rf bias, rearrangement of the SiO$_2$ ring structure for increasing ion energy appears to occur even below the probe limit of ethanol (N<7), while for the p-s bias this process is missing.

In conclusion, the rf bias provides a more effective densification of plasma-deposited SiO$_2$ films than the p-s bias. Considering the distinct characteristics of the two biasing systems this reveals that the ion energy and ion-to-growth flux ratio are not interchangeable parameters in film densification. Provided that the ions possess enough energy, the densification process is mainly driven by the ion-to-growth flux ratio.
5.2 Recommendations

In this section some recommendations are given for future research or improvement of the experimental setup. A general remark is that the optical, chemical and microstructural characterization of any film should be performed shortly after deposition to prevent the influence of irreversible ageing or contamination.

- In order to probe smaller micropores than is possible with ethanol, another solvent with smaller molecule size, e.g. methanol or water, should be used to perform the porosimetry measurements. The probing of smaller micropores could provide a better understanding of the densification process as function of ion energy at optimal growth flux. In order to actually obtain more accurate results the measurements in the lower pressure regime should be extended, i.e. using extra measurement points for the smallest micropores. Performing additional measurements using nitrogen adsorption at 77 K may also be useful as much information is available in literature for reference.

- At present the determination of ion flux from the plasma and the ion energy distribution (IED) is based on several assumptions most probably leading to deviations between the calculated and actual values. The bias properties of both the rf and p·s bias should, therefore, be examined into more detail. A promising technique to obtain the ion flux from a depositing plasma is the recently developed pulse-shaped capacitive probe, conceivably incorporated into the substrate holder. In order to obtain more knowledge about the IED the retarding field analyzer (RFA) has great potential. Measurements in non-depositing plasmas have already been successfully performed.

- When the bias properties are unambiguously determined the ion energy series should be repeated using both the rf and p·s bias to promote film densification. In this way, the conclusions drawn in this work can be confirmed and more insight about the differences in the densification process by the rf and p·s bias may be obtained. In order to provide even a deeper understanding of microstructural changes due to ion bombardment the p·s bias series should be performed at an ion-to-growth flux ratio similar to the rf bias. As the p·s bias allows to accurately scan the ion energy (single-peaked IED) this may provide insight into the exact transition in the microstructure as function of ion energy at optimal flux ratio.

- The ellipsometric porosimetry technique should be extended to allow for the microstructural characterization of diffusion barriers on polymer substrates. To prevent damage to the substrate the degassing of the barrier film should be performed at temperatures below the glass transition temperature of the polymer. Furthermore, the adsorption isotherms should be acquired up to the highest attainable relative pressures in order to promote capillary condensation in the largest mesopores present. This provides a more accurate hysteresis loop which will improve the calculation of the pore size distribution by means of the Kelvin equation. In case of barrier films this is important as the defect size is expected to be in the mesoporous regime.
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Bibliography


Bibliography


