A Novel Spectroscopic Ellipsometer in the Infrared

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Vivre,
c’est transformer en conscience
une expérience aussi large que possible.

- André Malraux
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Chapter 1

Introduction
1.1 Historical context

Polarization of light has been observed as early as in the 17th century. While Sir Isaac Newton (1642-1672) devoted himself to the development of a corpuscular theory of the propagation of light, Christiaan Huygens (1629-1695) extensively developed the wave theory. He was able to derive the law of reflection and refraction and even able to explain birefringence phenomenon. While manipulating calc-spar crystals, he observed that the two rays exiting a crystal could be recombined by rotating a second identical crystal in the same axis [1]. Later, Malus (1775-1812) showed that polarization phenomena occur also by reflection [2]. It is important to know that at that time the electromagnetic nature of light was not known. A parallel development of electricity and magnetism led Faraday and then Maxwell to establish a relationship between electromagnetism and light in 1873. Maxwell’s equations [3] finally showed that light was ”an electromagnetic disturbance in the form of waves.” Less than two decades later, Drude [4, 5] was able to study both absorbing and transparent layered films by measuring the phase difference between two mutually perpendicular polarized light beams [6]. Drude’s work is considered as the first experiment of ellipsometry.

A monochromatic electromagnetic wave is a transverse wave constituted of both electric $\vec{E}$ and magnetic $\vec{B}$ fields. They are mutually perpendicular and both are perpendicular to the direction of propagation. Polarization is defined as the trajectory described by the electric field vector when varying in time in the plane defined by $\vec{E}$ and $\vec{B}$. In the general case, this trajectory is an ellipse. The technique of ellipsometry takes its name from this shape [7]. Ellipsometry is a technique which measures the change of polarization state of a light beam when it is reflected at a surface. This change is related to the physical, optical, and chemical properties of the material. The trajectory of the beam lies in a plane normal to the surface of the sample, called plane of incidence. By convention, the electric field is expressed in two perpendicular directions, one being in the plane of incidence and associated to the index $p$, the other is indexed $s$.

![Figure 1.1: Principle of ellipsometry.](image)

Ellipsometry allows for the determination of the complex reflectance ratio $\rho$ of a surface. This quantity is defined as the ratio of $p$ and $s$ reflection coefficients, $r_p$ and $r_s$ respectively. Commonly, the reflectance ratio is expressed with the variables $\Psi$ and $\Delta$ [8].

$$\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta}. \quad (1.1)$$
One of the main advantages of ellipsometry is its non-intrusive nature. In contrast with other surface analysis techniques such as scanning electron microscopy (which often requires additional conductive coating), secondary ion mass spectrometry (SIMS), sputter Auger Electron spectrometry (AES), or ion beam analysis techniques, the sample is not destroyed during the measurements. Despite the pioneering work of Drude, the technique of ellipsometry only started flourishing in the 1960’s. The reason is that the directly measured parameters are not per se of interest. The properties of the material can only be extracted from the directly measured parameters by applying a model of the reflection and transmission of the light beam near the surface of the sample [9]. Such a model becomes rapidly complex and involves calculations that need the assistance of computers.

Single wavelength ellipsometry became soon popular and the first commercial ellipsometers were available from the early 1970’s. Because of the high sensitivity of this method, the development of new instrumentation appeared to be of the utmost importance. Several automated approaches to the measurement of the polarization state were proposed. The most successful was the so-called photometric ellipsometry in which the polarization of light is modulated by means of a linear polarizer, namely rotating polarizer (RPE) or rotating analyzer (RAE) ellipsometry [10]. Later, the introduction of additional optical elements in the ellipsometer, able to induce a phase shift in the polarization state of light, led to rotating compensator ellipsometry (RCE) [11], and phase modulation ellipsometry (PME). These techniques have been widely compared in literature ([8, 12] and references therein).

1.2 Spectroscopic ellipsometry

From this point three fields of research and development have been extensively explored.

1. Instead of using single-wavelength light sources, people began to investigate the consequences of light reflection on matter over a large spectrum from UV-visible [13–15] to infrared [16–20]. Spectroscopic ellipsometry, although based on the same principle than single-wavelength ellipsometry, requires generally a totally different instrumentation [21–23].

2. The enhanced performance of microprocessors offered the possibility of reducing the calculation time to a point that real-time ellipsometry became possible [24, 25]. The monitoring of elementary processes governing plasma surface interaction, for instance, has been successfully investigated using ellipsometry [26, 27].

3. The continuously better accuracy required in order to increase the sensitivity of the technique led to exhaustive investigation on calibration procedure and errors limitations [24, 28–30].

Spectroscopic ellipsometry is now a well established and widely used method. However, when compared to other spectral ranges, the development of spectroscopic ellipsometry in the infrared range only emerged in the beginning of the 1990’s, with the advent of Fourier transform techniques, allowing the use of infrared light for spectroscopic purpose [19]. Furthermore, polarizing optical elements (polarizers, retarders) still appear to be of poor quality when compared to those used in visible.

Infrared spectroscopic ellipsometry can provide nevertheless more information than when the technique is used in visible: molecular composition, derived from the analysis of absorption
resonance bands, can be obtained. This makes this technique particularly attractive for the study of oxides or organic materials. Unfortunately, the use of an ellipsometer in the infrared has too often been reduced to a highly sensitive tool giving information on vibrational properties of the material [31] and not on optical properties in this spectral range, or have been applied to a limited spectral range [32]. For the latter purpose, a study on a larger spectral range and a non ambiguous determination of the ellipsometric parameters (especially the phase shift $\Delta$) are required.

### 1.3 Content of the thesis

The aim of this thesis is the development and the utilization of a spectroscopic ellipsometer in the infrared range (2.5 to 12.5 $\mu$m) based on the principle of rotating compensator ellipsometry. The superiority of this technique over the others is demonstrated. This work is a continuation of the work of J.H.W.G. den Boer who established the foundations of the development of the ellipsometer [22]. The scope of this study can be divided in two parts:

- In the first part we will detail the design of the ellipsometer. We studied the different elements including the source, the polarizers, the compensator and the detector. The polarizers performance has been improved by using Brewster angle polarization principle [33] and a compensator functioning on a large spectral range has been design (Chapter 2). Particular attention has been payed on the alignment and calibration procedures and on the estimation of the errors and the the possible misinterpretation of the spectra (Chapter 3). For this purpose, thermally grown silicon dioxide films are investigated. Then a study on silicon sub-oxide films obtained by sputtering at low temperature has been carried out, showing the capacity of ellipsometry, when associated with accurate models, to determine optical (complex refractive index) and chemical properties (stoichiometry) of the films (Chapter 4). The evolution of the properties of the films from semiconductor to insulator, when the stoichiometry of oxygen is increased, is investigated.

- The second part of this thesis, is the report of a joint study on the consequences of non-thermal plasma treatment of biological tissue [34]. Bone tissue has been exposed to inductively coupled plasma (ICP). Bone represent a very complex material to study since it is constituted of both mineral and organic matter. Furthermore it is a challenging material for ellipsometric study since it is highly transparent. The analysis of the bone surface have been carried out using infrared spectroscopic ellipsometry and ions beam techniques like Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) (Chapter 5). The techniques show complementarity and allowed a better understanding of the mechanism of etching process of bone tissue (Chapter 6). A mechanism of the etching of organic material (essentially type I collagen) is proposed.

Finally, in Chapter 7, conclusions are summarized and new directions for the improvement of the ellipsometer are drawn.

### References


Part I

Design of a spectroscopic ellipsometer in the infrared
Chapter 2

Rotating compensator ellipsometer: Instrumentation

This chapter gives a general description of ellipsometry technique and focuses on Rotating Compensator configuration. The theory is based on the work of J.H.W.G den Boer [1]. First the polarizers are reviewed and a new design for Brewster angle transmission polarizers is proposed. The performance of this new type of polarizers is investigated. They exhibit a very high degree of polarization. The principle and the design of a spectroscopic compensator are detailed. The measured characteristics of this compensator differ strongly from the calculated ones. The divergence of the infrared beam appears to be the main cause of this discrepancy.
2.1 Principle of ellipsometry

Ellipsometry is a highly sensitive technique for surface analysis. The principle relies on the change of the polarization state of light when reflecting from a surface\(^1\). To characterize the polarization state, corresponding to the direction of the electric field of the electromagnetic wave, two directions are chosen as reference. The so-called p-direction (respectively s-direction) is defined as parallel (resp. perpendicular) to the plane of incidence. Using this convention, the change of polarization can be expressed by the ratio \(\rho\) between the Fresnel reflection coefficients \(r_p\) and \(r_s\). The ellipsometric angles \(\Psi\) and \(\Delta\) are then introduced as

\[
\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta}.
\]  

(2.1)

It is clear that \(\tan \Psi\) represents the ratio of magnitudes of \(r_p\) and \(r_s\), and \(\Delta\) the phase difference between the coefficients. The results are usually shown in terms of \(\Psi\) and \(\Delta\) spectra\(^2\). A model of the surface can then be applied to fit the experimental results and extract from them the surface parameters, such as refractive index, the dielectric functions, thickness of different layers, etc. The material under investigation may be solid or liquid, and the degree of complexity in terms of anisotropy or composition (bulk, stacked layers, porosity) can be very high. This depends on the complexity of the model elaborated for the surface under investigation.

As we already mentioned [2–4], ellipsometry offers the advantage of being non intrusive. This property contributes to the large development of the diagnostic technique in the research field but also in the industry. One of the most common applications of ellipsometry is process monitoring e.g. the treatment of a silicon wafer in a plasma reactor. The sample is treated by deposition, etching or even more complex processes. The ellipsometry diagnostic can consist of a simple beam from a monochromatic source (Helium Neon laser for instance) reflecting on the sample. The change in the polarization by the surface can be monitored in real-time. A rather simple numerical model is then used to correlate the polarization change to the thickness modification of the sample.

An ellipsometer consists of a source, different polarizing devices, and a detector. The source is in our case a globar connected to a Michelson interferometer. Several types of polarizing devices can be used. Linear polarizers are generally placed:

1. Near the source, to impose a polarization to the incoming light. Because of this function, the polarizer is effectively called **polarizer**.
2. Near the detector. In this case it is called **analyzer**. Its function is to fix the polarization of the beam reaching the detector.

A third optical element is added\(^3\) in the set-up along the optical bench. This can be an extra polarizer, a **compensator** (also called retarder), or a **photo-elastic modulator** (PEM). One or more of these elements can be rotating. The result is a sinusoidal variation of the intensity of the detected signal. The analysis of the signal leads to the determination of the change of

\(^1\)In a very strict definition, we should also mention the situation of transmission ellipsometry (or polarimetry), but usage led to the association of ellipsometry to actual reflection ellipsometry  
\(^2\)In some cases, a representation with \(\tan \Psi\) and \(\cos \Delta\) is preferred  
\(^3\)Some configurations allow the use of a polarizer and an analyzer only, but the results obtained suffer generally from ambiguity. This will not be discussed further in this thesis
polarization induced by the sample. In principle any of the optical polarizing devices can be the rotating element. We will see further, that a judicious choice has to be made, depending on the experimental conditions. The photo-elastic modulator represents a case apart. This is a crystal that, while submitted to pressure, becomes birefringent. When the crystal is coupled with a piezo-electric device, the birefringence can be adjusted by changing the voltage applied to the piezo. The crystal is in this case not rotated, but a sinusoidal voltage is applied to the piezo-electric device. There is thus a large range of configurations possible for an ellipsometer. We can mention: rotating compensator, rotating analyzer, rotating polarizer, rotating analyzer-fixed analyzer (The third element is here a rotating linear polarizer placed after the sample.) etc.

Our purpose is to develop an ellipsometer including a rotating compensator. This optical element generates a phase shift between the p and s components of the electric field. This phase shift can have any value as long as it is well determined. The ideal case, is a phase shift of $\pi/2$, because the equations, that will be derived later in this thesis, are significantly simplified (the cases of a phase shift of 0 or 180° are not of interest). If the shift equals $\pi/2$, the retarder is also called quarter wave plate. The ellipsometer is in this case composed of a fixed polarizer (P), a rotating compensator (C) (situated before or after the sample (S)) and an analyzer (A), in front of the detector. We distinguish two configurations, where the compensator in placed before (PCSA) or after (PSCA) the sample, respectively. The difference between both configurations is only a modification of equations giving the intensity of the light hitting the detector.

Figure 2.1: Two possible configurations for a rotating compensator ellipsometer

Figure 2.1 shows both configurations. This technique belongs to the photometric ellipsometry technique: the intensity recorded by the detector depends on the angular position (azimuth) of one of the rotating elements. In order to obtain the equation of the intensity of the signal, we need to introduce first a suitable formalism describing the polarization state of the light beam and the transformation of the polarization due to optical components.
2.1.1 Stokes Vectors and Mueller matrices

There are different methods to represent the polarization state of light. One of them is was presented by Clark Jones [5, 6]. This formalism is based on a representation of the electric field as a complex number, the components being two orthogonal directions perpendicular to the propagation direction. A transformation can then be represented by a $2 \times 2$ matrix.

Although it has been widely used, Jones formalism suffers some limitations in ellipsometry. The main drawback is the impossibility to express partial polarization with Jones matrices. A more appropriate representation of the polarization state of light was proposed earlier (1852) by G.G. Stokes. He used a 4-element vector, called Stokes vector. Each element is a linear combination of direct observables of the electromagnetic wave. These observables are irradiances, with the dimension of energy.

\[
\vec{S} = \begin{bmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{bmatrix} = \begin{bmatrix}
I_0 \\
I_x - I_y \\
I_{+\pi/4} - I_{-\pi/4} \\
I_r - I_l
\end{bmatrix}
\] (2.2)

Here, $I_0$ is the total irradiance of the beam. The other subscripts refer to a certain direction: $x$ and $y$ represent horizontal and vertical direction respectively, $+\pi/4$ and $-\pi/4$ are $+45^\circ$ and $-45^\circ$ relative to the horizontal direction., and $r$ and $l$ denote right and left circular directions respectively. The so-called horizontal direction may be arbitrary: the other directions are defined relative to this axis. When a sample is used for measurements, it is placed vertically outside the Michelson spectrometer as shown in Figure 2.1. By extension, the horizontal direction is defined by the direction of the plane of incidence, that is actually horizontal in our case. By convention, the positive rotation direction is counterclockwise when looking into the source [7].

The great advantage of the Stokes formalism is that every element of the Stokes vectors can be experimentally determined.

For example, $S_1$ can be determined by using a perfect linear polarizer successively in the $x$ and $y$ direction, $I_x$ and $I_y$ are then measured. With the same polarizer, placed along the $+45^\circ$ and $-45^\circ$ axes, one can determine $S_2$. The parameter $S_3$ is measured by using a circular polarizer. As examples, we can give the Stokes vector of a linearly polarized beam along the vertical direction:

\[
\begin{bmatrix}
1 \\
-1 \\
0 \\
0
\end{bmatrix}
\] (2.3)

Another example is a linearly polarized beam at an angle $\varphi$ with respect to the x-axis:

\[
\begin{bmatrix}
1 \\
\cos(\varphi) \\
\sin(\varphi) \\
0
\end{bmatrix}
\] (2.4)

From the Stokes formalism, Mueller introduced a representation of optical devices by using $4 \times 4$ matrices [8], the so called Mueller matrices. A Stokes vector representing a polarization condition is transformed to another Stokes vector by the multiplication of a Mueller matrix. This type of matrix is a generalization of the Jones matrix. If a Jones matrix can always be
derived into a Mueller matrix, the reciproque is not necessarily true [9]. If an optical system exhibits depolarization, it cannot be associated to a Jones matrix. Another interesting point of the Mueller matrix formalism is that all the components of the matrix are real. Although it involves more operations, the computation of different matrices is easier. The representation of some simple optical element may however look somewhat more complex. Table 2.1 shows the associated Mueller matrix of some optical components which will be used in this thesis.

If we consider now a system of optical devices in cascade, the beam emitted from a source can be originally fully, partially, or not polarized, it will be represented by the Stokes vector \( \vec{S} \). If the beam passes through several optical devices, the resulting polarization will be modified \( \vec{S}' \).

We can associate a Mueller matrix \( (\overline{M}_1, \overline{M}_2, \ldots) \) to each optical device. The overall transformation can be expressed by a Mueller matrix \( (\overline{M}) \), which is the multiplication of the different optical devices matrices.

\[
\overline{M} = \overline{M}_N \cdot \overline{M}_{N-1} \ldots \overline{M}_2 \cdot \overline{M}_1 = \prod_{l=1}^{l=N} \overline{M}_l
\] (2.5)

### 2.1.2 A rotating compensator ellipsometer into equations

As we already mentioned, a rotating compensator offers several advantages compared to other techniques [10]. One of them is the isolation of the rotating element from the source and the detector. Ellipsometers are diagnostic instruments very sensitive to polarization, or depolarization. If the source suffers from partial polarization, and if the rotating element is installed directly next to the source, the detected signal would reflect the polarization of the source. This particular aspect would be studied in detail in a next section. A stationary polarizer immediately following the source defines unambiguously the polarization of the beam. Because of the possible sensitivity of the detector to polarization, the problem is the same with a rotating element just next to the detector, and the solution is to use a fixed analyzer next to the detector. Then the compensator can be rotated independently, without any perturbation due to the polarization of the source or the detector. Another advantage is the possibility of using any optical instrument before the polarizer and after the analyzer. This property enables an easier positioning of the elements, particularly for in situ measurements.

Let us consider now a perfect rotating compensator ellipsometer composed of:

- perfect polarizer at azimuth \( P \)
- sample under investigation with, as parameters, the ellipsometric angles \( \Psi \) and \( \Delta \)
- compensator, at azimuth \( C \), and horizontal fast axis \( \delta \)
<table>
<thead>
<tr>
<th>Optical component</th>
<th>Mueller matrix</th>
</tr>
</thead>
</table>
| Perfect linear polarizer with horizontal transmission axis | \[
\frac{1}{2} \begin{pmatrix}
1 & 1 & 0 & 0 \\
1 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\] |
| Partial linear polarizer with horizontal transmission axis and attenuation coefficient $\alpha$ and a phase difference between the main axis $\delta$ | \[
\frac{1}{2} \begin{pmatrix}
1 + \alpha & 1 - \alpha & 0 & 0 \\
1 - \alpha & 1 + \alpha & 0 & 0 \\
0 & 0 & 2\sqrt{\alpha} \cos \delta & 2\sqrt{\alpha} \sin \delta \\
0 & 0 & -2\sqrt{\alpha} \sin \delta & 2\sqrt{\alpha} \cos \delta
\end{pmatrix}
\] |
| Perfect retarder with horizontal fast axis and retardation $\delta$ | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & \cos \delta & \sin \delta \\
0 & 0 & -\sin \delta & \cos \delta
\end{pmatrix}
\] |
| Imperfect retarder with a horizontal fast axis, a retardation $\Delta_c$, and a relative amplitude change $\Psi_c$ | \[
\begin{pmatrix}
1 & \cos 2\Psi_c & 0 & 0 \\
\cos 2\Psi_c & 1 & 0 & 0 \\
0 & 0 & \sin 2\Psi_c \cos \Delta_c & \sin 2\Psi_c \sin \Delta_c \\
0 & 0 & -\sin 2\Psi_c \sin \Delta_c & \sin 2\Psi_c \cos \Delta_c
\end{pmatrix}
\] |
| Ellipsometric reflection sample where the major axis is determined by the plane of incidence. Angles $\Psi$ and $\Delta$ are the obvious ellipsometric quantities. | \[
\begin{pmatrix}
1 & \cos 2\Psi & 0 & 0 \\
\cos 2\Psi & 1 & 0 & 0 \\
0 & 0 & \sin 2\Psi \cos \Delta & \sin 2\Psi \sin \Delta \\
0 & 0 & -\sin 2\Psi \sin \Delta & \sin 2\Psi \cos \Delta
\end{pmatrix}
\] |
| Rotation matrix to represent a component in another frame of reference. The new frame is obtained after rotation of an angle $\theta$ from the old frame | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & \cos 2\theta & \sin 2\theta & 0 \\
0 & -\sin 2\theta & \cos 2\theta & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
\] |

Table 2.1: Mueller matrices for several optical components
2.1 Principle of ellipsometry

- perfect analyzer at azimuth A.

Table 2.1 gives the Mueller matrix for polarizing components with their optical axis aligned horizontally. To obtain the corresponding matrix into a reference frame at azimuth P (resp. A) we need to multiply the matrix by a set of rotation matrix with the following fashion:

\[
\overline{R}(-P) \cdot \overline{M}_P \cdot \overline{R}(P) \quad \text{(2.6)}
\]

\[
\overline{R}(-A) \cdot \overline{M}_A \cdot \overline{R}(A) \quad \text{(2.7)}
\]

The same remark stands for the compensator. The incident beam, hitting the polarizer is considered unpolarized. The corresponding Stokes vector is identical to 2.3. The resulting Stokes vector of the beam at the detector is

\[
\vec{S}_D = \overline{R}(-A) \cdot \overline{M}_A \cdot \overline{R}(A - C) \cdot \overline{M}_\delta \cdot \overline{R}(C) \cdot \overline{M}_{\Psi \Delta} \cdot \overline{R}(-P) \cdot \overline{M}_P \cdot \overline{R}(P) \cdot \vec{S}_0. \quad \text{(2.8)}
\]

Note the relation:

\[
\overline{R}(A) \cdot \overline{R}(-C) = \overline{R}(A - C) \quad \text{(2.9)}
\]

The intensity, obtained from the first component of the Stokes vector, is dependent on the azimuth of the compensator C:

\[
I(C) = A_0 + A_2 \cos 2C + B_2 \sin 2C + A_4 \cos 4C + B_4 \sin 4C \quad \text{(2.10)}
\]

where \(A_0, A_2, A_4, B_2,\) and \(B_4\) are Fourier coefficients. The different Fourier coefficients are defined by:

\[
A_0 = \frac{1}{\pi} \int_0^{\pi} I(C) dC
\]

\[
A_2 = \frac{2}{\pi} \int_0^{\pi} I(C) \cos(2C) dC
\]

\[
B_2 = \frac{2}{\pi} \int_0^{\pi} I(C) \sin(2C) dC
\]

\[
A_4 = \frac{2}{\pi} \int_0^{\pi} I(C) \cos(4C) dC
\]

\[
B_4 = \frac{2}{\pi} \int_0^{\pi} I(C) \sin(4C) dC.
\]

For a perfect rotating compensator ellipsometer it is rather easy to calculate the different Fourier coefficients:

\[
A_0 = 1 - \cos 2P \cos 2\Psi + \frac{1}{2}(1 + \cos \delta)[\cos 2A(\cos 2P - \cos 2\Psi) + \sin 2A \sin 2P \sin 2\Psi \cos \Delta]
\]

\[
A_2 = -\sin \delta \sin 2A \sin 2P \sin 2\Psi \sin \Delta
\]

\[
B_2 = \sin \delta \cos 2A \sin 2P \sin 2\Psi \sin \Delta
\]

\[
A_4 = \frac{1}{2}(1 - \cos \delta)[\cos 2A(\cos 2P - \cos 2\Psi) + \sin 2A \sin 2P \sin 2\Psi \cos \Delta]
\]

\[
B_4 = \frac{1}{2}(1 - \cos \delta)[\cos 2A \sin 2P \sin 2\Psi \cos \Delta + \sin 2A(\cos 2P - \cos 2\Psi)].
\]

(2.12)
By choosing an appropriate set of values for \( P \) and \( A \), equations 2.12 can be simplified considerably. Thus, if we choose \( P=45^\circ \) and \( A=0^\circ \) (i.e. in the plane of incidence), these equations become:

\[
\begin{align*}
A_0 &= 1 - \frac{1}{2}(1 + \cos \delta) \cos \Psi \\
A_2 &= 0 \\
B_2 &= \sin \delta \sin 2\Psi \sin \Delta \\
A_4 &= -\frac{1}{2}(1 - \cos \delta) \cos 2\Psi \\
B_4 &= \frac{1}{2}(1 - \cos \delta) \sin 2\Psi \cos \Delta.
\end{align*}
\] (2.13)

We will not consider the case of \( \delta = 0^\circ \) or \( \delta = 180^\circ \) because there is no interest to have a compensator with such a phase shift in the ellipsometer. By introducing the quantities:

\[
\begin{align*}
X_1 &= \tan 2\Psi \cos \Delta = -\frac{B_4}{A_4}, \\
X_2 &= \tan 2\Psi \sin \Delta = -\frac{B_4}{A_4} \left(\frac{1 - \cos \delta}{2 \sin \delta}\right),
\end{align*}
\] (2.14)

we obtain

\[
\begin{align*}
\tan 2\Psi &= \sqrt{X_1^2 + X_2^2} \\
\tan \Delta &= \frac{X_1}{X_2}. \quad (2.15)
\end{align*}
\]

Unfortunately, the ellipsometer cannot be considered perfect: several parameters are responsible of imperfections. Among them, the the non-achromatic character of the compensator. The value of the retardation \( \delta \) is dependent of the wavelength. Furthermore, the other optical components (polarizer, analyzer, detector...) cannot be considered perfect either. in the following, we will focus on the improvement of the polarizers, and the design of a spectroscopic retarder.

### 2.2 Source: Fourier transform infrared spectrometer

We define the "source": anything in front of the first element of the ellipsometer, the polarizer. This includes the actual light source, the interferometer, and the possibly used optical devices (mirrors or lenses) before the polarizer in order to align the beam.

The emitting source is a globar \(^4\) i.e. a silicon carbide bar, heated to a temperature around 1500K. The spectral profile of the source (Figure 2.2) is close to the one of a black body. For wave numbers of 3500 cm\(^{-1}\) and higher and 1100 cm\(^{-1}\) and lower, the intensity is weak. The signal to noise ratio is thus small. The stability of the source has been evaluated by consecutive absorbance measurements on a relatively long time scale. We report these measurements later in this chapter. The measurements obtained are shown on fig. 2.7.

#### 2.2.1 Definitions and principle

Spectroscopic ellipsometry (SE) in the infrared range suffered for a long time of a lack of efficient sources and optical materials. The sources available were not sufficiently bright. Concern-
2.2 Source: Fourier transform infrared spectrometer

Figure 2.2: Emission spectrum of the globar. Water and carbon dioxide absorption areas have been indicated.

The main optical element of a Fourier transform spectrometer is a Michelson interferometer (Figure 2.3). A set of mirrors and diaphragm is used in front of the source to generate a collimated beam. This beam is divided by a beam splitter in two parts of equal intensity. One of these two beam is reflected at a fixed mirror (M1), while the second is reflected at a moveable mirror (M2).

Then both beams pass again through the beam splitter and recombine. The resulting beam reaches eventually the detector. The beam splitter consists of two plates, the first one hit by the incident beam is called compensator, the second is the actual beam splitter. The latter is a semi-transparent plate. The role of the compensator plate (identical in its bulk part to the beam splitter plate) is to enable both separate beams to pass four times through the plates. Without the compensator, the reflected beam (going to M1) would pass through the beam splitter plate only once, and the transmitted one, three times.

If the mirror M2 is moved over a the distance \( x \), the intensity for a monochromatic source is modulated according to a cosine form:

\[
i(L) = 2j \cos(\pi \sigma L)^2,
\]

where \( j \) = intensity of light source, \( \sigma \) = wave number, \( L = 2x \), and \( x \) = displacement of mirror M2. Note that the optical path difference is \( L \) in our case, the source is a Globar, and has a continuous spectrum. This means that \( j = j(\sigma) \). The equation 2.16 must be integrated over
the wavenumber range:

\[ i(L) = 2 \int_{-\infty}^{+\infty} j(\sigma) \cos(\pi \sigma L) d\sigma \]  

(2.17)

or

\[ i(L) = \int_{-\infty}^{+\infty} j(\sigma) d\sigma + \int_{-\infty}^{+\infty} j(\sigma) \cos(2\pi \sigma L) d\sigma. \]  

(2.18)

The first term does not provide any relevant information concerning the spectrum, and will be ignored. The second term represents the Fourier transform of the spectrum \( j(\sigma) \) under investigation. By considering \( L = 2x \) the optical path difference, we obtain the set of Fourier transform equations:

\[ i(L) = \int_{-\infty}^{+\infty} j(\sigma) \cos(2\pi \sigma L) d\sigma; \]  

(2.19)

\[ j(\sigma) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} i(L) \cos(2\pi \sigma L) dL. \]  

(2.20)

It is clear that equations 2.19 and 2.20 are only theoretical: an integration to infinite values is not realistic. The mirror can only move through a certain distance \( L_M \) and an actual source has also a limited spectral range. To overcome this problem, an apodization function is used to calculation the integrals.

### 2.2.2 Influence of the temperature

The source emits black-body radiation. The globar is water cooled but the emitted heat influences the surrounding temperature inside the spectrometer and the heat transfer must be regulated. It takes thus a certain time for the source to stabilize once it is switched on.

Another cause of instabilities of the source is the oxidation of the surface of the globar if it is not heated for a long time. This can modify the efficiency of the source and the spectral profile. A solution to this specific problem is obviously to let the source burning permanently.
2.2 Source: Fourier transform infrared spectrometer

Since the thermal exchange between the inside of the interferometer, where the globar is placed, and the outside plays a critical role concerning the stability, it is important to monitor (and if possible control) the temperature in a large area around the set-up. This can lead to large problems in the case of investigation in in-situ configuration. The proximity of a reactor can result in strong perturbations due to the change of the room temperature.

The measurement duration may also be limited because of the temperature fluctuation. The calibration procedure that will be described (sections 3.4 and 3.5) needs a rather long time (of the order of 3 hours, for a complete procedure). One might be tempted to keep the same calibrated configuration for a long period. Unfortunately, we will show that, the calibration does not only consist of determining geometrical angle giving the relative azimuth of the different elements of the ellipsometer. These elements are calculated by Fourier coefficients obtained from the measured beam intensity. The latter can be influenced by the temperature. Thus the operator should find a compromise between the duration of the measurements and the number of scans per measurements (A larger number of scans offers generally a better signal to noise ratio). Also, a calibration should be carried out regularly.

2.2.3 Polarization due to interferometer

It is important to know the state of polarization of the beam leaving the interferometer (i.e. entering the ellipsometer). Even though the polarization state is fixed by the first optical component of the ellipsometer (i.e. the polarizer), if the light source is strongly polarized in a direction normal to the polarizer azimuth, the signal will be weak. Furthermore, polarized light source is not compatible with the use of a rotating polarizer ellipsometer. The source itself, a Globar, is assumed to emit unpolarized light, the use of mirrors inside the Bruker prevent these optical devices from generating polarization. The main element that is expected to polarize the beam is the beam splitter [11]. We measured the polarization degree of the source. For this purpose, we placed a polarizer and an analyzer along the optical path, and rotated the polarizer (fig. 2.4). The use of an analyzer was necessary to eliminate the influence of the polarization sensitivity of the detector and a possible polarizing property of the mirror placed in front of the detector. This sensitivity will be investigated in a later section.

![Figure 2.4: determination of the polarization of the source](image.png)

In the case of an unpolarized beam at the output of the interferometer, and assuming that the polarizers are perfect, the signal should be a perfect sinusoid. The deviation of the signal compared to the perfect sinusoid characterizes the partial polarization of the light. The signal obtained is...
shown on figure 2.5.

![Figure 2.5: Intensity of the signal detected as the polarizer is rotated of 360°. The signal was recorded for a wavelength of 2000.50 cm\(^{-1}\) but the same behavior is observed all along the spectral range. The analyzer is fixed to an arbitrary position.](image)

The light appears to be strongly polarized. In our set-up, the direction of polarization is horizontal, which will correspond to a \(p\) direction, i.e. parallel to the plane of incidence for our samples. Another particularity is that the polarization is independent of the wavelength. The signal displayed in figure 2.5 is obtained at 2000.5 cm\(^{-1}\) but is identical for all wavelengths.

### 2.2.4 Beam profile

The interferometer is functioning with a fast moving mirror. The mirror is driven with compressed air and the scanning is triggered by a He-Ne laser. In fact the laser plays two roles: in its first role, it is used as alignment laser, in order to roughly situate the infrared beam, especially when the beam is used on a path outside to the spectrometer. However, the laser spot does not correspond to the center of the beam. The laser is just parallel to the beam. This is a major drawback for the alignment of the different optical elements of the ellipsometer, since we are using rotating elements that required a quasi-perfect alignment.

In its second role, the He-Ne laser is used to trigger the data acquisition of the interferometer. On the other side of the Beam splitter, a detector cell is placed. A consequence of this necessary detection system is an alteration of the beam profile. Figure 2.6 shows a horizontal section of the beam at the output of the interferometer, and at a longer distance. Note that the beam is not distorted at the output but the profile looses its cylindrical symmetry at a longer distance. This is could be connected to an intentional focus of the beam from the manufacturer in order to have a correct beam profile at the output of the spectrometer or in the center of the analysis chamber inside the spectrometer block.

We also note the divergence of the beam, which is estimated to 1.6°. This divergence seems to be a consequence of the focusing that we just described. These elements concerning the beam...
2.3 Detector

2.3.1 Choice of detector

Basically, two types of detectors are in use in the infrared range: thermal detectors and photon detectors. Thermal detectors such as deuterated triglycine sulfate (DTGS) detectors, are based on the principle of absorption of radiant energy, which leads to a rise in temperature and a related modification of the electric properties of the sensor. This type of detector has the advantage of never being saturated, but the disadvantage of being rather slow. In photon detectors, the photons directly interact with the semiconductor material of the detector cell. They are generally very fast, but they must be handled very carefully because a saturation of the signal, due to a too large photon flux, can be fatal. Several considerations have to be taken into account for the choice of the detector. The most important are:

- spectral range
- synchronization with a fast scanning speed
- noise equivalent power (N.E.P.)

The spectral range in our study is mainly determined by the common transmission range of the optical components that we will use on the set-up. Typically, the restriction will be due to the Zinc Selenide (ZnSe) polarizers and retarder prism and the Silicon polarizer that we developed (cf. following sections). Roughly, the spectral range can be considered between $4000 \text{ cm}^{-1}$ and $700 \text{ cm}^{-1}$. This covers a large range of molecular resonance frequencies. A typical emission spectrum is shown in figure 2.2. Some areas are already identifiable:

- A large absorption band characterizing $CO_2$
- Two areas of perturbation as signature of water
The measurements need to be processed as fast as possible, but in synchronization with the scanning of the interferometer. The Bruker IFS66 allows a sampling frequency up to 200 kHz. For technical reasons, we limited our measurements to a sampling frequency of 160 kHz.

The time constant, $\tau$, which is the time required for the detector to respond to an abrupt change in input optical power. For DTGS detectors, $\tau$ is of the order of 50 ms. The class of DTGS detectors would allow a sampling frequency of the order of 10 kHz. Mercury Cadmium Telluride (also shortly named MCT) detectors offer a time constant smaller than 1 $\mu$s and a synchronization with a sampling frequency of 160 kHz is possible.

The noise equivalent power (N.E.P) represents the lower detection limit of the detector. It is the quantity of incident light equal to the quantity of intrinsic noise, i.e. the quantity of incident light when the signal-to-noise ratio is unity. In order to compare the performances between different detectors, the normalized detectivity ($D^*$) is introduced, and is defined by:

$$D^* = \sqrt{A \Delta f / N.E.P}.$$  \hspace{1cm} (2.21)

where $A$ is the optical area of the detector and $\Delta f$ is the bandwidth of the detection electronics. $D^*$ is nominally independent of the size of the detector and the bandwidth of the measurement circuit. The correcting factor $\sqrt{A \Delta f}$ is used to normalize parameter of different detectors in order to compare them. Typical $D^*$ values for DTGS detectors are $2 \times 10^8$ cm Hz$^{1/2}$/W and for MCT detectors $2 \times 10^{10}$ cm Hz$^{1/2}$/W for a detector size normalized to 1 cm$^2$ and a bandwidth of 1 Hz. The MCT detector delivers thus a much higher detectivity. To summarize the MCT detector seems to be the most suitable detector for our ellipsometric measurements.

### 2.3.2 Sensitivity to polarization

We have already discussed the polarization of the source [2] preventing the use of an ellipsometer in the rotating polarizer configuration. The detector can also be sensitive to the polarization state. The cause is the presence of a lens inside the window of the detector, in order to focus the beam on the 1 mm$^2$ detector cell. The lens may induce a certain polarization. Furthermore, if the beam is not perfectly collimated, it hits the detector lens with a non normal incidence. This can lead to a modification of the polarization of the detected light. In other words, the detector will not react in the same fashion if the analyzer position is changed. To evaluate the sensitivity of the detector to the polarization state, we used the same experimental configuration than in figure 2.4, but this time, the polarizer is fixed and the analyzer rotates. No deformation of the signal due to polarization sensitivity could be observed. It is nevertheless possible that another rotating element (compensator) generates some wobbling when rotating. The angle of incidence of the focused beam hitting the detector cell would then be modified and the lens inside the detector would generate a modulated phase shift.

### 2.3.3 Water inside the detector

While determining the stability of the source, a certain spectroscopic signature was detected around 3000 cm$^{-1}$. The signature was increasing in time and seemed to be characteristic of a liquid of a solid element. (Figure 2.7(a))
Figure 2.7: Absorbance spectra measured at the output of the interferometer (2.7(a)) and obtained for water at 80K (2.7(b))
We compared our measurements with spectra of water measured in Leiden Observatory at the University of Leiden\(^5\). A spectrum corresponding to a temperature of 80K is shown in Figure 2.7(b), which is very similar to the spectral shape of Figure 2.7(a).

This led us to the conclusion of the presence of water inside the chamber of the detector cell, which is cooled with liquid nitrogen (77K). The fact that the amount of water is increasing can be due to either a leak inside the detector cell, or a progressive cooling down of the water. This presence of water was detected inside several detectors. However, the consequences on the measurements are not so critical since the measurements are rarely longer than a few minutes, and the disturbance of the spectra within this time frame is relatively small (less than 2% after 1 hour). Thus, we decided to use these detectors anyway and if necessary, we would take this phenomenon into account while measuring in this spectral range.

### 2.4 Brewster angle transmission polarizer (BATP)

Polarizers in the infrared generally suffer from poor performance. Few materials showing good transmission in this spectral range are available. The quality of the polarizers are however of the utmost importance for ellipsometry. If the extinction coefficient appears to be poor, errors could lead to difficult interpretation of the spectra. Furthermore, the calibration procedure that will be detailed in the next chapter, will is based on the assumption of perfect polarizers. To improve the polarization coefficient of the linear polarizers used in the ellipsometer, and to increase the amount of transmitted light, we designed new polarizers based on the principle transmission at Brewster angle. Such type of polarizer has been already designed in the group of Prof. D. van der Marel [12] at the University of Groningen.

#### 2.4.1 Principle

Let us consider an electromagnetic wave (electric field amplitude \(E_p\) and \(E_s\)) initially propagating in a medium of refractive index \(n_0\) and hitting the surface delimiting a medium of index \(n_1\), with the angle of incidence \(\theta_0\). Part of this electromagnetic wave is reflected (\(E''_p\) and \(E''_s\)), another part is transmitted and propagates through the second medium (\(E'_p\) and \(E'_s\)), with an angle of refraction \(\theta_1\). Using the convention that one always looks against the direction of propagation of the wave, and considering only the electric field that determines the polarization state, we can express the Fresnel amplitude transmission coefficients:

\[
\frac{E'_s}{E_s} = t_s = \frac{2n_0 \cos \theta_0}{n_0 \cos \theta_0 + n_1 \cos \theta_1},
\]
\[
\frac{E'_p}{E_p} = t_p = \frac{2n_0 \cos \theta_0}{n_1 \cos \theta_0 + n_0 \cos \theta_1}. \tag{2.22}
\]

By using Snell’s law, we can eliminate \(n_0\) and \(n_1\):

\[
t_s = \frac{2 \sin \theta_1 \cos \theta_0}{\sin (\theta_0 + \theta_1)},
\]
\[
t_p = \frac{2 \sin \theta_1 \cos \theta_1}{\sin (\theta_0 + \theta_1) \cos (\theta_0 - \theta_1)}. \tag{2.23}
\]

The **intensity** transmission coefficients are defined by:

\[
T_s = \frac{n_1 \cos \theta_1 t_s^2}{n_0 \cos \theta_0 t_s^2} = \frac{4n_0 n_1 \cos \theta_0 \cos \theta_1}{(n_0 \cos \theta_0 + n_1 \cos \theta_1)^2} = \frac{\sin 2\theta_0 \sin 2\theta_1}{\sin^2 (\theta_0 + \theta_1)},
\]

\[
T_p = \frac{n_1 \cos \theta_1 t_p^2}{n_0 \cos \theta_0 t_p^2} = \frac{4n_0 n_1 \cos \theta_0 \cos \theta_1}{(n_1 \cos \theta_0 + n_0 \cos \theta_1)^2} = \frac{\sin 2\theta_0 \sin 2\theta_1}{\sin^2 (\theta_0 + \theta_1) \cos^2 (\theta_0 - \theta_1)}.
\]

These coefficients depend on the angle of incidence as shown in figure 2.8 In this case, the coefficients represent those of silicon. The intensity reflection coefficients are also shown as obtained by the following relations:

\[
R_s = 1 - T_s,
\]

\[
R_p = 1 - T_p.
\]

Figure 2.8: Intensity transmission and reflection coefficients for silicon at a wavelength of 5 µm, the ambient is air.

Silicon presents suitable properties of transmission in our spectral range. It is also easy to handle and can be purchased in the form of double side polished wafers, very appropriate for this purpose. When the angle of incidence approaches the Brewster angle, light polarized parallel to the plane of incidence (p) is fully transmitted whereas the s-component is only partially transmitted (around 30 %) The Brewster angle \( \theta_B \) is defined by:

\[
\tan \theta_B = \frac{n_1}{n_0}.
\]

From now, we will consider only air and silicon, with \( n_1 = 1 \) and \( n_2 = n \), respectively. For Silicon, \( \theta_B = 73.7^\circ \) for a wavelength of 5 µm. At this angle, transmission coefficients have considerably simplified expressions:

\[
T_s = \left( \frac{2n}{1 + n^2} \right)^2,
\]

\[
T_p = 1.
\]
The silicon wafer must be considered as a parallel plate with two air/silicon interfaces. Thus, when the beam light passes through a silicon wafer, the transmission coefficient in the p-direction is given by:

\[ T_{wafer}^s = T_s^2 = \left( \frac{2n}{1 + n^2} \right)^4. \]  

(2.28)

When transmitted through \( m \) wafers, the transmission coefficient is then the \( m \)-th power of \( T_{wafer}^s \). By using a set of wafers, one can build a linear polarizer with a polarization direction parallel to the plane of incidence of the silicon wafers. The aim is to decrease the s transmission coefficient to an undetectable value\(^6\). For this purpose we use several parallel plates in cascade.

The efficiency of a polarizer is calculated by the intensity ratio between the extinction azimuth (where the transmitted intensity reaches a minimum) and the transmission azimuth (perpendicular to the extinction one). This value is called polarization ratio, or polarization coefficient. Our first measurements have shown that a better polarization coefficient is obtained for an angle of incidence slightly larger than the Brewster angle [13]. This is confirmed by Bird et al. [14] who have shown that the best polarization coefficient is obtained with an angle of incidence 4 degrees larger than the Brewster angle \( \theta_B \). This property can easily be explained from figure 2.8. At an angle \( \theta = \theta_B + 4^\circ \), the transmission coefficient \( T_p \) is slightly smaller because of the horizontal curve at \( \theta_B \), but \( T_s \) is much more reduced because of a stronger slope at \( \theta_B \). However, the aim of the development of this type of polarizer is to obtain a higher transmitted intensity \( T_p \) compared to wire grid polarizers. We have to impose a certain limit to keep sufficient transmitted signal. The limit can be obtained by calculating the difference between the transmission coefficient in the p direction and the one in the s direction,(cf. Fig. 2.9) and it shows a maximum for \( 79^\circ \). According to our first measurement, we decided to use an angle of 78\(^\circ\). When comparing results obtained at Brewster angle and at 78\(^\circ\):

- p-component transmission coefficient \( T_p \) is reduced from 1 to 0.978.
- s-component transmission coefficient \( T_s \) is reduced from 0.292 to 0.224.

Until now, we did not consider any interference or absorption effect. Silicon wafers should be considered as parallel plates. Interferences are generated within the plates and it is virtually impossible avoid them. Internal interferences can be modelled by the following equations [15]:

\[ T_s = \left( \frac{2n^2}{1 + n^4} \right)^m, \]

\[ T_p = 1, \]

(2.29)

where \( m \) is the number of silicon plates. Silicon is also a partially absorbing medium in the infrared, and the absorption efficiency is varying along the spectrum. The effect can be modelled by the following equations [15]:

\[ T_s = \frac{\left( \frac{2n}{1+n^2} \right)^{4m} e^{-\alpha d}}{1 - \left( \frac{n^2-1}{n^2+1} \right)^4 e^{-2\alpha d}}^m, \]

\[ T_p = e^{-\alpha d} \]

(2.30)

\(^6\)An alternative solution would be to choose a material with a larger refractive index, in this case the s-component that is transmitted is even lower. A larger refractive index leads however to a larger Brewster angle, and for a suitable extinction, the Brewster angle would approach 90\(^\circ\), and the construction of the polarizer would be unrealistic.
2.4 Brewster angle transmission polarizer (BATP)

Figure 2.9: Difference between the transmission coefficients in p and s directions at $\lambda = 5\mu m$.

with $\alpha$ the absorption coefficient and $d$ the thickness of the wafer. The consequences are nevertheless small considering the thickness of the wafers.

Another effect that can alter the measurements is the interference between plates, aligned in cascade. Because the angle of incidence must be close to the Brewster angle for each wafer, the latter have to be parallel to each other. This parallelism can generate interferences. A solution is to tilt the wafers to avoid a perfect parallelism, and still take care that the angle of incidence is close to the Brewster angle. Thus we can practically calculate the transmission coefficients by taking into account only interferences within plates.

Figure 2.10: Brewster angle in the infrared range for Silicon in air

The transmission coefficients have been calculated at a wavelength of $5 \mu m$. Since the Brewster angle is defined by the index of refraction, one should consider the influence of the wavelength on the efficiency of the polarizer. Figure 2.10 shows the dependency of the Brewster angle
with the wavelength. The variation is rather small, one should not expect strong discrepancies from the calculations performed at 5 µm. Thus the wavelength dependency does not have a strong influence on the properties of the polarizer and the maximum of efficiency does not vary significantly. The chosen angle of incidence at 78° seems suitable for the polarizer.

2.4.2 Design

The transmission of a light beam through a parallel plate generates a shift $e$ of the outgoing beam. The shift is calculated by:

$$e = d \sin (i - r) / \cos r,$$

(2.31)

where $d, e, i, r$ are shown on figure 2.11

![Figure 2.11: Transmission through a parallel plate.](image)

This is a major drawback in the design of such polarizers because they must be able to rotate without exhibiting any wobbling or translation. The detector cell area of the MCT detector is of the order of 1 mm$^2$, and even a minor wobbling of the beam while the polarizer is rotating would be a problem. A solution to avoid this shift is to cross the parallel plates in order to get the same number of Silicon wafers with an angle of incidence $i$ and -$i$ respectively. The displacement of the transmitted light beam is then compensated. Another requirement is to have a polarizer as compact as possible.

Another parameter that has to be taken into account is the divergence of the beam. We have already shown (section 2.2.4) that, because of the large size of the globar, the beam cannot be perfectly collimated. The residual divergence was measured at 1.6°. The effective angle of incidence will then be slightly changed, altering the polarization coefficient.

We present the design of a polarizer in which 9 parallel plates are used with an angle of incidence of 78°. The parallelism between plates is slightly imperfect in order to avoid interferences. Three long wafers are inserted in one trench, and two sets of smaller wafers are inserted in order to intersect the long ones at the point of contact of the wafers, these are cut with an angle of 24° for a better continuity of the beam. The design is made in such configuration that the beam always passes through 3+3 wafers with an angle of incidence $+i$ and -$i$). Therefore, a shift is necessary between the trenches for the smaller wafers set (cf. close-up in Figure 2.12).

2.4.3 Performance

The polarization coefficient of the polarizers has been measured. For this purpose, a Brewster angle transmission polarizer (BATP) was placed behind a tandem wire-grid polarizer. The
Brewster angle transmission polarizer was then positioned successively parallel and perpendicular to the wire grid polarizer. The tandem wire grid polarizer has been studied by den Boer et al. [16] Specifications of single wire grid polarizers are given in Chapter 3, table 3.1. The tandem polarizer has a rather high polarization coefficient and has the property of transmitting over a large spectral range. It suffers however of a strong back reflection effect, because the beam hits the surface of the polarizer perpendicularly. The loss is estimated to 30%, to which we have to add, in an ideal case, 50% due to the polarization of the light at the output of the polarizer. When placed in tandem, the loss due to back reflection becomes 50%. Thus, the intensity of a light beam transmitted from a tandem wire grid polarizer collapses to 25% of the impinging beam. The ellipsometer is using two identical polarizers (polarizer and analyzer), and obviously, such loss of intensity becomes quickly critical. This intensity loss effect is not visible with a Brewster angle polarizer, since 100% of the light in the in the p-direction is transmitted, whatever the number of parallel plates are used (The absorption within the plates is neglected).

The measurement of the polarization coefficient relies on few assumptions. The first one is that there is no polarization sensitivity of the detector, and no polarization of the source. To avoid this problem, a reference polarizer is placed between the source and the Brewster angle polarizer, and is fixed. In such a configuration, the beam entering the BATP exhibits the same polarization state. The polarization sensitivity of the detector is much weaker, but can also overcome by placing another fixed polarizer between the BATP and the detector, this second polarizer is positioned parallel to the first one. Finally, another assumption is that the reference polarizers (here the tandem wire grid) are perfect, which means with an infinite polarization coefficient. This assumption is obviously never met.

The measurements are shown on Figure 2.13. The values obtained from this measurement, appeared to be lower than what we could expect, especially for the low wavelength (high wave number) The polarization coefficient varies by more than a factor 10, whereas we expected a rather homogenous distribution of the values. The explanation comes from the third assumption that we presented above, concerning the perfection of the reference polarizers. The tandem wire grid, although suitable for most of infrared polarization applications, suffers from a “leak”, in the sense that even in crossed position, residual light goes through. This leak is strongly dependent on the wavelength [16]. As none of the polarizers (reference or BATP) can be considered
Figure 2.13: Polarization coefficient of a Brewster angle transmission polarizer. The polarizer is placed between two tandem wire-grid polarizers and is isolated from the polarization influence of the source and the detector.

Figure 2.14: Polarization coefficient of a Brewster angle transmission polarizer: Two Brewster angle polarizers are used in this case. Only one is rotated, and positioned successively parallel and perpendicular to the other one.

perfect, the polarization coefficient measured is more related to the less perfect polarizer. In the present case, it seems that the Brewster angle polarizer exhibits a better performance than the wire grid polarizers.

In order to overcome this situation, we simply used two BATP positioned successively parallel and perpendicular to each other. This time, the polarization coefficient doesn’t suffer from strong variations and exhibits higher values between 1000 and 2000. However, considering the procedure we used, a correction on the polarization coefficient has to be made. If we consider
both polarizers identical, thus with the same attenuation coefficient $\alpha$ defined in table 2.1 position 2 (we will not consider an induced phase shift), the intensity measured when the polarizers are crossed at $90^\circ$, is $4\alpha$. Thus the polarization coefficient measured has to be corrected by a factor 4. Which means that the BATP polarizer, has a polarization coefficient varying from 4000 to 8000 (Figure 2.14), over a spectral range from 4000 to $800 \text{cm}^{-1}$.

The signal is noisy however. This is due to the very low intensity recorded when the polarizers are crossed. In this extinction configuration, the signal to noise ratio is very low, close to the unit. The fluctuations on the measurement of the polarization coefficient are directly related to the fluctuation of the noise. In fact, the values of the polarization coefficient are limited by the low intensity of the source.

We have been able to design an compact Brewster angle transmission polarizers allowing a utilization in a rotational mode. The theoretical analysis of the polarizer predicts a polarization coefficient of 65 000 (cf. eq. 2.29). We have been able to measure values between 4000 and 8000. There are several reasons that could explain these discrepancy. First, the polarizer is designed for a specific wavelength, since the Brewster angle is wavelength dependent. The application of the polarizer to a wide spectral range will necessarily generate deviations from the theoretical values. Second, we did not take into account the absorption of silicon in the infrared range. The light beam is transmitted through 6 silicon wafers of 0.48 mm. This has certainly an influence on the outgoing intensity. Third, the divergence of the beam will also generate some leak, because the Brewster angle principle is based on a accurate positioning between the beam and the silicon wafer. A deviation from the Brewster angle of 1 to $2^\circ$ can have a large consequences on the polarization coefficient. Finally, because of the weak intensity of the infrared source, the signal measured in low and the noise limit is quickly reached. This generates significant fluctuations when measuring the minimum intensity with crossed polarizers, leading to even negative values for the measured intensity. Figure 2.14 shows actually the polarization coefficient calculated with the absolute value of the extinction signal. In conclusion, we have built a polarizer good enough to hardly distinguish leaking signal from the noise when the angular position corresponds to the extinction.

2.5 Design of a spectroscopic compensator

2.5.1 Principle

As we already explained, a compensator is an optical element that generates a phase shift in the electromagnetic wave. Common compensators are quarter wave plates ($\lambda/4$) leading to a phase shift of $\pi/2$ between the electric field in two perpendicular directions. This type of optical devices is in general very accurate, but is limited to a very narrow spectral range. In fact they are generally designed for a specific wavelength and not for a spectroscopic application.

It is nevertheless possible to obtained a phase retardation over a large spectrum, by designing a so-called achromatic retarder. There are different ways of designing these retarders. One is to use the principle of total internal reflection [17]. This very simple principle results directly from Snell’s laws: When a beam propagating in a prism hits the wall with an angle of incidence larger than a critical value, none is transmitted and the entire beam is reflected, at least optically. This phenomenon is only possible if the index of refraction in of the medium where the beam propagates has a index of refraction larger than the outer medium. But this condition is not
sufficient. The angle of incidence \( i \) must be larger than the critical angle, defined by:

\[
\sin i > \frac{n_2}{n_1}
\]  

(2.32)

where \( n_1 \) and \( n_2 \) are the indices of refraction of the medium where the incident beam propagates and the outer medium, respectively.

Figure 2.15: Principle of total internal reflection. The inner medium (in gray) has the larger index of refraction. According to Snell’s laws, when the angle of incidence is large enough (cf eq. 2.32), the light is fully reflected and the outgoing beam polarization exhibits a phase shift.

In our case the outer medium is air. The light polarization is then modified by a phase shift. The latter depends on the angle of incidence and the wavelength, but if the material is chosen with small dispersion (i.e. an almost constant index of refraction), it hardly varies within the considered spectral range.

The choice of this optical principle has a major disadvantage, that actually prevented the development on a larger scale of such retarders: the beam must be deviated by internal reflection. The use of the compensator in rotation yields the addition of mirrors to redirect the beam in the rotation axis. The mirrors, depending on the angle of incidence of the beam, will add a phase shift, that has to be taken into account. Thus, the compensator should contain the smallest number of mirrors, with the smallest possible angle of incidence.

Our group already developed a spectroscopic compensator based on the principle described above [1, 18]. One total internal reflection was performed inside a crystal of KRS-5, and three mirrors were used in order to redirect the beam. Unfortunately, it turned out that the KRS-5 crystal was not suitable. As most of the crystals, it exhibits birefringence properties when submitted to pressure. But because it is rather soft, KRS-5 is quite sensitive to this effect. Furthermore, it has been shown that the large thermal expansion of this crystal leads to a strong variation of the compensator behavior if the ambient temperature is changing.

### 2.5.2 Design

For our purpose we used a rhomb prism of Zinc Selenide (ZnSe). The choice of the material was made by considering several parameters:
2.5 Design of a spectroscopic compensator

- rather non-dispersive material with a large index of refraction in the spectral range under investigation.
- low thermal expansion and low elasticity. These properties prevent from deformation and distortion that might lead to imperfections of the phase shift.
- easy to manufacture and is not as toxic as KRS-5.

We determine the geometry of the prism by considering two internal reflections within the prism. Figure 2.16 shows the index of refraction of Zinc Selenide for the spectral range we want to investigate (2.5 to 13 $\mu$m). We opted for a Fresnel rhomb type prism.

![Figure 2.16: Index of refraction of Zinc Selenide](image)

The material ZnSe is slightly dispersive, the refractive index value remains however close to 2.42 on a large spectrum. The angle of incidence for the internal reflection is chosen at 65 degrees. Two mirrors are used to realign the beam to the rotation axis of the compensator. The angle of incidence of the beam hitting the mirrors is close to 12.5 degrees and is adjustable over an angular range of 3 degrees, with micrometer screws. The design of the compensator is shown on Figure 2.17. Note that with a length of 22 cm, and a weight of around 2 kg, such a retarder is totally different than a usual mono-wavelength quarter wave plate. The motor allowing the rotation of the compensator block has a rotation frequency of 20 degrees per second. The compensator must be as stiff as possible to avoid any wobbling. A calculation of the theoretical optical characteristics of the complete compensator is given in table 2.2 for several wavelengths. To evaluate the properties of the compensator, we positioned the ellipsometer in a straight through position. In such a configuration, both branches of the ellipsometer are aligned, and no sample is placed between the polarizer and the compensator. The characteristics of the compensator are determined by the total phase shift $\Delta_c$ and the amplitude ratio $\Psi_c$ induced by compensator. These two parameters obviously depend on the wavelength and should be accurately determined. Den Boer et al. have determine a procedure allowing the determination of $\Delta_c$ and $\Psi_c$, when the following assumptions are respected [19].
<table>
<thead>
<tr>
<th>wave number</th>
<th>$\Psi$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1030 cm$^{-1}$</td>
<td>44.76°</td>
<td>89.82°</td>
</tr>
<tr>
<td>1500 cm$^{-1}$</td>
<td>44.74°</td>
<td>89.90°</td>
</tr>
<tr>
<td>2500 cm$^{-1}$</td>
<td>44.75°</td>
<td>89.78°</td>
</tr>
<tr>
<td>4000 cm$^{-1}$</td>
<td>44.71°</td>
<td>89.60°</td>
</tr>
</tbody>
</table>

Table 2.2: Theoretical values of the induced $\Psi_c$ and $\Delta_c$ after the beam passes through the complete retarder.

Figure 2.17: Rotating compensator mounted on a stepper motor. The beam reflects twice inside the Zinc Selenide prism and is realigned by means of two bare gold mirrors, so that the complete bloc can rotate, without any shift or wobbling of the beam.

- The polarizer and the analyzer are considered perfect, and perfectly aligned. With regard to the performance of the Brewster angle transmission polarizers described earlier, we can consider this assumption realistic.

- Perfect collimation of the beam. We already know that this assumption is not correct. But the influence on the characteristics determinations will be discussed later.

- The compensator does not suffer from any other imperfections such as wobbling, or internal reflection between the wall of the prism. Once again, it is very likely that this assumption is not fulfilled.

- The source and the detector are considered perfect.
2.5 Design of a spectroscopic compensator

The description of the procedure and the calculations are already described in [1, 19]. Imperfect components related to the compensator are introduced, namely $x_c$, $y_c$, and $z_c$, defined as:

$$
x_c \equiv \cos 2\Psi_C,
$$
$$
y_c \equiv \sin 2\Psi_C \cos \Delta_C,
$$
$$
z_c \equiv \sin 2\Psi_C \sin \Delta_C.
$$

(2.33)

One can easily see that these parameters are linked by a quadratic relation:

$$
x_c^2 + y_c^2 + z_c^2 = 1.
$$

(2.34)

For a perfect compensator, i.e. with $\Delta_C = 90^o$ and $\Psi_C = 45^o$, we obtain:

$$
x_c = 0;
$$
$$
y_c = 0;
$$
$$
z_c = 1;
$$

(2.35)

The Mueller matrix of the compensator $M_{\Psi_C,\Delta_C}$ is given in table 2.1. In the case of a straight through configuration $\Psi = 45^o$ and $\Delta = 0$. The Stokes vector at the detector is given by:

$$
\vec{S}_D = \overline{R}(-A) \cdot \overline{M}_A \cdot \overline{R}(A - C) \cdot \overline{M}_{\Psi_C,\Delta_C} \cdot \overline{R}(C) \cdot \overline{R}(-P) \cdot \overline{M}_P \cdot \overline{R}(P) \cdot \vec{S}_0
$$

(2.36)

The intensity can be expressed in the same form than eq. 2.10. If the polarizer is positioned at the azimuth $P=45^o$ and the analyzer at $A=0$, the expression for the different Fourier coefficients are substantially simplified. By assuming that the azimuth of the compensator is unknown, den Boer et al. have shown that the different Fourier coefficients can be expressed as [19]:

$$
A_0 = 1,
$$
$$
A_2 = x_c(\cos 2C + \sin 2C),
$$
$$
B_2 = x_c(-\sin 2C + \cos 2C),
$$
$$
A_4 = \frac{1}{2}(1 - y_c) \sin 4C,
$$
$$
B_4 = \frac{1}{2}(1 - y_c) \cos(4C).
$$

(2.37)

The compensator characteristics are then given by:

$$
x_c = \pm \sqrt{\frac{2A_2^2 + 2B_2^2}{2A_0}},
$$
$$
y_c = 1 - 2\sqrt{\frac{A_2^2 + B_2^2}{A_0}}.
$$

(2.38)

The values for $\psi_C$ and $\Delta_C$ are obtained from eq. 2.33:

$$
\cos 2\psi_C = x_c,
$$
$$
\cos \Delta_C = \frac{y_c}{\sqrt{1 - x_c^2}}.
$$

(2.39)

The parameter $z_c$ is calculated from eq. 2.34. One can note that $x_c$ is not fully determined, but only its absolute value is known. This is actually not a real problem since the sign of $x_c$ can be
Figure 2.18: Parameters of the compensator (2.18(a)) and the corresponding amplitude ratio $\Psi_C$ and phase shift $\Delta_C$ (2.18(b)) determined by experiment.

deduced from a test measurement in a straight through configuration. In this case, one should measure a phase shift $\Delta$ of 0°, once the detected signal is corrected with $x_c$. By trying calculation with both signs, we can determine the appropriate one, that remains of course the same for the rest of the measurements.

Figure 2.18 shows the experimental values of the characteristics of the compensator. It shows a large discrepancy with the theoretical values. This is at first glance rather surprising. The theoretical calculations show a variation as function of the wavelength of the order of 1 degree for $\Delta_C$, whereas the experimental value is more than 12°. Furthermore, the measured data are lower than expected. As we already mentioned, one of the most critical aspects of the ellipsometer is the divergence of the beam, estimated between 1 and 3 degrees. The angle of incidence for the internal total reflections (ideally 65°) inside the Zinc Selenide prism should be considered broadened, within a range from 63° to 69°. Figure 2.19 shows the variation of the phase shift generated by the two reflections inside the prism, as a function of the angle of
incidence and the wavelength. The figure shows a strong variation with the angle of incidence, whereas the wavelength has almost no influence on the phase shift. This is in contradiction with the measured values of the characteristics of the compensator, where the wavelength dependency seems important. Until now we can only give some suggestions to explain this result: The divergence of the beam is linked to the light wavelength. The short wavelengths seem to follow more diverging directions than long wavelengths.

![Graph](image.png)

Figure 2.19: Theoretical phase shift generated by 2 internal total reflections inside a Zinc Selenide prism. The angle of incidence is optimized at 65°, for a phase shift of 90°

The divergence of the beam originates from an off-axis parabolic mirror redirecting and collimating the beam in front of the beam splitter. The partial beam, directly transmitting through the beam splitter hits a moveable mirror, whose function is the modulation of the beam according to the wavelength. The optical path, as we already mentioned, is determined by the amplitude of the linear oscillation of the moveable mirror. If the beam is not well collimated, the modulation is imperfect. Depending on the position of the moveable mirror, the external parts of the beam may not be reflected. This means that the optical path will not be homogeneous on the complete cross section of the beam, especially on the external, or the most diverging, parts of the beam. This phenomenon can lead to an inhomogeneous repartition of
the wavelength inside the beam. Indeed, Figure 2.20 shows measurements of spectra performed at different positions within the beam. For these measurements, the detector is placed directly facing the beam, without the use of focusing mirror. The repartition of the intensity with the wavelength varies slightly for the different spectra. It seems difficult to correct this problem since it is directly related to the divergence of the beam, which cannot be totally prevented.

Another cause that might explain the strong discrepancy between theoretical and experimental results is the depolarizing property of zinc selenide. Röseler mentioned a depolarization degree of $P = 0.4$, after multiple internal reflections in KRS-5 ATR crystal [20]. KRS-5 is a crystal with optical properties close to those of ZnSe. Unfortunately, the measurements of the degree of polarization requires the use of ATR crystal, and this measurement was not possible in our laboratory. We can thus only suggest this depolarization phenomenon to explain the behavior of our retarder.

![Figure 2.20: Comparison of different spectra measured within the beam. The detector cell is placed directly in the beam without focusing mirrors. The spectra has been normalized. The wavelength distribution within the beam appears to be non-homogenous.](image)

One should note that the rather large difference between the theoretical and the measured parameters of the compensator are not critical at all. In the following chapter, we will show that ellipsometry measurement can be performed, by introducing corrections on the compensator behavior. The characteristics of the compensator can be measured with an excellent accuracy. In fact, any generated phase shift can be used, as long as the latter is well known. Only few conditions are required: the phase shift $\Delta_{C}$ should be sufficiently different from $0$ (360°), and 180°. These conditions are obvious if one want to keep the interest of using a compensator. Furthermore, the measured values should be stable, in order to be defined once before the measurement session.
References


Chapter 3

Imperfect ellipsometer: alignment, calibration, measurements

The imperfections of the ellipsometer are investigated. The consequences on the alignment and the calibration are studied. In particularly, the case of the calibration of the compensator is studied in detail. It is shown that it is possible to use imperfect optical components and to use suitable corrections to perform accurate measurements. Ellipsometric spectra are performed on samples of silicon oxide on silicon. The influence of the thickness of the oxide layer and of the angle of incidence on the spectra are investigated. In particular, the shift of the longitudinal and transversal optical modes of silicon oxide is studied in detail.
3.1 Introduction

Because of the high sensitivity of ellipsometry, the alignment and calibration procedure is of prominent importance. Any imperfection in the set-up can generate errors in the measurement that are disastrous for further interpretation. It is thus absolutely essential to minimize imperfections, and to have a good and accurate estimation of these. Furthermore, the application of ellipsometry for a spectroscopic purpose introduces much more parameters, which requires an even higher level of control during the calibration and the measurement procedures. Several studies have already been performed in order to characterize the imperfections, generated by misalignment and their consequences on the calibration of the ellipsometers [1–5]. Unfortunately, a generalization of these results to any type of ellipsometer would be vain. Each configuration (e.g. null ellipsometry, rotating analyzer/polarizer, rotating compensator, photo elastic modulation . . . ) will be more sensitive to one specific parameter, and the sources of imperfection may also be different.

The functioning is based on a rotating compensator ellipsometer, associated to a Fourier transform infrared spectrometer (FTIR). The spectrometer is a Bruker IFS66. This ellipsometer allows a spectral study over a range varying from 4000 cm$^{-1}$ to 800 cm$^{-1}$ (2.5 to 12.5 $\mu$m). The advantage of the combination of FTIR and ellipsometry is the capacity to gather information, not only on the optical (index of refraction), electrical (dielectric function), of the physical (layers thickness) structure of the material under investigation, but also on its chemical composition by monitoring the chemical signature of the different elements [6, 7].

The key element of the ellipsometer is the spectroscopic compensator. The difficulty of building such a retarder is precisely its spectroscopic property. It is technically nearly impossible to design a retarder with a constant phase shift over a large spectral. This is due to the lack of achromatic (or non dispersive) material in the infrared. In the next part, we will list the parameters that might be sources of errors if they are not well known and estimated. Then an investigation of the alignment procedure will be discussed. The calibration of the compensator will be studied in detail, and particularly the consequences of misalignment.

In order to qualify the ellipsometer, and study its behavior, we performed a series of measurements of amorphous silicon oxide ($a-SiO_2$) deposited on silicon $<100>$ wafers. The choice for such sample was driven by the large amount of publications on this subject [8–12], which allows easy comparison of measured data. Furthermore, silicon oxide is a transparent material in the infrared and silicon is a reflective crystal. A direct consequence of the combination of these two materials is a strong wavelength dependent variation of the phase shift $\Delta$. Furthermore, silicon oxide exhibits some absorption signatures around 1000 cm$^{-1}$, these bands should be visible on the spectra.

3.2 Sources of imperfection

The ellipsometer is used in a PSCA configuration, where P, S, C, and A designate the polarizer, sample, compensator, and analyzer respectively. The first step is thus to detail the different sources of imperfection in the ellipsometer.
3.2 Sources of imperfection

Source

The first element of the ellipsometer is the source. By source, we mean any optical element positioned before the polarizer. This includes the actual source, a globar, and the FTIR spectrometer, and optionally some aligning and collimating elements. With this definition, the source is partially polarized, essentially because of the presence of a beam splitter in the Michelson interferometer. The effect of such a device has been studied by Röseler [10]. In a more general case, the source can also exhibit a phase shift between the p and s polarization components. The source can be represented by a perfect source Stokes vector associated to a partial polarizer Mueller matrix $\overline{M}_{POL}(\alpha_D, \delta_D)$, with attenuation coefficient $\alpha_S$ and a phase shift coefficient $\delta_S$.

Polarizer

Any linear polarizer, especially for spectroscopic applications, undergoes some leak, which means that an unwanted transmission occurs in the cutting direction of the polarizer. For some experiments, wire grid polarizers have been used. This type of polarizer consist of a parallel plate or material transmitting in infrared, and coated with metallized oxide. The coating has a sinusoidal profile and forms a grating at the surface. The polarizer absorb the light light polarized in the direction parallel to the lines and let the perpendicular light passing through. The efficiency of the polarizer depends on the spacing of the lines of the grating. We used two types of wire grid polarizers, one set made of Barium fluoride (BaF$_2$) and one set made of Thallium Bromide Iodide (KRS5). The latter has the advantage of being transparent on a very large spectral range, but the line spacing is larger than for the BaF$_2$ substrate.

<table>
<thead>
<tr>
<th>Material</th>
<th>BaF$_2$</th>
<th>KRS-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aperture</td>
<td>25 mm</td>
<td>25 mm</td>
</tr>
<tr>
<td>Transmission efficiency</td>
<td>85%</td>
<td>70% (10 $\mu$m) - 50% (3 $\mu$m)</td>
</tr>
<tr>
<td>Grid period</td>
<td>0.25 $\mu$m</td>
<td>0.4 $\mu$m</td>
</tr>
<tr>
<td>Transmission of unwanted radiation</td>
<td>1% (3 $\mu$m)</td>
<td>4% (3 $\mu$m) - 0.25% (10$\mu$m)</td>
</tr>
</tbody>
</table>

Table 3.1: Characteristics of wire grid polarizers

Table 3.1 gives the different characteristics of the polarizers. Note the low extinction coefficient of the polarizer: a maximum value of 50, over a large spectral range (2 to 11 $\mu$m). It is possible to greatly improve the efficiency of such a polarizer by using them in tandem [13]. The extinction coefficient is then squared, and reaches decent values. Unfortunately, the transmission is then strongly affected and the percentage of light passing through can be very low. Thus in some situations, the use of tandem wire grid polarizers is not possible. The wire grid polarizer presents also the drawback of introducing a phase shift between the transmitted and the absorbed components [14]. A phase shift coefficient has to be introduced in the Mueller matrix representing the polarizer.

These conclusions led us to the design of new polarizers described in the previous chapter in order to improve the extinction coefficient and transmit the maximum of light. These Brewster angle transmission polarizers have a much larger polarization coefficient, and offering a smaller dependency to the wavelength. However, to keep a more general approach, we consider to this point this polarizer imperfect. Using the concept of Mueller matrices, a polarizer can be...
represented by the matrix described in Table 2.1, position 2, with a attenuation coefficient $\alpha_P$ (resp. $\alpha_A$), and a phase shift $\delta_P$ (resp. $\delta_A$) for the polarizer (resp. analyzer).

**Detector**

The detector response can also be a source of error. Polarization-dependent photo-detector sensitivity has been mentioned by Azzam & Bashara [15]. This can be a major problem, in the case of a rotating analyzer configuration. The analyzer impose a linear polarization to the beam reaching the detector. If the analyzer rotates, the efficiency of the detector can be modified. The effect could be misinterpreted as a modification of the polarization due to the sample surface. The effect of the polarization sensitivity of the detector is strongly attenuated if the ellipsometer is used in a rotating compensator and fixed analyzer configuration, since the polarization direction after analyzer is fixed and thus the efficiency of the detector remains the same. In the general case, the detector can be represented, like the source, with a partial polarizer of matrix $\mathbf{M}_{POL}(\alpha_D, \delta_D)$ with an attenuation coefficient $\alpha_D$, and phase shift $\delta_D$.

**Compensator**

As we already mentioned, the ellipsometer is functioning with a rotating compensator. The principle of such a retarder is based on a double internal total reflection inside a Zinc Selenide prism. Two bare gold mirrors are added to realign the beam, to avoid wobbling of the beam during the rotation of the compensator (Figure 2.17). The compensator can be represented by introducing a retardation $\Delta_c$ and and a relative amplitude change $\Psi_c$. In the case of a quarter wave plate, $\Delta_c = 90^\circ$ and $\Psi_c = 45^\circ$. The Mueller matrix representing such a compensator is given in Table 2.1. We have already shown that the parameters of the compensator strongly differ from the calculated values. This is not only due to faults intrinsic to the retarder, but also to the accumulation of imperfections of the other optical elements, that were considered perfect while calculating the properties of the retarder.

**Beam profile**

Another source of imperfection is the beam profile. The IFS 66 uses a alignment laser which is parallel to the infrared beam, but is slightly shifted from a the center. This laser is used to trigger the scanning of the interferometer. A little mirror, situated after the beam splitter, and attached to a small arm, positions the laser beam inside the beam. As a consequence, the beam suffers from a ”shadowing” on a larger distance (cf. Fig. 2.6). The non symmetrical profile of the beam can be prejudicial for the measurements, since we use a rotating element. By a $180^\circ$ rotation of the compensator the value of the detected intensity will not be the same as it should be according to the theory.

**Beam divergence**

Finally, the beam is not collimated, and suffers from a slight divergence calculated at $1.6^\circ$. The divergence cannot be corrected, it results from the fact that the source is not, and cannot be considered as, a point source. The globar has a characteristic dimension of 10mm, and the source intensity is too weak to consider the use of small diaphragm to reduce the image of the source.
3.3 Model

3.3.1 General model

We can now introduce a new model of ellipsometer taking most of these imperfections into account. Let us then consider a rotating compensator ellipsometer consisting of:

- A partially polarized source, that can be modelled with a perfect source Stokes vector associated with a partial polarizer Mueller matrix \( \overrightarrow{M}_{POL}(\alpha_{D}, \delta_{D}) \), as defined above.

- An imperfect polarizer. The associated matrix is: \( \overrightarrow{M}_{POL}(\alpha_{P}, \delta_{P}) \).

- A sample characterized by the ellipsometric parameters \( \Psi \) and \( \Delta \).

- An imperfect compensator, with the associated imperfect components \( \Psi_{C} \) and \( \Delta_{C} \). The azimuth of the compensator is \( C \) with the error \( dC \). The associated matrix is: \( \overrightarrow{M}_{CMP}(\Psi_{C}, \Delta_{C}) \).

- An imperfect analyzer, with azimuth \( A \) and error \( dA \): \( \overrightarrow{M}_{POL}(\alpha_{A}, \delta_{A}) \).

- An imperfect detector: \( \overrightarrow{M}_{POL}(\alpha_{D}, \delta_{D}) \).

The azimuth of the optical elements are given relative to the plane of incidence, with the convention that a positive azimuth each element is represented by a Mueller matrix in combination with rotation matrices to take into account of the different azimuth of the principal axis, as it is explained in equations (2.6) and (2.7). The Stokes vector corresponding to a rotating compensator ellipsometer with imperfect components is then obtained by:

\[
\overrightarrow{S}_{D} = \overrightarrow{M}_{POL}(\alpha_{D}, \delta_{D}) \cdot R(D - A - dA) \cdot \overrightarrow{M}_{POL}(\alpha_{A}, \delta_{A}) \cdot R((A + dA) - (C + dC)) \cdot \overrightarrow{M}_{CMP}(\Psi_{C}, \Delta_{C}) \cdot R(C + dC) \cdot \overrightarrow{M}_{\Psi\Delta} \cdot R(-P - dP) \cdot \overrightarrow{M}_{POL}(\alpha_{P}, \delta_{P}) \cdot R(P + dP) \cdot \overrightarrow{M}_{POL}(\alpha_{S}, \delta_{S}) \cdot \overrightarrow{S}_{0}. \tag{3.1}
\]

The expression of the intensity measured at the detector is obtained by taking the first component of the calculated Stokes vector. The development of the general expression of the intensity would not be appropriate: several tens of pages would be required unless some simplifications are introduced.

3.3.2 Simplified model

First, the azimuths of the analyzer and the polarizer are fixed, at 0 and \( \pi/4 \) respectively. These angular positions are classical for such type of ellipsometer. It is known that under the assumption that the different optical elements are perfect, the above azimuths considerably simplify the expression of the intensity. Furthermore, if we consider the elements actually constituting our ellipsometer, the polarizers could be considered perfect. We have shown that the polarization coefficient for a Brewster angle transmission polarizers, is very high, above 4000, and is rather homogeneous over a large spectral range (4000-800 cm\(^{-1}\)). Moreover, in extinction position,
the signal detected, which corresponds actually to the leak of the polarizer, can barely be dis-

tinguished from the noise level. Thus, the attenuation coefficient can be neglected. Concerning

the phase shift potentially generated by the polarizer, this phenomenon occurs generally with

wire grid polarizers [14], and is not expected with Brewster angle transmission polarizers. A

first calculation shows however that even when introducing a phase shift in the characteristics

of the polarizer and the analyzer, there is no influence on the final result, since these phase shifts

vanish in the calculation. \( \delta_P \) and \( \delta_A \) do not appear in the final expression of the intensity.

Finally, the only important parameters that we have to take into account are the errors on

the azimuths of the polarizer, the analyzer and the compensator, respectively, \( d_P \), \( d_A \), and \( d_C \).

Another difficulty is the properties of the beam. It is difficult to model the divergence and the

profile of the beam in terms of Mueller matrices. To solve this problem, we should consider a

perfectly collimated beam with a homogeneous cross-section, associated to an optical element

whose Mueller matrix translates the beam divergence and the anisotropic profile. For this, a

large computing work and an accurate profile image are required. This will not be developed

further in this thesis.

The consequences of a imperfect beam on the compensator have been extensively studied

in Chapter 2. Conserving the polarizer, the measurements performed did not show a strong

influence of the divergence of the beam. One of the effect is nonetheless a lower polarization

coefficient. In theory, the Brewster angle transmission coefficient exhibits a polarization coef-

ficient of the order of 65 000, but experimental values are only between 1000 and 2000. These

values correspond however to a rather high efficiency. The profile of the beam is in the case

of the polarizer and the analyzer a minor problem since both optical devices are fixed during

the measurements. The anisotropy of the beam profile can be harmful only if the elements are

rotating.

In conclusion, it is possible to simplify the expression of the intensity by taking into account

the most critical parameters, that are the errors made on the azimuths of the polarizer, the

analyzer, and the compensator, namely \( d_P \), \( d_A \), and \( d_C \) respectively. With these restrictions, the

expression of the intensity becomes:

\[
\vec{S_D} = \vec{M}_{POL}(0, \delta_A) \cdot \vec{R}((dA - C - dC) \cdot \vec{M}_{CMP}(\Psi_C, \Delta_C) \cdot \vec{R}(C + dC) \cdot \vec{M}_{\Psi \Delta} \cdot \vec{R}(-\pi/4 - dP)) \cdot \vec{M}_{POL}(0, 0) \cdot \vec{S_0}.
\]

Before studying the influence of the different errors on the azimuths, we will describe in the

following section the calibration procedures. The first argument of the Stokes vector, the intensity

can be expressed as a sinusoidal function with harmonics of the second and fourth order in

the compensator azimuth \( C \).

\[
I(C) = A_0 + A_2 \cos 2C + B_2 \sin 2C + A_4 \cos 4C + B_4 \sin 4C.
\]

### 3.4 Alignment of polarizer and analyzer

The calibration of the ellipsometer requires several stages. Every optical component (Polarizer,
analyzer and compensator) must be aligned with high precision and accuracy. The azimuth

of these optical elements is by convention defined relative to the plane of incidence when the

beam reflects on the sample. The sign of the azimuth is defined following the convention that

the positive rotation angle is counterclockwise when looking into the source [16].
3.4 Alignment of polarizer and analyzer

3.4.1 Polarizer azimuth

The first element to be inserted in the ellipsometer and to be aligned is the polarizer. There are different methods allowing an accurate alignment of the polarizer. Some of them require the simultaneous use of an analyzer. One technique is rather straightforward, but requires the condition that the position of the sample is well known. In our set-up, the sample is placed vertically relative to the table carrying the ellipsometer. The idea is to use a large surface of silicon, placed vertically, which is relatively easy to obtain, and placed at Brewster angle relative to the beam. When inserting and rotating the polarizer, extinction is obtained for a polarizer azimuth perpendicular to the plane of incidence. This is due to the fact that only the p-component of light is transmitted at Brewster angle. One should note here that the p-component is defined relative to the Silicon plate, but also corresponds to a p-component for the sample position. One of the characteristics of this technique is that it is used in straight through configuration. Since, the rest of the calibration of the ellipsometer is also performed straight through, it simplifies the entire procedure. One of the disadvantages is that the extinction azimuth might be not accurately defined. When approaching extinction, the signal to noise ratio drops dramatically, resulting in a rather large angular region of uncertainty. The minimum can be difficult to determine if one focusses on the minimum, but it is better to fit the sinusoidal shape of the detected signal when the polarizer is rotated. In this case, the accuracy on the polarizer azimuth is of the order of 0.15 degrees.

Others techniques are used to determine the polarizer azimuth, most of them require the use of a sample. Most of these techniques have been initially developed for single wavelength ellipsometers. Theoretically, the transfer of these techniques to spectroscopic application should not be problematic, since the different elements azimuths are geometric objects, and thus should not be wavelength dependent. Best known procedures are residue and phase calibration. These two procedures have been described in several papers [4, 5, 17], and it has been shown that both methods are complementary to each other, differing by the properties of the sample used for the calibration. We chose to use residue calibration in our case.

For the calibration of the polarizer, the compensator is removed from the set-up. The configuration is then equivalent to a rotating analyzer ellipsometer. Only second order Fourier coefficients ($A_2$ and $B_2$) are considered. The residue is then defined as:

$$R \equiv A_2^2 + B_2^2.$$  \hspace{1cm} (3.4)

It is shown that $R$ is reaches an extremum when the polarizer is in the plane of incidence. Figure 3.1 shows a typical result of the measurement of residue in order to determine the position of the polarizer. In this case, the accuracy is lower than 0.05°. Den Boer et al. [5] have demonstrated that the choice of a sample exhibiting an ellipsometric angle $\Psi$ more or less constant and greater than 30° for all wavelengths and a phase shift $\Delta$ varying as a function of the wavelength over a large range, would be adequate for such calibration procedure. A metallic substrate coated with transparent film is one of the possible candidates. The accuracy of the determination of the polarizer azimuth strongly depends on the quality of the sample. This is nevertheless the sole criterion: The quality of the polarizer plays also an important role. We have seen that polarizers are not perfect, and specially, their behavior tend to be wavelength dependent. During our measurements, we used two different types of polarizers: wire grid associated in tandem [13], and Brewster angle transmission polarizers. The latter have shown higher performances and a comparison with wire grid has been realized. As a result, the Brewster angle polarizers show a better accuracy.
The choice of the spectral range is also important. We already mentioned that azimuths should not depend on the wavelength, but strong variation of the spectra due to the presence of water and carbon dioxide may alter the results. To overcome this difficulty, we opt for a restricted spectral range, where no interference is expected between the components on the sample surface and others elements in possibly in the beam path.

### 3.4.2 Analyzer azimuth

The analyzer azimuth is determined in a straight through configuration. The source, the polarizer, the analyzer, and the detector are aligned (the sample holder is removed or is designed to let the beam go through when no sample is placed). It is possible to perform the analyzer calibration by using a sample, but our experience led us to the conclusion that a higher accuracy is reached when measurements are performed straight through. The analyzer azimuth is generally determined with an accuracy of the order of 0.01°. The restrictions about the spectral range used for the calibrations are the same than for the polarizer calibration, in order to avoid disturbance due to the presence of water and CO₂.

### 3.5 Compensator calibration

Two types of calibrations are necessary for the compensator. The alignment and positioning of the compensator azimuth, relative to the plane of incidence defined by the sample, and the optical parameters of the retarder, i.e. the ellipsometric parameters $\Psi_C$ and $\Delta_C$ induced by the compensator.

The azimuthal position of the compensator is determined in a straight through configuration, where polarizer, compensator, and analyzer are aligned in this order. The polarizer is placed at
the azimuth $\pi/2$, and the analyzer in the plane of incidence. By performing a rotating compensator measurement in this configuration, eq. 3.2 can be simplified by considering $\Psi = \pi/4$, and $\Delta = 0$, the corresponding Fourier coefficients are then:

$$
\begin{align*}
A_0 &= [1 + \frac{1}{2}(1 + y_c) \sin(2dA + 2dP)](1 - \sin(2dP)), \\
A_2 &= x_c[\cos(2dA - 2dC) + \sin(2dP + 2dC)](1 - \sin(2dP)), \\
B_2 &= x_c[-\sin(2dA - 2dC) + \cos(2dP + 2dC)](1 - \sin(2dP)), \\
A_4 &= \frac{1}{2}(1 - y_c) \sin(2dP - 2dA + 4dC)(1 - \sin(2dP)), \\
B_4 &= \frac{1}{2}(1 - y_c) \cos(2dP - 2dA + 4dC)(1 - \sin(2dP)),
\end{align*}
$$

(3.5)

where $x_c$ and $y_c$ are defined in eq. 2.18(a).

If we consider in a first stage that the polarizer and the analyzer are perfectly aligned, then $dP = 0$ and $dA = 0$. The position of the compensator can then be determined by:

$$
dC = \frac{1}{4} \arctan \frac{A_4}{B_4}.
$$

(3.6)

The accuracy is very high if a non perturbed spectral area is chosen.\(^1\)

If we consider now the a misalignment of the polarizer and the analyzer, we obtain:

$$
dC = \frac{1}{4} \arctan \frac{A_4}{B_4} + \frac{dA - dP}{2}.
$$

(3.7)

Thus the error made on the determination of $dC$ is of the order of $dP$. The determination of the retardation $\Delta C$ and the amplitude ratio $\Psi_C$ of the compensator have been already detailed in the former chapter. An investigation of the influence of the misalignment is nevertheless interesting. From equations 3.5, we can determine the errors made when using previously obtained formulas, giving $\Psi_C$ and $\Delta C$ (eq. 2.39), or better, the associated quantities $x_c$, $y_c$, and $z_c$ (eq. 2.38). It is possible then to calculate $x_c$ and $y_c$ as a function of the Fourier coefficients and the azimuth errors, by considering only first order term in $dP$ and $dA$:

$y_c$ is solution of an second degree polynomial equation

$$
y_c = \frac{1}{2} \sin(2dA + 2dP) + y_c = 1 - \frac{2\sqrt{A_4^2 + B_4^2}}{A_0} + \frac{1}{2} \sin(2dA + 2dP)
$$

(3.8)

and $x_c$ can then be calculated by:

$$
x_c = \frac{\sqrt{2A_2^2 + 2B_2^2}}{2A_0} [1 + \frac{1}{2}(1 + y_c) \sin(2dA + 2dP) - \sin(2dP - 2dA + 4dC)].
$$

(3.9)

Naturally, if $dP = 0$, $dA = 0$, and $dC = 0$ expression of $y_c$ and $x_c$ are reduced to eq. 2.38. It is quite remarkable that $y_c$ does not depend on $dC$, i.e. the misalignment of the compensator. $x_c$ is however influenced by the errors on the azimuths of the polarizer, the analyzer, and the compensator. The behaviors of $x_c$ and $y_c$ are plotted in Fig 3.2. Arbitrary values for the Fourier

\(^1\)it is in theory possible to use $dC = \frac{1}{2} \arctan \frac{A_4 - B_4}{A_2 + B_2}$ but $A_2$ and $B_2$ are very small numbers, (because of $x_c$) and the result will suffers from a low signal to noise ratio.
coefficients have been chosen, the amplitudes of $x_c$ and $y_c$ do not correspond necessarily realistic values. Only the variation is to be considered. These calculations show a small influence of the errors on the alignment over the values of the characteristic parameters of the retarder.

The calibration procedure is shown to be accurate enough for ellipsometric measurements. It requires however high attention, specially concerning the position of the polarizer. The compensator appears to be the most sensitive element of the ellipsometer, but its calibration, if compared to that of the polarizer, is easy and accurate. In the following part, a classical study of amorphous silicon oxide thermally deposited on crystalline silicon is performed.
3.6 Modelling of ellipsometric spectra

Ellipsometry is a non direct technique, the ellipsometric parameters $\Psi$ and $\Delta$ are not interesting parameters themselves, from the physical point of view. From the measured data, the aim is to retrieve information on the optical and physical constants of the material under investigation. The parameters that can be determined in a most direct way are, the layer thickness if relevant, the (complex) index of refraction, the associated dielectric function. Other parameters can also be extracted, such as the roughness or the porosity, depending of the model. In fact, to obtain these parameters, depends on the complexity of the model. The procedure is always based on a fit of the measured spectra with curves obtained from a theoretical model. Depending on the properties of the material, such as the composition, its expected absorption features, and the location of the absorption features in the spectrum, the thickness of the material, the purity, the porosity..., a model is developed. Although some of them can be extremely complex, most are based on the theory of the Lorentz oscillator. The principle of this model is an oscillator driven by an external force, and subjected to a damping force.

An electromagnetic beam reflecting on a surface exhibits a polarization modified by the induced dipole moments of the atoms or molecules of the medium. The motion of an electron bound to a nucleus driven by an oscillating electric field $\vec{E}$ is given by:

$$m \frac{d^2 \vec{r}}{dt^2} + m \Gamma \frac{d \vec{r}}{dt} + m \omega_0^2 \vec{r} = -e \vec{E},$$

(3.10)

where $m$ is the electronic mass, $e$ represents the electronic charge (or rather is amplitude $e > 0$), $f$ is the oscillator strength, $\omega_0$ is the resonant frequency corresponding to the frequency that the oscillator should have if not subjected to a damping effect ($\Gamma$) or a driven oscillation. By using Maxwell’s equations, one can determine the complex dielectric function $\tilde{\varepsilon}$, of the material. This calculation has been detailed elsewhere [18].

The dielectric function is directly derived from the expression of the displacement field $\vec{D}$ as a function of the electric field $\vec{E}$.

$$\vec{D} = \tilde{\varepsilon} \vec{E}. $$

(3.11)

In the general case, the dielectric function is a tensor, but here, the medium is considered isotropic and $\tilde{\varepsilon}$ is a complex scalar. The expression of the dielectric function is then:

$$\tilde{\varepsilon} = \tilde{\varepsilon}_\infty + \frac{4\pi \mathcal{N} e^2}{m} \frac{1}{(\omega_0^2 - \omega^2) - i \Gamma \omega},$$

(3.12)

where $\mathcal{N}$ is the number of oscillators per unit volume. The asymptotic limit $\tilde{\varepsilon}_\infty$ correspond to the value of the dielectric function when $\omega \to \infty$. In the case of a model involving $\mathcal{N}$ oscillators, with different resonance frequencies eq. 3.12 can be extended:

$$\tilde{\varepsilon} = \tilde{\varepsilon}_\infty + \frac{4\pi e^2}{m} \sum_i \frac{\mathcal{N}_i f_i}{(\omega_0^2 - \omega^2) - i \Gamma \omega},$$

(3.13)

where $\sum_i \mathcal{N}_i = \mathcal{N}$.

The dielectric function $\tilde{\varepsilon}$ represents the degree to which the material maybe polarized by an applied external electric field, and is related to the complex refractive index by the relationship:

$$\tilde{\varepsilon} = \tilde{N}^2.$$

(3.14)
The real and imaginary parts of $\tilde{\varepsilon}$ are given by:

$$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$$

(3.15)

and for a population of identical oscillators are:

$$\varepsilon_1 = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)\omega_0^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2},$$

$$\varepsilon_2 = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega_0^2\omega^2\Gamma}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2}$$

(3.16)

with:

$$\varepsilon_0 - \varepsilon_\infty = \frac{4\pi N e^2}{m\omega_0^2} f.$$  

(3.17)

The imaginary part is the resonance term for the energy dissipation, when the electromagnetic wave of the beam, interacts with the medium. Figure 3.3 shows the behavior of the real and imaginary parts obtained for a oscillator with constants:

Also represented the corresponding real and imaginary part of index of refraction:

$\tilde{N} = n + ik$, whose expressions are given by:

$$n = \left[\frac{1}{2}\left(\sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1}\right)\right]^{1/2},$$

$$k = \left[\frac{1}{2}\left(\sqrt{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}\right)\right]^{1/2}.$$

(3.18)

One can note that at $\varepsilon_1 = 0$, $n=k$ and this defines the LO mode. The TO mode is defined by the maximum of $\varepsilon_2$. The link between the complex refractive index and the ellipsometric

Figure 3.3: Frequency dependency of the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) part of the dielectric function for the Lorentz oscillator (3.3(a)). Also represented, the real (n) and imaginary (k) part of the refractive index(3.3(b)). The resonance frequency is chosen at 1000 cm$^{-1}$, the damping is fixed at 15 cm$^{-1}$, and $\varepsilon_\infty$ at 2.1
parameters is given by the expression of the complex Fresnel reflection coefficients

\[
\tilde{r}_p = \frac{n_1 \cos \theta_0 - n_0 \cos \theta_1}{n_1 \cos \theta_0 + n_0 \cos \theta_1},
\]

\[
\tilde{r}_s = \frac{n_0 \cos \theta_0 - n_1 \cos \theta_1}{n_0 \cos \theta_0 + n_1 \cos \theta_1},
\]

and the ratio is:

\[
\rho = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan \Psi e^{i\Delta}.
\]

In practice, one knows the values of \(\Psi\) and \(\Delta\) determined experimentally, and wants to calculate the refractive index or the dielectric function, which means, to perform inverse operations of those above. The models are generally much more complex than the one exposed above. Depending on the nature of the medium, (metal, transparent or absorbing medium) one should expect different behavior of the dielectric functions in the infrared. In this spectral area, the molecules play the role of oscillator, therefore metals do not exhibit resonance. Moreover, their index of refraction is very high (at 10 \(\mu\)m, \(n \geq 10\) and \(k \geq 40\), and almost constant on a large spectral range. The modelling of stratified media implies other considerations, such as multiple reflections inside each layer, and different thickness and optical parameters for each layer. Theories have been developed on complex media. For simulation, we used a commercial software SCOUT2, developed by MTheiss [19]. It offers the advantage of not being solely devoted to ellipsometry, but for a large variety of spectroscopic diagnostic such as: Transmission and reflection absorption, ATR, and from UV to infrared.

### 3.7 SiO\(_2\) on Si-sample

Different samples of amorphous silicon dioxide thermally grown on crystalline silicon were used for this series of measurements with oxide thickness varying from 105nm to 1030nm. The thicknesses were determined by using 632.8 nm single wavelength ellipsometry, with an accuracy of \(\pm 5\) nm.

The configuration of the infrared spectroscopic ellipsometer is the same as described in the previous chapter. We used for these measurements Brewster angle transmission polarizers. Since time dependence is not an issue in this case, we could used a long measurement time. During the measurement, the compensator is rotating by steps. Only a 180° rotation is necessary in an rotating compensator ellipsometer (RCE) configuration. The total rotation is achieved in 10 steps of 18°. The sampling rate is 160 kHz and 500 scans are performed at each step. The resolution is fixed at 4 \(\text{cm}^{-1}\) on a spectral range from 4000\(\text{cm}^{-1}\)to 800\(\text{cm}^{-1}\).

Figure 3.4 shows the spectra of the ellipsometric parameters \(\Psi\) and \(\Delta\), for a silicon oxide layer of 1030 nm. As expected, \(\Delta\) exhibits a strong wavelength dependency, over a large range. The angle of incidence was here fixed at 70°. The spectrum can be split in two spectral areas. Over a range between 1300\(\text{cm}^{-1}\) and 900\(\text{cm}^{-1}\), one can find the main absorption features. Two transverse optical (TO) modes, corresponding to an asymmetric stretching vibration of the oxygen atoms of 2 adjacent Si-O-Si (TO\(_3\)) units at around 1075\(\text{cm}^{-1}\), and the symmetric stretching motion of adjacent sites (TO\(_4\)) at 1170\(\text{cm}^{-1}\). The associated longitudinal optical modes, LO\(_3\) and LO\(_4\), are located at 1223\(\text{cm}^{-1}\) and 1140\(\text{cm}^{-1}\) respectively.

The rest of the spectral range (4000-1300\(\text{cm}^{-1}\)) does not exhibit absorption features, but a large variation of \(\Delta\) centered at 2300\(\text{cm}^{-1}\). This strong variation corresponds to a maximum of
Figure 3.4: Spectra of ellipsometric angles obtained for a layer of 1030 nm of amorphous silicon oxide on crystalline $<100>$ silicon substrate. Experimental data and curve fitting are represented.

$\Psi$. This is a general statement in ellipsometry, that an extremum of one ellipsometric parameters (zero of the first derivative) corresponds to a bending point of the other parameter (zero of the second derivative).

A first fit is performed on the basis of the theory developed above. Several oscillators are taken into account. The curve fitting is shown on Fig.3.4. From this, we can extrapolate different parameters such as the thickness of the oxide layer, the dielectric function and the refractive index (both are complex values). The model does not fit the experimental curve perfectly, especially in the spectral areas where $\Delta$ is subjected to strong curvatures. The main reason is the slight divergence of the beam reflecting in the sample surface. The angle of incidence is integrated during the measurements and this smoothens the curvature of $\Delta$. Furthermore we have shown that the wavelength distribution inside the beam is linked to the divergence, and the wavelengths at the extremity of the spectrum are thus more affected by the consequences of the divergence. The thickness could nevertheless be measured at 1033.9 nm. The value is in perfect agreement with the value determined by single wavelength ellipsometry. For the fitting of the spectra, we used a model based on bulk fused silica. The properties are supposed to be the same for a thin film [20]. In the next part, we will see that this equivalence is not obvious. The dielectric function and the refractive index are shown in figure 3.5. The spectral range has been limited (875-1400 cm$^{-1}$), since no important features are present beyond 1400 cm$^{-1}$.

3.7.1 Thickness related frequency shift

The region near the absorption resonances (900-1500 cm$^{-1}$) is the most interesting to investigate since this is where the dielectric function exhibits the strongest changes. Another series of measurements have been performed after a new calibration of the compensator limited to this spectral region. Figure 3.6 shows the spectra obtained for three different oxide thicknesses, the measurements were both performed with an angle of incidence of 70$^\circ$. The silicon oxide
was thermally grown on a crystalline silicon wafer. The oxide layer thicknesses are 1030 nm, 730 nm, and 346 nm respectively. The latter sample was obtained after etching of a thicker oxide layer with an $SF_6$ plasma. These thicknesses have been accurately measured with single wavelength ellipsometry in the visible. The preparation is assumed to keep the films at identical properties.

A first remark is the slight shift of the zero position of $\Delta$ around 1260 nm. According to Ossikovski et al. [12], the shift of delta corresponds to a shift of the LO$_3$ mode of silicon oxide due to asymmetric stretching$^2$. In general, deviations of peak positions depend on the film stress,

$^2$In their article [12] Ossikovski et al. do not mention the presence of symmetric stretch TO$_3$/LO$_4$, that is considered by others, but this resonance pair is overlapped and has an intensity much lower than that of TO$_3$/LO$_3$.

Figure 3.5: Real (solid curve) and imaginary (dashed curve) part of the calculated dielectric function of the a-SiO$_2$ film deposited on silicon substrate (Fig. 3.5(a)). The energy loss function ($\text{Im}(1/\varepsilon)$) has been also represented. Its maximum corresponds to the LO mode frequency. Fig 3.5(b) shows the corresponding real (solid) and imaginary (dashed) part of the refractive index.
Figure 3.6: Ellipsometric spectra of silicon oxide layer of 1030 nm and 730 nm thickness. The shift of the zero position of $\Delta$ indicates a displacement of the LO$_3$ mode.

porosity [21], or stoichiometry of the film. Stress effect becomes measurable only for $\mu$m-thick oxide layers. Because of the identical preparation conditions of the samples, the frequency shift can only be related to the difference of oxide layer thickness between both samples. This shift has also been mentioned in earlier articles [22–24]. Results obtained are shown in table 3.2 The

<table>
<thead>
<tr>
<th>Sample thickness</th>
<th>LO$_3$ position</th>
<th>TO$_3$ position</th>
</tr>
</thead>
<tbody>
<tr>
<td>1030 nm</td>
<td>1279 cm$^{-1}$</td>
<td>1130 cm$^{-1}$</td>
</tr>
<tr>
<td>730 nm</td>
<td>1271 cm$^{-1}$</td>
<td>1131 cm$^{-1}$</td>
</tr>
<tr>
<td>346 nm</td>
<td>1266 cm$^{-1}$</td>
<td>1127 cm$^{-1}$</td>
</tr>
<tr>
<td>106.5 nm</td>
<td>1257 cm$^{-1}$</td>
<td>1096.5 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Table 3.2: Position of the transverse and longitudinal mode for different oxide layer thicknesses

LO mode peak was determined by the position of the zero of $\Delta$, and the TO mode was determined as a local maximum on the $\Psi$ curve, around 1130 cm$^{-1}$. The displacement is clear concerning the LO mode. The peak position is quasi linearly dependent on the thickness. The displacement is estimated to 2.2 cm$^{-1}$ every 100 nm. For the TO mode, however, the displacement is different; for a thickness larger than 350 nm the TO peak position is fixed, whereas it drops to lower values for a thickness of 106.5 nm. The behavior of the peak positions have been studied by different authors but essentially for the transverse optical mode, since the LO mode can only be seen with an large angle of incidence. On this point ellipsometry is an innovative technique, even though Fourier transform P-polarized infrared reflection absorption spectroscopy allows also the observation of both modes [25].

It has been shown that the displacements of the TO-LO modes are actually not due to the physical properties of the silicon oxide but to a purely optical effect [26, 27]. More precisely, internal reflections at the ambient-film and film-substrate interfaces are responsible for the frequency shifts. This theory is not developed in this thesis; Ossikovski et al. presented a model.
3.7 SiO$_2$ on Si-sample

based on classical electromagnetic theory [12] for reflection measurement, thus also ellipsometry. According to this model, the TO mode frequency stabilizes at 1130 cm$^{-1}$ for thicknesses larger than 350 nm but the LO mode frequency is continuously shifted for larger thickness value. The values measured above are in perfect agreement with their model. This is however valid only for reflection measurements techniques and not for transmission. Klanjšek Gunde et al. [27] developed a model for transmission, where the TO mode peak stabilizes around 1094 cm$^{-1}$. This difference in the peak position measured by transmission or reflection techniques is due to the fact that the beam crosses twice the silicon oxide film (without considering multiple reflections within the film). The Fresnel equations are thus modified and the optical effect leading to the peak frequency shift is more important when the measurements are performed by reflection. Moreno et al. have modelled this phenomenon [28]. The real frequencies of the TO and LO are actually determined by extrapolating the frequency for oxide thickness equal to zero.

3.7.2 Variation of the angle of incidence

The set-up of the ellipsometer allows measurements at different angles of incidence. Depending on this angle, the sensitivity of the ellipsometer to certain optical features will be different. By changing the angle of incidence, one can chose the most sensitive configuration according to the material under investigation.

The measurements has been preformed on a sample of 730nm thick silicon oxide layer thermally grown on silicon. The thickness has been previously determined by single wavelength ellipsometry at $\lambda = 632.8$ nm (730 nm) and spectroscopic ellipsometry in visible (731 nm). Figure 3.7 shows the changes of the ellipsometric angles over a large spectral range (4000-800 cm$^{-1}$) for different angles of incidence.

A first remark is the strong variation of the ellipsometric parameters, with the angle of incidence. A direct consequence is the necessity of an accurate determination of the angle of incidence during the measurement session, in order to avoid strong deviation in the spectra. Looking at the behavior of $\Delta$, one can note a transition between measurements below 70°, where $\Delta$ is continuous in the region of 3400-3200 cm$^{-1}$, and measurements above 70°, where a discontinuity is observed. This discontinuity can be observed also by simulation and the limit corresponds to the a value close to the Brewster angle associated to silicon (around 73.6°). It is also interesting to note that for the different angles from 45 to 65°, the transition occurs at the same frequency, i.e 3230 cm$^{-1}$, but this transition, is shifted when discontinuity occurs.

The transition of $\Delta$ corresponds to a maximum of $\Psi$ as already reported above. The maximum of $\Psi$ is the sharpest for an angle of incidence of 70°, which means that this angle is the most suitable for the determination of parameters such as layer thickness. Unfortunately, more noise appears on the curve, and maybe even some interference effect near the transition region at 3250 cm$^{-1}$. The cause of these interferences is not clear.

Another interesting point is the behavior of the TO-LO modes around (1400-900 cm$^{-1}$). For angles lower than 60° an inversion of the LO peak in observed.

This inversion has been previously observed and discussed [28], although investigation were using absorption or transmission measurements rather than ellipsometry. For an angle of incidence of 45°, the presence of a second pair of resonances between LO$_3$ and TO$_3$ is obvious. It has been identified as a LO$_4$-TO$_4$ pair at 1165 cm$^{-1}$ and 1200 cm$^{-1}$ respectively, and attributed to disorder within the SiO$_2$ layer [29, 30]. Note the inverted order of TO$_4$-LO$_4$ frequencies.
Figure 3.7: Variation of the ellipsometric parameters as function of the angle of incidence. The sample is an amorphous silicon oxide layer of 730 nm deposited on crystalline silicon compared to the TO$_3$-LO$_3$ pair.

Figure 3.9 shows the position and the amplitude of TO and LO modes, for an oxide layer of 730 nm. The TO mode frequency is more sensitive to the angle of incidence than the LO mode. Over a range from 45° to 80° the shift of the transverse mode is 25 cm$^{-1}$, whereas it is of 8 cm$^{-1}$ for the longitudinal mode. The values for an angle of incidence larger than the brewster angle (73.6°) are remarkable for the TO mode: they exhibit a shift to larger wave numbers. It
Figure 3.8: Variation of the TO and LO mode intensity when the angle of incidence in changed. The inversion of the LO mode is clearly visible for an angle of incidence of 45°. For this angle, the presence of a TO\textsubscript{4}-LO\textsubscript{4} is also visible.

Figure 3.9: Dependence of the TO and LO peak frequency on the angle of incidence and corresponding amplitude of the peaks measured on Ψ curve.

should however be noted here that the position of the TO mode is more difficult to determine for large angle of incidence. The amplitude of the peak were measured as the amplitude on the Ψ curve. This gives only relative values between LO and TO mode. This latter mode exhibits a rather stable amplitude over the angular range. The amplitude seems to decrease slightly when the angle of incidence increases until the Brewster angle of the substrate, and then increases for larger angles. The LO mode however increases continuously and on a larger amplitude over the range of angle of incidence.
3.8 Conclusion

In this chapter, the problems due to the possible imperfections of the ellipsometer have been identified. The most critical part of the calibration has been shown to be the angular position of the different elements. The azimuth of the polarizer, compensator, and analyzer are mostly affected by the fact that the beam cannot be perfectly collimated. This is due to the actual surface nature of the source. It has been shown however that the ellipsometer can be calibrated with high accuracy.

The small divergence of the beam lead to some deformation of the spectra as it has been shown on the measurement of amorphous silicon oxide (a-SiO$_2$) layer deposited on crystalline silicon (cf. Fig. 3.4). These effects have however a small influence to determine the different parameters of the film. Some other influences, like the thickness of the layer, the angle of incidence, have been studied. They reveal a thickness dependent frequency shift of the transverse and longitudinal optical modes that is purely an optical effect and have been previously pointed out with infrared spectroscopic ellipsometry, but also with other techniques. Furthermore, the ellipsometer shows a high accuracy in the determination of parameters such as oxide thickness when compared with other techniques (single wavelength or visible spectroscopic ellipsometry).

References


REFERENCES


Chapter 4

Investigation on silicon sub-oxides by infrared ellipsometry

Silicon rich suboxides ($\text{SiO}_x, x < 2$) have been obtained by plasma sputtering at low temperature. Different types of substrates have been used, chromium, silicon, and glass. The stoichiometry has been analyzed by infrared spectroscopic ellipsometry. The refractive index has also been investigated. It appears that the bonding process changes with the stoichiometry of the film. For films with a low stoichiometry, the $\text{Si}_2\text{O}_3$ absorption band is dominant whereas, for higher stoichiometry, the $\text{SiO}_2$ band corresponding to in-phase motion of $\text{SiO}_4$ tetrahedra becomes predominant for higher stoichiometry.
4.1 Introduction

Amorphous silicon dioxide (a-SiO$_2$) remains an important component in the semiconductor industry, and a subject of intensive research. Several techniques have been recently developed in order to obtain oxide films at low temperature. These new development are driven by technical needs. Hard coatings on plastic or polymer surfaces require for instance the use of low deposition temperature (below 100°C). Another example is the coating on Infrared detector windows, which are often made of hygroscopic material, and which cannot endure high temperature. Among the methods used for deposition are rf glow discharge [1], low pressure chemical vapor deposition (CVD) [2], plasma enhanced CVD (PECVD) [3], photo CVD [4], remote plasma enhanced CVD (RPECVD) [5, 6], laser ablation [7], sputtering [8]. Contrary to classical, thermally grown, oxides, the films show porosity and the stoichiometry does not correspond to that of silicon dioxide. The refractive index is often the most important parameter, and is wanted to be as close to the one of a-SiO$_2$ as possible. Sub-stoichiometry is also found at the Si/SiO$_2$ interface [9] and can have strong consequences for the properties of ultra-thin films [10, 11]. Furthermore, the optical properties of silicon sub-oxide films have been studied [12]. Applications such as passivating film for protecting Large Scale Integrated circuits surface as well as gas barrier material for food and pharmaceutical technology [13] become of interest. It has been shown that, in a spectral domain far from absorption bands, the refractive index is directly related to the stoichiometric coefficient $x$ of silicon suboxide (SiO$_x$) [2].

Ellipsometry consists of the measurement of the modification of the polarization of an impinging beam reflecting from a surface. This polarization is a characteristic of the optical, electrical, and chemical properties of the material. It is expressed in terms of two variables $\Psi$ and $\Delta$ defined by:

$$\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta},$$

(4.1)

where $\rho$ is the ratio of complex Fresnel coefficients $r_p$ and $r_s$, in a direction respectively parallel and perpendicular to the plane of incidence, defined by the trajectory of the impinging and the reflected beam from the surface. To be more specific, $\tan \Psi$ is the ratio of magnitudes of $r_p$ and $r_s$, and $\Delta$ is the phase difference between the coefficients. Ellipsometry, being a non intrusive technique, requires however a model of the sample under investigation in order to obtain the characteristics of the material from $\Psi$ and $\Delta$.

The aim of this study is to investigate silicon sub-oxide films with infrared spectroscopic ellipsometry. This technique offers the possibility of combining the advantages of spectroscopic ellipsometry, specially to determine refractive indices of films, and the information provided by infrared spectroscopy, such as absorption resonance bands of the main chemical constituents of the material. For this study, silicon suboxide films have been deposited by sputtering on three different types of substrates. We used a metal (chromium), a semiconductor (silicon), and an insulator (glass). The substrates used for this study have been separately analyzed because they represent interesting subjects by themselves in terms of ellipsometry measurements. Metals like chromium have a strong reflectivity in the infrared and exhibits very large values for the complex refractive index [14]. Silicon can also be problematic since the theoretical values of $\Psi$ and $\Delta$ are critical, 5° and 179° respectively. These value can be subject to particularly high inaccuracy. Concerning the last substrate, glass, it is transparent in the infrared, but exhibits signature of absorption bands, characteristic of Silicon oxide.
4.2 Experimental conditions

The silicon suboxide films have been obtained by sputtering at a temperature of $50^\circ C$. The conditions of deposition have been identical for the three substrates. Seven types of films have been deposited; they are summarized in table 4.1. The process was controlled in order to obtain an oxide thickness close to 600 nm for all the samples. The thickness was measured afterwards by step height measurement. Before treatment, a small part of the sample was covered with a mask. Once removed, the thickness of the deposited oxide is measured.

<table>
<thead>
<tr>
<th>sample</th>
<th>stoichiometric coefficient $x$</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.01</td>
<td>574</td>
</tr>
<tr>
<td>b</td>
<td>0.27</td>
<td>581</td>
</tr>
<tr>
<td>c</td>
<td>0.55</td>
<td>605</td>
</tr>
<tr>
<td>d</td>
<td>0.73</td>
<td>605</td>
</tr>
<tr>
<td>e</td>
<td>1.00</td>
<td>605</td>
</tr>
<tr>
<td>f</td>
<td>1.26</td>
<td>602</td>
</tr>
<tr>
<td>g</td>
<td>1.41</td>
<td>593</td>
</tr>
</tbody>
</table>

Table 4.1: Samples used for this study. The stoichiometric coefficient was measured by EDX technique, the thickness was obtained by step height measurement.

The stoichiometry of the oxide has been determined by EDX. From now, we will consider depth and the stoichiometry as well defined and use the values as constants.

The ellipsometer consists of a rotating compensator spectroscopic ellipsometer in a PSCA configuration, that is: a fixed polarizer (P) defines polarization of the beam that hits and reflects on the sample (S) surface and passes through a rotating compensator (C). A fixed analyzer (A) imposes again the polarization before the beam reaches the detector.

![Figure 4.1: Representation of the ellipsometer in PSCA configuration.](image)

The source is a globar combined with a Fourier transform interferometer (BRUKER IFS66). The spectral range extends from 800 to 4000 cm$^{-1}$, and the resolution is set at 4 cm$^{-1}$. The compensator is rotating step by step, and the data acquisition is performed at each step. The measurement are performed in open air, thus the spectra may suffer from small variations of CO$_2$ (around 2350 cm$^{-1}$) and water (3300 cm$^{-1}$ and 1600 cm$^{-1}$).

For all the measurement the angle of incidence is fixed at $70^\circ$. The fit of the spectra is performed by using the commercial software package SCOUT2.
4.3 Analysis of the substrates

4.3.1 Chromium

Chromium is a body-centered cubic metal, antiferromagnetic at room temperature. In contact with air, it immediately oxidizes and a 30 Å thin layer of \( \text{Cr}_2\text{O}_3 \) is formed at the surface [15]. This layer can generate perturbation in the infrared during the acquisition of the spectra. The samples have been industrially prepared and consist of a thick layer of chromium on glass. The layer is thick enough (several \( \mu \text{m} \)) to be considered as infinite, this is particularly valid in the infrared where the index of refraction is high, and no light is transmitted. Very few data on chromium are available, especially in the infrared ([16] and references therein, [17]).

![Ellipsometric spectra of thick chromium films](image)

Figure 4.2: Ellipsometric spectra of thick chromium films, (\( \Psi \) in solid line and \( \Delta \) in dashed line. Chromium is naturally covered by a thin native oxide layer, the signature of the oxide appears at 1250 cm\(^{-1} \).

The ellipsometric parameters are shown in figure 4.2. As expected, perturbations due to the presence of water and carbon dioxide in the ambient are visible. The value of \( \Delta \) are higher than 160 over most of the spectral range and increase with the wavelength. \( \Psi \) shows values between 30 and 34 °. One can notice a sharp resonance at 1250 cm\(^{-1} \), which we attribute to the thin chromium oxide layer \( \text{Cr}_2\text{O}_3 \). Until now, we have not been able to identify this line. It appears in all the sample we used for the measurements. It is possible that it corresponds to impurities inside the substrate or at the surface.

Chromium appeared to be very difficult to model in the infrared. The usual way is to develop a Drude model, corresponding to an adapted Lorentz oscillator. For metals, the resonance is due to free electrons. The restoring force (cf. Fig. 3.10) is neglected, which means, \( \omega_0=0 \). Strong discrepancy has been reported between the different recorded measurements, even though few of them concern our spectral range [16]. Furthermore, the presence of the oxide layer, even very thin, may complicate the interpretation on the spectrum. It was not possible to correctly model the data of chromium. By using a simple Drude model, a fit was obtained giving values of the real part of the refractive index (\( n \)) larger than the imaginary part (\( k \), specially for...
small wave number (around 1000 cm\(^{-1}\)). This is in contradiction with the literature and theoretical expectations. We are however confident with our experimental data, which are very reproducible. We think, that the difficulty comes from finding an appropriate model. Lynch et al. [15] report that Drude model may not be suitable because chromium is a transition metal, of which the interband transitions occur at particularly long wavelengths (20 \(\mu\)m and further). Furthermore, the particularly strong signature of the oxide, if identified as so, allows us to think that the contribution of Cr\(_2\)O\(_3\) on the \(\Psi\) and \(\Delta\) spectra is important despite a thickness estimated to 30 Å.

### 4.3.2 Silicon

The silicon substrate consists of a silicon wafer with <100> orientation. The wafers have not been treated prior to deposition, thus the presence of native oxide has to be taken into account. Obtaining a spectrum of silicon is also challenging with infrared ellipsometry. The reason is the extreme values of \(\Psi\) and \(\Delta\), close to 0 and 180° respectively. In contrast to rotating analyzer or rotating polarizer ellipsometers, the rotating compensator ellipsometer which we use is able to generate reliable data for \(\Delta\) in the region of \(\Delta = 180°\) (cf eq. 2.15).

![Figure 4.3](image)

**Figure 4.3:** Ellipsometric spectra of silicon. The silicon native oxide resonance, normally around 1240 cm\(^{-1}\), is overlapped by water perturbation

We measured the ellipsometric parameters of silicon in a spectral range from 4000 to 800 cm\(^{-1}\). The spectra look relatively noisy. This is due to the low values of the reflection coefficients. Furthermore, the polarization of the beam reflecting from the sample surface is strongly oriented along the s direction and after the compensator, it forms an ellipse elongated in the s direction too. The analyzer azimuth being positioned in the p direction, only a weak signal reaches the detector. The consequence is a low signal to noise ratio. A strong water signal, mainly in the \(\Delta\) spectrum, is observed. Unfortunately, the presence of water, in the 1800-1200 cm\(^{-1}\) area overlaps the native oxide absorption peak around 1240 cm\(^{-1}\). The spectra are fitted by taking into account the native oxide. In fact, the contribution of the native oxide is also visible on the values of \(\Delta\) over the spectral range. The presence of native oxide results in a lower value
4.3.3 Glass

The glass substrate is in fact a microscope slide, without specific treatment. It appears that this type of glass shows different characteristics than fused silica. Because of its transparent properties, the light reflected is strongly attenuated. The slides were 1 mm thick.

Figure 4.5: Experimental (solid lines) and fit (dashed lines) of the ellipsometric parameters of glass microscope slide.
Figure 4.5 shows the experimental and fitted values obtained by ellipsometry. There is clearly a good agreement. One should note that the spectrum does not correspond to that of classical amorphous silicon oxide, where TO$_3$ and LO$_3$ and clearly split. The exact composition of the microscope slides is not known. Other discrepancies between the experimental data and the model are also observed. The values of $\Delta$ and $\Psi$ for high frequencies become slightly higher than those of the model, specially for $\Delta$ where a convergence to 0 is expected. This could be due to imperfections of some optical elements of the ellipsometer or residual misalignment after calibration procedure. These errors are emphasized because of the low intensity of the reflected beam. Another interesting feature is the strong variation noticeable on $\Psi$ at 1275 cm$^{-1}$, which is also visible on $\Delta$. It might be an interference effect, due to multiple internal reflections within the transparent slide.

Measurements were performed nevertheless considering the glass slides as a substrate. They have been compared with models obtained from transmission measurement on the same type of microscope slides (data included in SCOUT2 software, from private communication).

![Dielectric function and refractive index](image)

(a) Dielectric function  
(b) Refractive index

From the model, we have obtain data on the dielectric function and the absorption coefficient, which are presented in figure 4.6. The spectral range has been reduced to 2500-800 cm$^{-1}$, since no special features appear at higher wave numbers. Slight changes compared to amorphous silicon oxide can be noticed. The absorption coefficient does not, or hardly, exhibit a shoulder at the base of the TO$_3$ peak, for wave number around 1200 cm$^{-1}$, characterizing the TO$_4$ peak.

### 4.4 SiO$_x$ on Si-substrate

#### 4.4.1 Measurements

We will first focus on the SiO$_x$ films deposited on silicon, since a lot of applications might be related to the use of such substrates.

Fig 4.7 shows the spectrum of two different suboxides deposited on silicon. The oxide thickness is identical, and the only parameter that has been intentionally changed is the stoichiometry.
Figure 4.7: Ellipsometric parameters obtained for two samples: sample d (x=0.73, solid line) and sample f (x=1.26, dashed line)

The phase shift $\Delta$ shows strong variation along a 0-360° range. $\Psi$ is also subject to important variations. The spectrum should be divided in two separate areas. One (from 1300 to 800 cm$^{-1}$) is related to chemical signature, and deals with the composition of the layer. The second spectral area (4000-1300 cm$^{-1}$) provides information on the reflectivity and the optical properties of the sample. Obviously, both areas are modified, which suggest a change of the chemical composition of the oxide layer leading to a change of the optical characteristics.

A first clear observation, is the absence of Si-H (around 2150 cm$^{-1}$) and Si-OH (3400-3600 cm$^{-1}$) absorption signature in both samples. Once the sub-oxide film is in contact with air, normally water enters naturally the material and Si-OH bonds occurs in sub-stoichiometric sites. In this case, we supposed that the matrix formed by the silicon atoms is dense enough to prevent the penetration of water inside the film. This property has been also observed in remote PECVD experiments [6]. The plasma stoichiometry plays then an important role. The control of the deposition temperature can also influence the purity of the film.

### 4.4.2 Analysis of the absorption spectral region (900-1300 cm$^{-1}$)

Observing the low wave numbers region, the spectra exhibit structures which are similar to those of thermally grown silicon dioxide, but some differences are noticeable. In SiO$_2$ film spectra, there is a clear splitting between the LO and the TO modes (cf. Figs. 3.4 and 3.8). The absorption resonance peaks around 900 and 1250 cm$^{-1}$have been already studied and deconvolutions into several absorption sub-bands have been proposed [7]. Compositions were also determined by means of X-ray photoelectron microscopy [2].

We used the deconvolution proposed by Drinek et al., based on the model of Aspnes et al. [18, 19]. The resonance absorption band can be deconvoluted into 5 sub-bands listed as:

- $\delta$ Si-O absorption corresponding to Si-SiO$_3$ bonds [4] or non bridging SiO groups [20]. The resonance frequency is around 870 cm$^{-1}$ (I).
- $\nu$Si-O related to Si-Si$_3$O or Si-Si$_2$O$_2$ bonds, around 980 cm$^{-1}$ (II).
- strong Si$_2$O$_3$ absorption band around 990 cm$^{-1}$ (III).
• strong SiO$_2$ band corresponding to the in phase motion of oxygen atoms in Si-O$_4$ bonding units, around 1080 cm$^{-1}$ (IV).

• weak absorption band, corresponding to the out-of-phase motion of oxygen atoms, around 1175 cm$^{-1}$ [5] (V).

Figure 4.8: Model of deconvolution of the absorption band with five sub-bands, corresponding to the Si-O bands in different bonding configurations. See the text for the description of the different sub-bands. The absorptions bands corresponds in this case to a stoichiometry x=1.

The sub-bands have been modelled by Brendel oscillators [21], where the susceptibility of each band $j$ is given by:

$$\chi_j(\nu) = \frac{1}{\sqrt{2\pi}\sigma_j} \int_{-\infty}^{+\infty} \exp\left( \frac{(x - \Omega_{0,j})^2}{2\sigma_j^2} \right) \frac{\Omega_{p,j}^2}{x^2 - \nu^2 - i\nu\Omega_{\tau,j}} \, dx.$$  \hspace{1cm} (4.2)

Here, $\Omega_{0,j}$ is the oscillator frequency, $\Omega_{p,j}$ the oscillator strength, $\Omega_{\tau,j}$ the damping constant, and $\sigma$ the width of the Gaussian distribution. These variables represent the four input variables for each of the five sub-bands. The fits were performed from the ellipsometric spectra, using the software SCOUT2. The spectra corresponding to the sample a (x=0.01) were not suitable for such a fit since no absorption bands were visible (see Fig. 4.9). The Brendel oscillator model is generally useful to treat disordered systems, that we would expect in the formation of strongly sub-stoichiometric silicon oxides.

From each of the other samples, the dielectric function is calculated and the the refractive index of each sample is deduced. The other parameters used for the fit are the oxide layer thickness and the real background value of the dielectric function ($\epsilon_\infty$). Variation of these parameters have only little influence on the spectra over the 1300-850 cm$^{-1}$ range, since the absorption bands are predominant here. A consequence is that one should not used the absorption band spectral region to determine the oxide thickness or $\epsilon_\infty$, since the accuracy would be very poor. The results obtained for the dielectric function and the refractive index are shown in figures 4.10 and 4.11 respectively. The transition of the optical properties of the oxide when the proportion of oxygen increases is clearly visible. For a low stoichiometry, (i.e. x low), the film has a behavior close to a reflecting semiconductor, and becomes more and more an insulator when x
reaches higher value. One can note that the case $n=k$ is obtained only for a stoichiometric coefficient $x$, higher than 1.25. This is an important fact since the longitudinal optical (LO) mode position is defined by the relation $n = k$. The extrema of $\epsilon_1$ become more distant in amplitude when the stoichiometry increases, but the position of these extrema in terms of wavelength is however not significantly modified. The minimum becomes even negative for values of $x$ higher than 1.25 (see fig 4.10(e)). At the same time the average value of $\epsilon_1$ decreases regularly. This is related to the value of $\epsilon_\infty$ and will be studied more accurately in the next section.

The maximum of $\epsilon_2$ increases with the stoichiometry it becomes even larger than the maximum of $\epsilon_1$ for sample g. This increase is also visible in the extinction coefficient $k$, varying from 0.5 (at $x=0.27$) to around 1.5 ($x=1.41$). This increase translates a showing a lower reflectivity of the oxide layer as the amount of oxygen increases.

The position of the maximum of the imaginary part $\epsilon_2$ of the dielectric function is slightly changing with the stoichiometry. The maximum is shifting towards higher wave numbers as seen on figure 4.12(a). The shift seems linear for a stoichiometry higher than 0.75, but lower values do not follow the linear behavior. The values obtained differ from those measured by Pai et al. ([5] and references therein). However, their silicon sub-oxide films were obtained with a different process (RPECVD) and exhibited IR absorption bands related to SiN, SiH and SiOH bonding groups due to adsorbed water, whereas none of such additional bands could be observed in our films. This suggests that films prepared by sputtering, even at low temperature, have a silicon matrix which is denser than that of PECVD films. A consequence of these properties is the generation of more stress in the silicon oxide network and a shift of the absorption bands [22]. The shift of the absorption coefficient can be explained by the relative contribution of the two mains sub-bands (III) and (IV). For low stoichiometry, the absorption due to Si-O bands in $\text{Si}_2\text{O}_3$ sites seems dominant, and as the oxygen concentration increases, the influence of vibration of Si-O in $\text{SiO}_4$ tetrahedra becomes more important. This is logical if we consider that a silicon atom has more chance of being linked to 4 oxygen atoms in a tetrahedron when the stoichiometric coefficient (i.e. the concentration of oxygen) increases. In addition to the frequency shift, the increase of the absorption peak amplitude is observed(Figure 4.12(b)).

A shoulder is also visible in the absorption spectra, and it evolves with stoichiometry. Whereas it cannot be identified for $x=0.27$, it is clearly visible for higher values. This shoulder
Figure 4.10: Evolution of the dielectric function of the suboxide films with the stoichiometry. Solid line: \( \varepsilon_1 \), dashed line: \( \varepsilon_2 \).
Figure 4.11: Evolution of the complex refractive index (n+ik) of the suboxide films with the stoichiometry. Solid line: n, dashed line: k.
4.4 SiO$_x$ on Si-substrate

is attributed to out of phase relative displacement of oxygen atoms in SiO$_4$ sites. This shoulder, is particularly visible for x=0.73 as shown of figure 4.13.

This corresponds to the stoichiometry where an important shift in the absorption maximum frequency is visible. It is possible that around this stoichiometry, the number of SiO$_4$ sites increases drastically. The out of phase motion within these tetrahedra seems to be relatively more important (one should consider also that sub-band V has a low oscillator strength compared to sub-band IV). Then, for higher x, the shoulder, although still visible, is not as strong and in-phase motion is again predominant.

4.4.3 Analysis over a large spectral range (900-4000 cm$^{-1}$)

We have already mentioned that the absorption region is not suitable for an accurate determination of dielectric background value ($\epsilon_\infty$) and the oxide layer thickness. The determination of these value should be made on a larger spectral range. The consequence of such a choice is a lower accuracy on the absorption bands: the algorithm will base its fit on the complete
Investigation on silicon sub-oxides by infrared ellipsometry

range and some important features in the absorption bands areas, especially shoulders, may be ignored because of their low weight in the regression calculation. Thus, once the parameters concerning the 1300-850 cm$^{-1}$ area have been determined, one can proceed with the calculation of $\epsilon_\infty$. The most important factor determining the dielectric background value is the position of the maximum of $\Psi$, which corresponds also to the bending point of $\Delta$. Figure 4.7 shows that the difference of stoichiometry induces a strong shift in the zero of $\Delta$. Unfortunately, a modification of the thickness of the film will have sensibly the same effect on the model. Therefore, either the thickness or the dielectric background has to be determined by another method. In our case, the thicknesses were obtained by step height measurement. Fixing these values, we can then fit the spectra. The values of $\epsilon_\infty$ are gathered on figure 4.14. The values corresponding to crystalline silicon have been obtained from the measurements of silicon substrates and those corresponding to silicon dioxide have been measured on a former experiment (cf. chap 3). These values are 11.64 and 2.12 respectively and are in total agreement with literature data [23, 24] For a stoichiometry $x=1.41$, the dielectric background is already close to that of silicon dioxide, but the value of $\epsilon_\infty$ seems to evolve slowly towards the value of amorphous silicon oxide. The particular properties of the films due to the sputtering process, can also play a role in the value of $\epsilon_\infty$, specially because of the stress in the silicon oxide network.

The values measured are strongly linked to the accuracy of the determination of the oxide layer thickness. The model shows that an error of 5 % on the thickness at 600 nm yields a variation of $\pm 8 \%$ in the value of $\epsilon_\infty$. The determination of the thickness can however been achieved with an accuracy better than 5%.

4.4.4 SiO$_x$ on chromium and glass

We have applied the model of the films to other substrates. Figures 4.16 and 4.17 show the model of silicon sub-oxide on silicon obtained for a stoichiometry of 1.00, applied on chromium and glass respectively. The experimental data obtained by ellipsometry are also represented. Very good agreement between the model and the experimental data is observed. No parameters have been adjusted, except the angle of incidence within a margin of $\pm 0.1^\circ$ due to experimental
4.4 SiO$x$ on Si-substrate

conditions. It is clear that the experimentally determined positions of the maxima of $\Psi$ coincide with the model. This means that, assuming that the thickness is the same for each sample, the optical properties of the film is the same regardless the substrate. One could remark that

![Graph showing fitting of the silicon sub-oxide (x=1) layer, on silicon substrate. The experimental measurement is represented in dashed line.](image1)

Figure 4.15: Fitting of the silicon sub-oxide (x=1) layer, on silicon substrate. The experimental measurement is represented in dashed line.

![Graph showing fitting of the silicon sub-oxide (x=1) layer, on chromium substrate. The experimental measurement is represented in dashed line.](image2)

Figure 4.16: Fitting of the silicon sub-oxide (x=1) layer, on chromium substrate. The experimental measurement is represented in dashed line.

the model and the experimental curves do not coincide near the maxima of $\Psi$ and the spectral area where variations of the ellipsometric parameters are strong. This can be explained by the divergence of the beam of the ellipsometer. To proceed to a accurate fit, one should use an angle spread model. This effect has been treated in literature [25]. The correction has not been applied for this work. On the large spectral range, the most important parameter is the different features position frequency, such has the zero (or 180° for chromium) position of $\Delta$. Stronger deviations are observed on on figure 4.17, for high wave numbers. We think that this is due to the errors on the fit of the glass substrate. Such deviation are effectively visible on figure 4.5.

Models elaborated with other values of $x$ give also good results when applied to other substrates, with discrepancies slightly more important for $x=0.27$. It is however difficult to identify
the causes of discrepancy: layer thickness, angle of incidence, different initial reactions of predominant silicon atoms with substrates, etc. The effect is however rather small. An important conclusion is that the film properties are not significantly affected by the nature of the substrate. In fact, discrepancies between films could occur in the very first layers of the deposition process since the first silicon and oxygen atoms will not interact in the same way with chromium atoms or with silicon or silicon dioxide networks. In order to study this phenomena, much thinner oxide layers (of the order of few nanometers) have to be considered.

4.5 Concluding remarks

Infrared spectroscopic ellipsometry has proved its capability in the study of films such as silicon oxides, at various stoichiometric conditions. The interest of such a technique is to provide accurate information on the general optical properties of the film (e.g. $\epsilon_\infty$) and on some more local spectral structures like absorption bands.

Concerning the silicon sub-oxide films, we have modelled the evolution of the dielectric function and the refraction index with the stoichiometry of the film. The relative distribution of the $\text{Si}_2\text{O}_3$ and $\text{SiO}_4$ tetrahedra bands, within the overall absorption band in the 1300-850 cm$^{-1}$ spectral range, has been observed. Furthermore, models of the films obtained show that the properties of the film are not significantly modified by the nature of the substrate.

Differences in the position of the absorption frequencies with other $\text{SiO}_x$ films in the literature have been observed. These discrepancies have been attributed to a denser network, preventing from water adsorption and generating stress in the network. This observation led us to a new investigation on PECVD of silicon oxide at low temperature [26]. The oxide stoichiometry is close to 2, but resonance frequencies measured with infrared ellipsometry do not coincide with those of amorphous silicon dioxide. A study of stress properties, network density and porosity is currently realized together with an ageing study of the films.
References


Part II

Surface analysis of bone tissue treated by non-thermal plasmas
Chapter 5

Diagnostic techniques for bone tissue analysis

Bone tissue has been investigated after treatment by a low pressure non-thermal plasma. This chapter gives a short introduction to bone tissue and describes the plasma treatment process. Several diagnostic techniques have been used to analyze the surface of the bone including infrared spectroscopic ellipsometry, Rutherford backscattering spectrometry (RBS), and elastic recoil detection analysis (ERDA). The information given by each of the techniques and their mutual complementarity for the analysis of bone tissue are shown. In particular, ellipsometry in the infrared can give accurate information on the chemical composition of the plasma treated bone, whereas ion beam analysis show the modification of the stoichiometry.
5.1 Introduction

The work presented in the following chapters is a part of a larger project on the development of bio-compatible plasmas. [1–3]. The last few years, much effort has been carried out to develop bio-compatible plasma sources. Plasma technology is directly derived from material surface processing science [4], and has been the prominent technique for deposition and etching in semiconductor industry. New trends in the development of biomaterials have been already taken advantage of plasma treatments. These have been applied on e.g. polymer surfaces, in order to develop bio-compatible surfaces [5] with applications such as implants or artificial organs. But plasmas have not yet been used directly on biological tissues and the interaction between ionized gases and living tissues is barely understood. However, it is expected that new developments such as plasma-based cure for diseases like restenosis, osteoporosis or eczema, could make a valuable contribution to medical science in the near future. Because living cells are extremely sensitive to heat damage, only non-thermal plasmas, operating at ambient temperature, are suitable for such applications.

Several types of non-thermal plasma sources have been developed. These include the atmospheric pressure plasma jet (APPJ) [6, 7], the plasma pencil [8] and the one atmosphere uniform glow discharge plasma (OAUGDP) [9]. These three example are working under atmospheric pressure. Unfortunately, none of these plasmas could be considered as bio-compatible. The energies transmitted to species populating the plasma are often too high to expect any living tissue to survive plasma treatment. Other examples of plasmas, such as capacitively coupled plasmas, or inductively coupled plasmas (ICP) can be generated at low pressure, in a sealed reactor. But in this case, the vacuum conditions prevent any application on most of the tissues.

Recently, a non-thermal plasma source functioning under atmospheric pressure has been developed [10]. The non-aggressive nature of the source has been demonstrated. This will hopefully enable new applications in e.g. dentistry or skin treatment. The plasma needle is described on figure 5.1. The size of the plasma needle (0.1 to 1 mm) represents however a major drawback in the study of plasma-tissue interaction. Only few diagnostic techniques would
be available for the analysis of the plasma phase. Moreover, the treated tissue area would be limited. To overcome this difficulty, we choose to utilize another plasma source: a non-thermal low-pressure Inductively Coupled Plasma (ICP). This large volume plasma is nowadays widely used in the semiconductor industry and has been extensively studied in the last decade. Moreover, a large range of diagnostic has been adapted for this type of reactor enabling gas phase and surface analysis. The interest of ICP lies in the large and uniform area that can be treated. This reactor is, however, operating under vacuum conditions (around 50 mTorr). This obviously limits the type of tissue that can be treated using an ICP. Bone tissue appeared to be a suitable material for this investigation, considering its stability, rigidity and low water content.

The aim of this research is not to find direct medical applications on a plasma treatment. Once again the vacuum conditions are not suitable for a medical treatment. With this study we want to understand how bone tissue would react when in contact with a non-thermal plasma. Several diagnostics have been used including infrared spectroscopic ellipsometry, Rutherford back-scattering (RBS), elastic recoil detection analysis, and scanning electron microscopy.

This chapter will begin with an introduction on bone tissue and its properties. Then a description of the different diagnostics will be given. In the following chapter the results of the measurements will be presented and discussed.

5.2 Bone tissue

5.2.1 Composition

The skeleton of vertebrates is constituted of individual bones and the connective tissues that joint them [11]. The essential difference between bone\(^1\) and the tissues surrounding them, are rigidity and hardness. Bone has several functions in the organism. It supports and gives shape to the body, it protect vital organs such as brain and heart and lungs thanks to the cranial and thoracic cavities respectively, it forms a strong structure where the bone marrow can develop, and transmits the force resulting from muscle contraction from one part of the body to another one. Rigidity and hardness of bone results from the prominent mineral composition of the tissue. These properties results from the mineral content of the bone tissue. Figure 5.2 shows the section of a typical long bone (humerus, femur or tibia). It is composed of a central part with a cylindrical shape, the diaphysis and two wider ends, the epiphiyses. A transition area between these two parts is named metaphysis. Diaphysis and the outer shell of metaphysis is mainly composed of cortical bone (also named compact bone) which has a dense structure and represent in mass 80% of the adult skeleton. The remaining 20% consist of more porous trabecular (or cancellous) bone. The relative distribution of cortical and trabecular bone differs between individual bones but also with the age. The function of cortical bone is mainly biomechanical and protective, whereas cancellous bone plays a prominent role in mineral regulation, thanks to its high density of blood vessels, and its higher effective surface, due to porosity.

A particularity of bone tissue is its mineralization process. Bone tissue consists of 65% mineral, 35% organic matrix, cells and water. The organic matrix is mainly a collagen network, where non organic salts deposit in an oriented fashion, but non collagenous proteins are also present and represent around 10% of the organic material. The main constituent of the mineral

\(^1\)Along this study the term bone will be used indifferently in order to designate the element of the skeleton and the matter constituting it.
network is poorly stoichiometric hydroxyapatite \((\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)\). The stoichiometry of the mineral component can be modified, by substitution of calcium site by different cations such as \(\text{Na}^+\), \(\text{K}^+\), \(\text{Mg}^{2+}\), \(\text{Sr}^{2+}\), or \(\text{Pb}^{2+}\). The \(\text{OH}^-\) anion can also be substituted by phosphatic acid \((\text{HPO}_4^{2-})\), carbonate \((\text{CO}_3^{2-})\), \(\text{Cl}^-\), and \(\text{F}^-\) radical. Typical values for the different components of mineral components are presented in table 5.1 for bovine bone. The presented values are results from different measurements on bone mineral using different techniques, for example gravimetry, IR spectroscopy and energy dispersive X-ray analysis. It should be noted that these values are averages of a variety of bovine. The exact composition may change with skeletal position, age, sex and diet. Type I collagen comprises 90 to 95% of the organic matrix of bone. A large range of non-collagenous protein are also present in traces. The remaining organic elements non-collagenous proteins, proteoglycans and phospholipids. The non-collagenous components play a role in bone homeostasis, for example growth factors and enzymes.

### 5.2.2 Physiology and mineralization

The most remarkable properties of bone tissue are its self-mineralization and its self-repairing capability [13]. Bone is irrigated by blood vessels, continuously developing in the tissue. The
5.2 Bone tissue

<table>
<thead>
<tr>
<th></th>
<th>Bovine Cortical Bone (wt% of whole bone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>26.7 ± 0.15</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>12.47</td>
</tr>
<tr>
<td>Carbonate</td>
<td>3.48</td>
</tr>
<tr>
<td>Citrate</td>
<td>0.863</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.731 ± 0.015</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.436 ± 0.009</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.077</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.072</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.055 ± 0.009</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Table 5.1: Chemical composition of bone mineral [12].

vessels cavities are formed by osteoclasts, that are bone-resorbing cells. Their are able to dissolve mineral as well as organic material of bone tissue. Beside drilling cavities during growth process, osteoclasts play an important role in the destruction of old bone matrix.

The effect of osteoclasts is balanced by other cells such as osteoblasts, osteocytes and bone-lining cells. These three types of cell are actually the same original cell at different development stages. Osteoblasts synthesize and lay down precursors of collagen I. They are also responsible of the production of osteocalcin, the most abundant non-collagenous protein in bone.

With the growth, some osteoblasts are buried in the bone tissue they have built and evolve to osteocytes, the latter represent by far the most abundant cell in bone. They generate network connections via microscopic channels (lacunae and canaliculi). Their role is monitor and regulate ionic concentrations inside bone, their are particularly sensitive to strain that would impose remodelling of the tissue.

Bone-lining cells play similar role than osteoblast, from which they are believed to derive. Their function is also closed to that of osteocytes, such as regulation of bone mineral, mass, and architecture.

The mineralization process takes place inside the organic bone matrix. Calcium cations and phosphate anions are supplied by blood plasma via nutrient arteries. Mineral crystals are deposited in alignment with bone collagen fibrils. The complex process in of mineralization is described in [12, 14].

Bone not only plays a mechanical role, it is also a mineral regulator for ion homeostasis. Reversely, bone disease are often originating from metabolic problems. Osteoporosis is perhaps the most prevalent example of bone disease. It affects an increasing number of people since it is closely related to ageing. It is defined as "a systemic disease causing an absolute decrease in the amount of bone and microstructural change, leading to skeletal fragility and consequent fractures after minimal trauma (low energy fractures)". There are several factors leading to osteoporosis [15], including : hormonal regulation, nutrition, heredity, lifestyle factors (tobacco, alcohol...), menopause and andropause, environmental factors (physical activity, nutrition, bodyweight...) Among these causes, many are not well understood. Furthermore the process of the loss of bone is not clearly explained yet, and this hinders the development of treatments. The consequences are biomechanical, leading to an increasing number of fractures.
occurring with a minimum stress [16]. The balance between the forming and the resorbing processes is the key of the explanation of such systemic disease. Elementary processes in the mineral and the organic compounds of bone tissue have to be investigated.

5.3 Samples

5.3.1 Preparation

We used for this study bovine bone from the knee bone or femur. These bones have a rather large size, allowing the preparation of several samples from the same bone, in order to obtain similar initial structures and properties. As we already discussed, bone does not have a homogeneous structure. We opted to focus our study on cortical bone. Our choice was driven by a higher density and lower porosity. Since the interaction with the plasma is expected to occur within a depth of few hundreds of nanometers, it is important to prepare a sample surface as smooth as possible, but by keeping nevertheless the original properties of the bone.

The samples were cut longitudinally in the bone in order to have an homogenous cortical bone tissue. Samples were cut with a precision diamond saw. We did not perform any polishing at the surface, because of the brittle structure of the bone. The precision saw do not modify significantly the roughness of the tissue. We measured the roughness on samples of cortical bone, and it has been estimated to 0.5 µm, which is of the order of the expected plasma penetration depth. Roughness is even much higher for cancellous bone as shown on the picture 5.3. Because of the required large analysis area for spectroscopic ellipsometry, the sample size was chosen at 2 × 1 cm with a thickness varying from 1 to 2 mm. Transversal cuts exhibit a too strong variation in the porosity as shown in figure 5.3. Blood and order tissue were removed by bathing the samples in water. The removal of these tissues is not really a problem since they would have been also removed under vacuum conditions. Before measurement, and specially for non treated ones, the samples were subjected to vacuum (around 10⁻¹ Bar) in order to remove excess of water.
5.3 Samples

5.3.2 Plasma treatment

The samples were exposed to ion bombardment in an inductively coupled plasma (ICP) [2]. The experimental set-up is a conventional "pancake-like" ICP. It consists of a 30 cm diameter large and 50 cm long chamber. On one of the axial ends, a water cooled 3-turn flat spiral antenna made of copper, with an outermost diameter of 15 cm, is powered by a 13.56 MHz rf source. The power is transferred to the chamber through a 2.5 cm thick and 33 cm diameter quartz plate. The magnetic field created by the current flowing into the antenna induces an inductive azimuthal electric field inside the chamber which heats the light electrons. The energy is then transferred from the hot electrons to the heavy particles (ions and neutrals) through various collisional processes. Inductively coupled plasmas are often referred as electrodeless plasmas as there is no direct contact between the powered antenna and the plasma itself. The rf source delivers an output rf power spanning from 0 W to 2 kW. In practice rf powers varying from 0 W to 800 W were used for these experiments. To reduce reflections, a matching network is placed between the source and the antenna.

![Inductively coupled plasma reactor, with the different diagnostics mounted: Langmuir probe, mass spectrometer (PPM422)](image)

A stainless steel electrode of 30 cm is positioned at 4 cm from the quartz plate. The back of the electrode has been designed so that a commercial energy resolved mass spectrometer from Balzers (Inficon) PPM422 can be pressed against it. On the plasma side a hole of 1 cm in the electrode allows the positioning of the extraction hood where the 100 mm entrance hole of the mass spectrometer is situated. The electrode is water-cooled and can eventually be dc biased. In the experiments described in this work, the electrode is grounded. The mass spectrometer enables detection of positive ions and radicals during processing and also of the energy of the ions reaching the electrode. A Langmuir probe installed on the top of the set-up measures the plasmas parameters. The base pressure achieved in the reactor is about 5.10-7 mbar and the usual working pressures in the chamber were ranging from 5 to 50 mTorr. These gas phase diagnostics are described elsewhere [2] and will not be detailed in this thesis.

During the treatment, the bone samples were positioned on the electrode.
5.4 Description of the diagnostic techniques

5.4.1 Infrared Spectroscopic ellipsometry

Ellipsometry has proven its powerful capacities of investigating the optical properties of surfaces [17, 18]. In the recent years, Fourier transform techniques enabled to enlarge the spectrum towards mid-infrared [19–21]. This allows the combination of the accuracy of ellipsometry with the large amount of information about chemical composition of the sample thanks to Fourier transform spectrometry.

Measurement are performed with an ex-situ spectroscopic ellipsometer in the infrared range, functioning with a rotating compensator. Ellipsometry is based on the measurements of polarization of light while reflecting on a surface. This change is expressed by determining the ratio of complex Fresnel coefficients \( r_p \) and \( r_s \), in a direction respectively parallel and perpendicular to the plane of incidence. Conventionally, the ellipsometric angles \( \Psi \) and \( \Delta \) are used.

\[
\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta}
\] (5.1)

In fact, \( \tan \Psi \) is the ratio of magnitudes of \( r_p \) and \( r_s \), and \( \Delta \) is the phase difference between the coefficients. The special configuration of a rotating compensator ellipsometer (RCE) offers several advantages compared to others techniques such as rotating analyzer / polarizer ellipsometers. It is for instance not affected by the possible polarization of the light source, or the polarization dependent response of the detector. Another advantage of RCE configuration is the fully determined value of \( \Delta \). With the other techniques the phase shift is calculated on a \( \pi \)-large range, but using RCE the value of \( \Delta \) on a 0-2\( \pi \) range. The ellipsometer we used has been already described and studied in the previous chapters, and its application on the study of thin films has been successful. Only a short description is given here.

![Representation of the ellipsometer in PSCA configuration.](image)

The ellipsometer is coupled to a Fourier Transform interferometer (Bruker IFS66), the detector is a Mercury Cadmium Telluride detector, Graseby, MCT-M16(cf. Fig 5.5). The Spectral range used during the measurements is 4000-870 cm\(^{-1}\), and the resolution is 4 cm\(^{-1}\).

Fourier transform infrared (FTIR) spectrometry has been already used on bone tissue [22–25], dental tissue [26] or synthesized tissue with close properties to those of bone [27], measurements have also been performed on organic components such as collagen [28] It has shown its capabilities of showing the effect of some bone diseases such as osteoporosis [29–32].
5.4 Description of the diagnostic techniques

This technique, sometimes adapted to micro-spectroscopy with an area of analysis of up to 50 \( \times \) 50 \( \mu \)m\(^2\), provides information on mineral (hydroxyapatite) and organic compounds (collagen). In all these studies, the measurement were performed by transmission, giving thus a line of sight measurement, along the whole thickness of the sample. This technique is thus not well adapted to our purpose since we expect modification in the tissue over only few hundreds nm in depth.

Ellipsometry offers the advantage of giving information on the first hundreds of nanometers under the surface. Furthermore, it provides more information than other comparative techniques such as attenuated Total reflection (ATR FTIR) [21]. The conditions of performing the measurements are however more critical, than for instance transmission or reflection FTIR spectroscopy. The determination of the angle of incidence of the infrared beam with high accuracy is of prominent importance. Furthermore, the nature of the sample (transparency, roughness, etc) can lead to some additional difficulty. The first measurements on bone samples show that the bone is highly transparent in the infrared range. This is a major problem for a technique such as ellipsometry, based on reflection. More specifically, our first measurements performed with an angle of incidence of 70° showed that no reflected signal was detected. in fact, the detected signal corresponded to the one of the substrate holder on the back side of the sample... To overcome this problem, we used a larger angle of incidence in order to obtain reflection at grazing incidence. Because of the weak intensity of the source and its non-punctual nature, the infrared beam hitting the sample has a diameter of around 1 cm. For a wider angle of incidence, the resolution is increased since reflection at grazing angle will provide more information on the structure of the surface (porosity, roughness...). However, if the angle of incidence becomes very large, the section of the sample become smaller than the beam, and the reflected intensity decreases. One must then find a balance between the resolution and the intensity of the signal. After several test measurements, we obtained a best signal with an angle of incidence of 80°. A typical spectrum is shown on figure 5.6:

![Figure 5.6: Typical ellipsometry spectrum of bone sample. The main features of the mineral and organic components are indicated in the \( \Delta \) spectrum.](image)

It clearly appears that the information is obtained mainly on the \( \Delta \) spectrum. This is due to the fact that, except on the absorption spectral areas, \( \Delta \) has a low and rather constant value. The most intense absorption bands have been indicated on the spectrum of \( \Delta \). One should be aware that the spectrum of \textit{Delta} is not an classical absorption spectrum. Although absorption bands
positions are obvious, a direct deconvolution into sub-bands is not possible. In theory, a model of the sample must be established and including the different mineral and organic components, the porosity and density a possible anisotropy and the microscopic structures of the tissue. It is however possible to identify changes in the peaks and to associated them to chemical bond modifications. In a general point of view, a change in amplitude of an infrared ellipsometry peak corresponds to a bond density change, while a shift of the peak corresponds to a change of chemical structure of the bond.

Contrary to other techniques used for this study (RBS, ERDA), ellipsometry in the infrared range is able to provide information on molecular composition of bone tissue. This will be the main objective of the ellipsometric measurements since optical parameters, such as the refractive index, are not of significant importance in this case.

5.4.2 Rutherford backscattering spectrometry

One of the most interesting parameters concerning bone tissue is the stoichiometry of the mineral or the organic compounds. In particular, the ratio between calcium and phosphor Ca/P, is useful indicator of the stoichiometry of hydroxyapatite. A technique like energy dispersive X-ray analysis (EDX) can provide such parameters. However it can not provide a depth profile of the sample. Moreover, detection limitations prevent from analysis of oxygen and lighter elements.

Ion beam analysis includes now well established techniques to characterize materials, such as Rutherford backscattering spectrometry (RBS), elastic recoil detection analysis (ERDA), nuclear reaction analysis (NRA), and particle induced X-ray emission (PIXE) [33]. For this study, we focussed on RBS and ERDA, which, when combined allow a study on the whole range of the periodic table. Measurements were performed at the Forschungszentrum Rossendorf, (FZR) in Dresden, Germany, at the center for Application of Ion beams in Materials Research (AIM).

Rutherford backscattering spectrometry consists of the measurement and the energy distribution of ions backscattered from atoms in the near-surface region of solids materials [33]. A detailed description of the technique is given in the appendix at the end of this thesis. Only the main results are shown here. The incident beam is a 1.7 MeV $^4$He$^+$ ion beam generated by a Van-de-Graaff accelerator. A projectile ion penetrates the sample through a depth $x$, where it collides with a heavier atom. Because of mass difference, the He ions can be backscattered and reach a detector. During this process the ion can lose energy by three fashions:

- Energy loss due to the stopping of the ion in the inward direction in the material ($\Delta E_{in}$)
- Energy lost during the collision with material’s atom.
- Energy loss due to the stopping of the ion in the outward direction in the material ($\Delta E_{out}$)

The stopping of the ion is define by the stopping power:

$$S(E) = \frac{dE}{dx}$$ (5.2)

It is shown that the energy $E$ of the ion recorded by the detector after the interaction with the material and by taking into account of the stopping effect is:

$$E = KE_o - \left( \frac{K}{\cos \theta_{in}} \left( \frac{dE}{dx} \right)_{in} + \frac{1}{\cos \theta_{out}} \left( \frac{dE}{dx} \right)_{out} \right) x = KE_o - [S]x$$ (5.3)
where $K$ is the kinematic factor, $\theta_{in}$ and $\theta_{out}$ are the angle with the sample normal of the incident and the outgoing ion respectively. The energy $E_o$ is the initial energy of the projectile ion before penetrating the sample, and $[S]$ is the energy loss factor. A typical RBS spectrum of bone is shown in figure 5.7.

Figure 5.7: Typical RBS sample on a thick bone sample. Ion beam 1.7 MeV $^4$He$^+$, $\theta_{in}=0^\circ$, $\theta_{out}=10^\circ$.

Each position of the steps is associated to an atomic element. The identification of the element is made by the relation defining $K$ (A.7) given in the appendix. By comparing the heights of the steps, it is possible to determine the atomic ratio between different atoms (eq. A.15). Equation 5.3 shows a dependency on the depth $x$. RBS allows depth profile consideration. Furthermore, by determining the atomic ratios before and after plasma treatment, it is possible to calculate the plasma penetration depth. at this depth the stoichiometry of the plasma treated sample equals that of the untreated sample.

5.4.3 Elastic recoil detection analysis (ERDA)

Elastic recoil detection analysis is another technique to RBS allowing the detection of lighter atoms. The projectile beam is a 35 MeV Cl$^{7+}$ ion beam from a 5 MV tandem accelerator. The detected particles are in this case recoils from the target sample. The energy loss due to stopping on both the inward and outward path is described by

$$\Delta E = \Delta E_{in} + \Delta E_{out} = \left[ \frac{K_2}{\cos \theta_{in}} \left( \frac{dE}{dx} \right)_{in} + \frac{1}{\cos \theta_{out}} \left( \frac{dE}{dx} \right)_{recoil,out} \right] x = [S]x \quad (5.4)$$

where $K_2$ is the kinematic factor for the recoil, defined in equation A.16, The angles $\theta_{in}$ and $\theta_{out}$ are defined as the angles, relative to the plane of the sample surface, of the incident and the outgoing beam, respectively. Note that $\left( \frac{dE}{dx} \right)_{in}$ and $\left( \frac{dE}{dx} \right)_{recoil,out}$ are the stopping powers of the target material for the incident ion and recoil respectively. The energy loss due to the collision described by the kinematic factor, $K_2$ in equation A.16 is used to identify the different elements.
Diagnostic techniques for bone tissue analysis

at the sample surface from the measured ERDA spectrum, similar to the element identification in RBS.

A Bragg ionization chamber, described in the appendix, is used as a detector. A typical ERDA measurement is shown in figure 5.8.

![ERDA measurement](image)

**Figure 5.8:** Typical ERDA measurement on a thick bone sample. Ion beam 35 MeV Cl$^{7+}$, $\theta_{in}=15^\circ$, $\theta_{out}=15^\circ$, $\phi_s = 30^\circ$, $Q = 3.4\mu$C.

Each branch corresponds to an atomic element. Here, the light element are (C,N) well resolved. For atoms with mass close to Cl mass, overlapping of the curves occurs and the measurements are not as accurate. Fortunately, Ca signal is easily observed by RBS. The concentration and depth profile of an element is obtained by selecting the corresponding branch. The intensity of the branch varies with the detected energy and can be associated to the depth $x$ inside the sample.

5.5 **Information content of analysis and concluding remarks**

We have seen that the complementary use of RBS and ERDA allows for the determination of the stoichiometry of the main atomic elements of bone tissue. Furthermore RBS can easily provide information on the plasma penetration depth. But both techniques does not give information on the molecular composition of bone tissue. This is a major drawback, since specific chemical functions, mainly deriving from collagen structure, play an important role in the tissue. Spectroscopic ellipsometry in the infrared can provide a solution to this problem. As seen in figure 5.6 many organic and mineral components can be identified. Furthermore, atomic elements such as oxygen, can belong to either organic or mineral part. Only ellipsometry is able to discriminate the origin of oxygen.

When compared to other FTIR techniques, only ellipsometry allows an analysis of the near surface area, of the order of several hundreds of nanometers. Because of the transparency of
bone tissue in the infrared, classical reflection spectroscopy seems unrealistic. Furthermore, transmission measurements provide line of sight measurement and the modification due to the plasma treatment will be overlapped by the signal of the bulk material. An alternative could be the preparation of very thin samples, but it is likely that very thin samples would not support vacuum conditions that are required for plasma treatment.

A quantitative interpretation of the ellipsometry spectra is however difficult and will not be performed. Ion beam analysis is thus necessary to determine the quantity of material effectively removed during plasma treatment. The decrease of an absorption peak on an ellipsometry spectrum can only be associated to an alteration of a chemical bond, one cannot however deduce from this the removal of atoms, molecules or radicals. For example, collagen is a very complex protein including cross-linking functions. The break of cross-linking bonds (visible in ellipsometry spectra, see next chapter) does not systematically involve the removal of elements, but can be associated to the formation of unsaturated (double) bonds.

Because of the complexity of the composition and the structure of the tissue, we did not apply a model for purely ellipsometric interpretation of the spectra. It was thus not possible to obtain a depth profile by this method. RBS measurements provided this information.

Summarizing, we have shown that ellipsometry can be applied to bone tissue analysis. The technique can provide information on the chemical composition of the mineral and organic compounds of the tissue. We believe that the depth that can be analyzed by ellipsometry is of the order of the plasma penetration depth, i.e. the depth of the material that will be modified by the plasma treatment. Ion beam analysis techniques, such as RBS and ERDA, provide depth profile of the stoichiometry, and give quantitative information of the atomic elements effectively removed during the plasma exposure. The unique combination of these techniques allows a complete study of the treatment of bone tissue by non-thermal plasma. It is thus possible to determine not only the quantity of material that is removed during the treatment but also the chemical functions that are the most affected by the plasma.

Acknowledgments

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References


Chapter 6

Bone tissue analysis

This chapter describes the analysis of bone tissue by spectroscopic ellipsometry, Rutherford Backscattering spectrometry and elastic recoil detection analysis. First the measurements obtained by infrared spectroscopic ellipsometry are discussed. They provide information on the effect of the etching of the bone surface. Particularly, a smoothing of the surface is observed. Furthermore, the specific effect of plasma treatment on the amide functions of collagen is visible with this technique. Rutherford Backscattering spectrometry and elastic recoil detection analysis provide information on the element specificity of the etching. Nitrogen is the element which is removed the most effectively. The influence of plasma gas, pressure, and input power is investigated. It is shown that the selectivity of the etching process can be depends on the nature of the feed gas and the applied power.
6.1 Introduction

The spectroscopy of the bone surface is investigated with rotating compensator ellipsometry as described in the preceding chapter. The measurements are performed ex-situ in open air. The sample suffer thus from water contamination. A typical $\Delta$ spectrum is shown in figure 6.1. The sample has been subjected to a moderate vacuum ($10^{-3}$ to $10^{-4}$ mbar) for several hours. By moderate vacuum, we mean vacuum conditions lower than those met during the plasma treatment; the sample can be subject to vacuum conditions of the order of $10^{-6}$ mbar, when the feed gas is not inserted in the vessel. The spectra were obtained with a resolution of 4 cm$^{-1}$ and at each step on the compensator, 2000 scans were recorded. This was necessary due to the fact that the intensity of the detected signal was weak. Bone tissue appears to be transparent and even at grazing incidence ($80^\circ$) only a small part of the light beam is reflected.

![Figure 6.1: Ellipsometric parameter $\Delta$ for an untreated sample of bone. The sample has been under vacuum conditions for 24 h before the measurements. The main features of the mineral and organic components are indicated.](image)

The main spectral signatures have been indicated on figure 6.1. These are situated at wavelengths comparable to the ones found using usual FTIR transmission absorption spectroscopy [1, 2]. The chemical signatures are more easily identified from the phase shift $\Delta$ spectra. The most intense contour represents $\nu_1\nu_3$ phosphate absorption (1200-900 cm$^{-1}$). Former studies have shown that this contour is actually composed of 11 sub-bands including PO$_4^{3-}$ and HPO$_4^{2-}$ absorption, depending on the stoichiometry [3, 4]. A substituting carbonate absorption band is also visible in a region from 850 to 890 cm$^{-1}$ ($\nu_2$CO$_3^{2-}$). This band is composed of 3 sub-bands corresponding to OH$^-$ substitution, PO$_4^{3-}$ substitution, and unstable carbonate [5]. Another $\nu_2$CO$_3^{2-}$ absorption band is situated between 1400 and 1500 cm$^{-1}$ but is overlapped by different organic components and it is difficult to distinguish the different features of this band. Concerning the organic structure of the tissue, visible in this spectral area, one can distinguish several amides:

- Amides A and B provide information on hydrogen bonding in collagen ($N - H$ stretch).
The bands are situated between 3200 and 3500 cm\(^{-1}\). Their intensities are weak. Unfortunately, these bands are perturbed by the presence of water (3400-3800 cm\(^{-1}\)). They will not be studied in this thesis, and the spectrum will thus be limited to a 1800-800 cm\(^{-1}\) range.

- Amide I corresponds mainly to a peptide bond \(C = O\) stretch (around 1650 cm\(^{-1}\)). Its contour can be deconvoluted into three sub-bands characterizing collagen structure, providing information on collagen helix and cross-linking structure [5].

- Amide II spectral band is due to a mixed \(C - N\) stretch and \(N - H\) in plane bending [4]. The contour is centered around 1550 cm\(^{-1}\).

- Amide III is much weaker. It corresponds to complex in-plane mode. The band is situated between 1200 and 1300 cm\(^{-1}\).

### 6.2 Plasma treatment

One of the first verifications that have to be made is the effect of vacuum conditions. For this purpose we perform a measurement on a sample before and after being subjected to vacuum. This comparative measurement is necessary for several reasons:

- To evaluate the contribution of water in the spectrum. Under vacuum conditions, bone tissue is dried, so that a large amount of water is removed. Once in open air again, a non-negligible quantity of water will be re-introduced in the porous material, but we believe that this quantity will be lower than originally present.

- To verify that the important organic elements of bone tissue are not removed simply because of vacuum conditions.

- To verify that the mineral structure is able to support vacuum conditions without suffering major damages.

- To differentiate the effect of the vacuum only and the plasma treatment.

Although the plasma treatment is considered non-thermal, heating of the surface of the sample is observed and a sample cooling system was installed [6]. The gases used are helium, argon, krypton, oxygen and a mixture argon/oxygen (50/50%). The input power can vary from 50 to 800 W, and the pressure inside the vessel from 5 to 50 mTorr. The exposure time was typically 20 minutes.

In contrast with transmission infrared spectroscopy, or spectro-microscopy, ellipsometry allows an analysis of the sample between several hundreds of nanometers and few microns under the surface. With this technique it is thus possible to visualize the changes due to the plasma. However, the plasma penetration depth is not expected to exceed 1 \(\mu\)m. The spectra obtained by ellipsometry include not only signatures due to the plasma treatment, but also signal of due to the composition of the bulk which is not modified by the plasma.
6.2.1 Influence of vacuum conditions

Since the $\Delta$ spectrum shows the interesting features most clearly, we will focus on the variations of $\Delta$. It has been shown that mechanical properties of bone tissue can be modified when exposed to drying process [7], but the chemical and organic structures are not expected to be modified. Figure 6.2 shows a comparison between an untreated bone sample and one exposed to vacuum. The spectrum of non treated samples seems to be more noisy. These perturbations are mainly due to the presence of water leading to interferences in this spectral area. Discrepancy between both spectra is observed in the region of the phosphate absorption band which coincides with a water absorption region. It is also possible that a certain amount of superficial collagen is removed with water. However, one can observe that the abovementioned peaks are still present and their sub-band structures are not modified. This proves that vacuum conditioning has only a minor effect on bone tissue. Some sites such as $\nu_2\text{CO}_3^2\cdot$ appear more clearly on the dried sample.

![Figure 6.2: Ellipsometric parameters of an untreated (dashed lines) sample and a sample exposed to vacuum ($10^{-4}$mBar) for 24 hours (solid lines). The different absorption broad bands are visible on $\Delta$ spectrum.](image)

One should note that a quantitative interpretation of the $\Delta$ spectrum is extremely complex. In a general point of view, a change in amplitude of an infrared ellipsometry peak corresponds to a bond density change, and a shift of the peak corresponds to a change of chemical structure of the bond. It is however difficult to put figures on these changes. A quantitative analysis of the spectra is only possible with a model including the contribution of the mineral and organic components. The porosity should also be modelled (by using a Bruggeman effective medium approximation for instance). A possible anisotropy has to be considered too. Furthermore, the microscopic structure of bone is not homogenous because of the presence of sites like osteons that have a completely different elemental composition. The development of a model of bone tissue for spectroscopic ellipsometry is thus far beyond the scope of this thesis. This study focuses on a qualitative evaluation of the bone tissue spectra. Quantitative results will be provided by RBS and ERDA.
6.2 Plasma treatment

6.2.2 Influence of plasma feed gas

Figure 6.3 shows at typical spectrum of a sample treated with an oxygen plasma at a pressure of 50 mTorr and with a power of 400 W. The spectrum, reduced to a 1800-800 cm\(^{-1}\) spectral range shows is compared to the spectrum of an untreated but dried sample. The main structure described above remains visible but some changes are observed. The peaks corresponding to amides I and II are slightly shifted. Amide III does not seem to be significantly affected. As for as the mineral constituent signatures, the peaks are not shifted but the intensity of the signal is weaker, especially for \(\nu_3\text{PO}_4^{3-}\) and \(\nu_1\text{PO}_4^{3-}\). This means that there is actually etching process of the mineral part of bone tissue. Carbonate \(\nu_2\text{CO}_3^{2-}\) at 880-860 cm\(^{-1}\) seems less affected. For the \(\nu_3\text{CO}_3^{2-}\) peak some some modifications are observed for the lower wave numbers, but the interpretation is difficult since, in this spectral region, overlapping with organic components (such as \(-\text{CH}_2\) and \(-\text{CH}_3\)) occurs [8].

As already mentioned, the contour of amides I and II can be deconvoluted in several sub-bands. Amide I consists of 3 components. The highest frequency at 1680 cm\(^{-1}\), is related to collagen cross-linking. The other lower frequency bands (1660 cm\(^{-1}\) with the highest intensity and 1633cm\(^{-1}\)) are sensitive to collagen secondary structure [9]. From Figure 6.3, it appears that the cross-linking is more affected by the plasma treatment.

![Figure 6.3: \(\Delta\) spectra of an untreated (dashed lines) sample and an oxygen plasma treated bone sample. The amides I and II peaks are the most affected by the treatment.](image)

Concerning the amide II, the peak maximum is shifted from 1551 cm\(^{-1}\) to 1530 cm\(^{-1}\). This amide is also related to the secondary structure of collagen and more precisely to the presence of nitrogen. It seems that an important amount of nitrogen is removed from the tissue, destructing the peptide function: \(-\text{CO} - \text{NH}-\).

The other changes are not significant enough to be interpreted as molecular modification of the tissue. The etching with an oxygen plasma is thus selective concerning the organic matter of bone tissue. The cross-linking of collagen is prominently affected as well as chemical bonds involving nitrogen atoms.
Influence of the plasma

We also studied the influence of the gas used for the plasma treatment. Figure 6.4 shows comparative spectra of bone samples exposed to different plasmas.

![Comparative spectra of bone samples exposed to different plasmas.](image)

Figure 6.4: Comparative spectra of the amide I and amide II regions for different plasma treatments.

The mineral components, phosphate and carbonate, are not affected by the etching. However, the amide II peak is shifted towards lower frequencies for all gases. The choice of the ions species does not seem to have an influence on the selectivity of the etching. The average value of \( \Delta \) is changing with the ion species, but it is difficult to identify the reason of this effect. In fact several factors can lead to this shift of \( \Delta \): the removal of water from the pores due to vacuum conditions should have as a result a shift of \( \Delta \) to lower values. This is observed in figure 6.2. The preparation of the sample, can also lead to different values of Delta. The phase shift measured by the ellipsometer is also very sensitive to concave or convex form of the sample surface. It is therefore not justified to compare the absolute values of \( \Delta \) in figure 6.4. However, by comparing the relative heights of the amide I and II peaks, a krypton plasma seems more efficient in the etching of amide I, since the amide I peak maximum is lower than that of Amide II for this gas treatment only.

Power dependence

The influence of the power has been also investigated. Figure 6.5 shows the spectra obtained after an argon plasma treatment at three different powers. The of phosphate absorption is not modified and will therefore not be displayed in this figure.

In these spectra, three phenomena appear clearly:

- After a treatment of a 400 W plasma, the amide III peak is still visible but reduced strongly.
6.2 Plasma treatment

Figure 6.5: Comparative spectra of the amide I, II, and III regions for argon plasma treatments at different powers. For a better readability, the curve have been shifted vertically.

- Amide II is much more affected with higher power treatment. The peak at 1550 cm\(^{-1}\) when untreated, becomes a plateau at 400 and 600 W, but this plateau tends to disappear at high power.

- The peak of amide I is slightly shifted towards lower frequencies when the power is increased (from 1645 to 1630 cm\(^{-1}\)).

The mineral components are however less affected by the plasma treatment even for higher power, as can be seen from the carbonate peak around 1450 cm\(^{-1}\). The shift of the amide I peak, is explained by an attenuation of the 1660 cm\(^{-1}\) sub-band. The role of this sub-band is not clear, but it is assumed to be linked to the secondary structure of collagen [5]. It seems thus that for low power plasma treatment (400 W) the cross linking nature of collagen is first affected. The plasma has an influence on the secondary structure for higher power only. The attenuation of amide II peak shows that chemical bounds involving nitrogen are relatively weak compared to, for instance, \(C=O\) bounds. An interpretation of the removal of amide III is more difficult because this band is related to the complex structure of collagen.

A last remark concerning the spectra can be made on signal to noise ratio. In figure 6.3 one can see that the spectrum of the treated sample appears less noisy than that of the untreated one. Ellipsometry can be sensitive to the roughness, if the characteristic dimension of the roughness is of the order of the wavelength of the beam of the ellipsometer. When the beam hits a rough surface, reflection will be more diffuse and the angular spread of the reflected beam will be larger. As a consequence, less light reaches the detector. Looking at figure 6.3 one can conclude that the plasma treatment has a smoothing effect on the surface.

We performed environmental scanning electron microscopy (ESEM) measurements (see figure 6.6) on the same sample before and after treatment. One can clearly see that, at a scale of several microns, the plasma treated surface is smoothened. This is an evidence that the mineral part of the issue is also etched. A selective etching of the organic components only would lead to an increased porosity of the material.
6.3 Elemental analysis using RBS and ERDA

Several techniques are available for elemental analysis of bone [10], among which electron dispersive X-ray microanalysis (EDX) became popular. One of the limitations of this technique is the need of a perfectly flat sample. This problem is overcome by the microanalysis that allows a reduction of the area under investigation. EDX is used to provide a mapping of the different elements in bone tissue, and to localize the different sites in bone, such as osteons. The detection of light atoms is also difficult with this technique and it is impossible for atoms lighter than oxygen.

In order to obtain a detection of a large range of atomic elements, we combined a study using Rutherford backscattering spectroscopy (RBS), and elastic recoil detection analysis (ERDA). The detection ranges of both techniques in terms of atomic elements overlap and we could easily verify that RBS and ERDA are providing consistent results. Using both techniques we were able to detect a large range of atoms including H, C, N, O, Na, Mg, P, Ca. Calcium and magnesium are visible by ERDA but the quantities are too small to be investigated further: a modification of the concentration of these atoms due to the plasma treatment would be highly inaccurate. Strontium, existing in traces in bone mineral, could not be detected by RBS.

6.3.1 Untreated bone

Comparative measurements have been performed on different untreated sample and on the same sample. It is common to express the results of elemental analysis in terms of atomic concentration ratio. These quantities characterizing the stoichiometry are important parameters that can diagnose bone diseases or ageing of bone tissue, but are also used for the synthesis of bone-like materials [11]. For example, the theoretical value of Ca/P ratio is 1.667 since calcium and phosphorus are expected to be found only in hydroxyapatite [12]. Measured values usually differ because of the poor stoichiometry of hydroxyapatite. When these ratios involve oxygen or hydrogen atoms, there is no theoretical values since oxygen and hydrogen belong to both mineral and organic constituents.
Figure 6.7: Reproducibility test: calcium-phosphorus and calcium-oxygen ration measured by RBS and ERDA (for Ca/O) on untreated samples. S1..S5 denote different samples, which should be identical, S2 and S2' are measurements performed on the same sample.

Figure 6.7 shows the measurement of the Ca/O and Ca/P ratios for untreated samples. These values were obtained after an integration of the depth profile from the surface to the detection limit depth of ERDA, that is smaller than that of RBS. Measurements show a good reproducibility. The ratios involving the different atoms are presented in table 6.1; they were obtained with an accuracy of 10%. Only comparative data of Ca/P ratio area available in literature [13].

| Atomic ratio |  
|-------------|---|---|---|---|---|
| Ca/P        | 1.63         |
| Ca/O        | 0.33         |
| Ca/C        | 1.62         |
| Ca/N        | 4.94         |
| Ca/H        | 2.54         |

Table 6.1: Measured atomic ratios for untreated bone.

6.3.2 Plasma penetration depth

We used the calculated atomic ratios for untreated bone to determine the plasma penetration depth with RBS. This technique allows for a larger penetration depth than ERDA. The plasma penetration depth is calculated as follows: we assume that the treated sample exhibits a layer of material affected by the plasma and a bulk part that kept the original stoichiometry of untreated bone. The atomic ratio is then measured near the surface of the treated sample. A model is applied based on a concentration gradient linear with the depth of the material, and varying from the atomic ratios at the surface to the ratios corresponding to the bulk. A fit to the experimental
Figure 6.8: Estimated plasma penetration depth for different samples obtained from simulations of the RBS spectra. See Table 6.2 for sample identification.

The measurements have shown that the plasma penetration depth varies from 470 to 700 nm. This range can be due to the plasma treatment conditions but also to the original properties of bone sample like the porosity. The roughness, of the order of several microns can be also a factor of strong variation of the plasma penetration depth. Furthermore, we have seen that the roughness is modified during the plasma treatment which complicates the interpretation of these variations. We can nevertheless conclude that the modified layer thickness is of the order of 500 nm.

Due to grazing incidence and sample roughness, the ERDA measurements only provide a mean concentration from a 300 nm thick layer near surface. In order to compare RBS and ERDA measurements, it is necessary to integrate the concentration of atoms determined by RBS over the depth of detection of ERDA. This is applied for the Ca/O ratio since it can be determined by both techniques [6]. The compared RBS and ERDA measurements agree within a range of 8%. Table 6.2 gives some of the conditions of plasma treatment that have been used for this study:

6.3.3 Calcium-phosphorus ratio

The atomic ratio between calcium and phosphorus is studied separately because it concerns only the mineral part of the bone, since neither Ca nor P are present in the organic constituents of the tissue. For this we measured the Ca/P ratio at the surface and we compared it to the bulk ratio, i.e. the ratio measured on untreated sample. From figure 6.9 on can see that the ratio is not significantly modified by plasma treatment, whatever the treatment conditions. Some samples (Ar5, Ar7) show larger values but cannot be really explained (for example, samples Ar4 and Ar5 are exposed to identical conditions). Sample O1 shows a lower Ca/P value. This sample has been exposed to the plasma over a longer time (40 min), and this could explain
the discrepancy. Unfortunately, all the other sample have been expose to plasma for the same time of 20 min. It is thus not possible to study further the influence of exposure time on the stoichiometry. From these measurements we can even though conclude that for an exposure

![Figure 6.9](image)

**Figure 6.9:** Ca/P ratio for untreated and plasma treated bone tissue, determined by RBS.

time of 20 min, the stoichiometry of the mineral constituent of the bone is not modified. Gas phase diagnostics have shown the presence of mineral constituent such as Ca and P in the plasma during the process [14]. The mineral matrix of the bone is thus etched. Figure 6.9 shows that
this etching is not selective: calcium and phosphorus are etched at the same rate when exposed
to the plasma. It is remarkable that change of gas, power or pressure do not influence these
relative etch rates.

6.4 Selectivity of plasma treatment

6.4.1 Influence of the gas

The influence of the feed gas of the plasma on the stoichiometry has been investigated. Four
gases were used: argon, krypton, helium and oxygen. Noble gases were chosen because of
their chemical non-reactivity. This simplifies the interpretation of the plasma bone interaction.
Only ion bombardment is considered. Concerning oxygen, it is believed that chemical etch-
ing is prevalent. We also used a mixture of 50\% argon- 50\% oxygen. All the treatments were
performed with a power of 400W, at 50 mTorr for 20 min. Figure 6.10(a) shows that calcium
and oxygen keep the same relative concentration with variations remaining within measurement
errors. In fact, oxygen is present mainly in the mineral constituent of bone. The mineral ma-
trix is predominant and oxygen is found in hydroxyapatite and carbonate anions. In contrast,
proteins content is generally, relatively poor in oxygen. We saw from the study of Ca/P ratio
that hydroxyapatite is evenly etched, independently on the plasma treatment conditions. As a
consequence, a change in oxygen stoichiometry of the organic component would not be clearly
visible from the Ca/O atomic ratio. Etching of nitrogen is, in contrast, more sensitive to the
feed gas of the plasma. It appears clearly that argon and oxygen (and Ar-O\textsubscript{2} mixture) provide
a more efficient nitrogen etching. The atomic ration Ca/N can in this case increase by a factor
2 (fig. 6.10(b)). Thus physical and chemical etching processes are efficient on nitrogen. With
oxygen plasma, NO or NO\textsubscript{2} can be formed and their presence is detected in the plasma by
mass spectrometry \cite{14}.

Argon is less efficient for the etching of carbon, whereas oxygen strongly modifies the car-on composition of the tissue. Oxygen is expected to remove carbon by forming CO or CO\textsubscript{2}.
This explain also the similar performance of Ar-O\textsubscript{2} mixture, close to that of oxygen plasma.
The removal of carbon should be clearly associated to a removal of hydrogen, since C – H
bounds are the most common in collagen. However, when an oxygen plasma is used, only
a slight change in the stoichiometry of hydrogen is observed. It is believed that via chemi-
cal reaction water or OH radicals are formed. Since hydroxyapatite has the property of being
hygroscopic, these products are \textit{trapped} in the mineral matrix (in poorly stoichiometric hydrox-
yapatite, anionic sites can be replaced by OH\textsuperscript{−} groups). Hydrogen atoms remain thus in the
tissue and hydrogen stoichiometry is unchanged. Also the use of argon does not significantly
affect the hydrogen concentration in the tissue. Physical etching is believed to be efficient only
if chemical etching occurs previously to produce water or OH radicals from C\textsubscript{x}H\textsubscript{y} groups. A
slightly higher value of Ca/H atomic ratio is observed when argon-oxygen mixture is used, the
efficiency of the mixture for the removal of hydrogen is still low.

To summarize, argon shows a strong selectivity in favor of nitrogen etching only, while
oxygen plasma, because of the chemical reactivity, are efficient on nitrogen and carbon, and
in a non direct way, on hydrogen. Krypton, the heaviest ion, has a poor selectivity, exhibiting
the lowest effects on the different atomic ratios. Mass spectrometry measurements performed
during plasma treatment have shown that krypton is the plasma feed gas removing the most of
Figure 6.10: ERDA measurements on bone tissue: influence of the feed gas of the plasma.
Figure 6.11: ERDA measurements on bone tissue: influence of the power of the plasma treatment.
6.4 Selectivity of plasma treatment

Due to their mass, krypton ions generate more damages at the surface and can break high as well as low energy bounds. This explain the low selectivity of the etching. Helium which is much lighter, has a better selectivity.

When comparing these results with ellipsometry spectra (fig. 6.4), it is clear that the changes of Ca/N ratio reflects the shift of amide II, and that this shift is visible for every gas.

6.4.2 Influence of pressure and power

Results obtained when varying the pressure of the plasma discharge are given in table 6.3. No significant influence on the stoichiometry of the tissue is observed. The effect of the plasma pressure on etching conditions is studied in more detail by C. Y. M. Maurice [14].

<table>
<thead>
<tr>
<th>Pressure (mTorr)</th>
<th>Ca/O</th>
<th>Ca/N</th>
<th>Ca/C</th>
<th>Ca/H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon 50</td>
<td>0.36±0.04</td>
<td>8.16±0.82</td>
<td>2.60±0.26</td>
<td>3.23±0.32</td>
</tr>
<tr>
<td>400 W 35</td>
<td>0.39±0.04</td>
<td>10.34±1</td>
<td>3.15±0.30</td>
<td>3.03±0.30</td>
</tr>
<tr>
<td>20 min 20</td>
<td>0.42±0.04</td>
<td>8.54±0.85</td>
<td>2.77±0.28</td>
<td>3.91±0.39</td>
</tr>
<tr>
<td>Argon 50</td>
<td>0.38±0.04</td>
<td>9.58±0.87</td>
<td>2.94±0.25</td>
<td>3.84±0.30</td>
</tr>
</tbody>
</table>

Table 6.3: Atomic ratios obtained with ERDA, with uncertainty, for different pressure conditions.

The influence of the power of the gas discharge has been studied with argon and oxygen. Both discharges were applied at 50 mTorr pressure for 20 minutes. The results of the measurements are shown in figure 6.11. Different behaviors are observed with argon and oxygen.

The stoichiometry of oxygen relative to calcium is only slightly affected by the power of the plasma. The etching of oxygen appears to be more efficient for 800 W power argon discharge, but variation remains small (cf. fig. 6.11(a)). As we already mentioned, changes in the oxygen stoichiometry of organic components are hardly visible in the Ca/O ratio. When oxygen is used as plasma, the power of the discharge seems to have no effect at all on oxygen etching selectivity.

In contrast, increasing power of oxygen discharges strongly modifies the relative stoichiometry between calcium and nitrogen. As we already mentioned, oxygen etchants react easily with nitrogen, producing gas compounds like NO or NO₂. Higher discharge powers are believed to increase the concentration of oxygen ions, and particularly atomic oxygen ions that favor nitrogen removal through chemical reactions. It is remarkable that the change of power does not have any effect on nitrogen when argon is used as a feed gas. It seems nevertheless that the presence of argon plasma already modify the stoichiometry of nitrogen, since the Ca/N atomic ration increase of a factor 2 when a 400W argon plasma is applied. It is believed that physical etching is efficient on nitrogen until a certain power beyond which the etching process saturates. This limit value is obviously lower than 400W.

Concerning the effect on hydrogen, and by applying the etching scheme developed earlier and involving chemical reaction and physical etching, it is suggested that chemical reactions occur in oxygen plasma but products remain adsorbed in hygroscopic [15] hydroxyapatite. The influence of power in argon plasma shows some unexpected results since physical processes in the removal of hydrogen are supposed to be necessary associated to chemical processes driven...
by oxygen plasma. In fact we think that for high power, the argon ions bombardment leads to a heating of the surface of the bone sample and water evaporates from the tissue. The plasma penetration depths that were calculated for 600 W and 800 W, corresponding respectively to samples Ar1 and Ar2, are deeper than for other conditions (see figure 6.8). We think that the heat is transferred through the sample reaching the bulk where water is evaporated from. As a result, the calculated stoichiometry of hydrogen decreases with the power of the plasma.

Considering the chemical etching potential of oxygen, one would expect a clear trend in the selectivity of carbon etching. Instead, the Ca/C ratio drops when the plasma power reaches 800 W. It is difficult to interpret this behavior. Further investigations are necessary, by studying the plasma conditions during the etching process with oxygen plasma.

To summarize these results, by changing the power of the discharge, and by carefully removing the gas mixture, one can tune the selectivity of bone tissue etching. Argon discharges seem to be adapted to the removal of hydrogen whereas oxygen plasmas are more efficient on nitrogen.

These results are compared with ellipsometry spectra. The power dependency has been studied with ellipsometry for argon plasma only. The comparison of spectra for different plasma powers has shown that the signature of amide II is the most affected. We have seen that this amide function is closely related to \( CN \) stretch and/or \( NH \) in plane bending. The variations of the spectral bands of amide II suggest that \( CN \) and \( NH \) bonds are broken during etching. The elemental analysis shows that the stoichiometry of carbon and nitrogen is not significantly modified when the power is increased. In contrast more hydrogen is released from the tissue for high power. We can deduce that the modification of the amide II band is mainly due to the break of \( NH \) bonds leading to the removal of hydrogen.

Concerning the amide I, we observe a small shift of the peak towards lower frequencies, which is more visible for 800 W treatment spectrum. Amide I is associated to the cross linking of collagen and to \( C = O \). For lower power, the cross linking is first affected, but the \( C = O \) bond remains. It is only for power larger than 600 W that this double bond is altered by the plasma, which explains the shift of the amide I band correlated by the (small) change in the stoichiometry of oxygen, highlighted by ERDA measurements.

### 6.5 Conclusion

This study has shown that ellipsometry can provide essential information on the effect of the etching of bone tissue. More specifically, we have shown that amide II and some sub-bands of amide I are the main molecular functions that are affected with the plasma. By comparing this observation with elemental analysis, we could identify that it is the \( N - H \) bond rather than \( C - N \) that is broken when the treatment is performed with an argon plasma. ERDA and RBS offer complementary quantitative analysis. More plasma treatment conditions have been investigated with both elemental analysis methods. It is shown that, depending on the feed gas, the depletion at the surface of the bone over a 500 nm thick layer can be due to physical (ion bombardment with argon plasma) or chemical processes (oxygen plasma). By modifying the feed gas mixture, it seems to be possible to significantly modify the etching selectivity. Increasing the plasma discharge power, it is possible to modify the selectivity of the etching depending on the feed gas that is used. High power argon plasma will strongly remove hydrogen that are believed to be associated to OH radicals or water molecules. The ion bombardment will
heat the surface and adsorbed water will evaporate. In contrast, oxygen plasma power will have an effect on nitrogen etching, inducing chemical reaction.

Concerning the Amide I, ellipsometry shows a modification of the $C=O$ bond only for high power argon discharges (800 W). Unfortunately, the removal of oxygen is not clearly visible with ion beam analysis because of the predominant amount of oxygen in the mineral constituents. For this type of analysis ellipsometry shows its superiority.

The variation of the plasma treatment conditions only concern organic material; it has been demonstrated that the mineral constituent are equally affected by the plasma and no change in the stoichiometry is observed.

These first results should lead to further investigation on plasma treatment of biological tissue, and applications with more bio-compatible atmospheric pressure plasmas.

Acknowledgment

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References


Chapter 7

Concluding remarks
7.1 Achievements

The first objective of this thesis was the design of a complete set-up of a spectroscopic ellipsometer functioning in the mid-infrared range (4000-800 cm\(^{-1}\)). The ellipsometer is based on the principle of a rotating compensator. For this purpose, a spectroscopic retarder and linear polarizers have been built.

- The compensator allows a phase shift varying from 70 to 85° over the complete spectral range. The variation, which proves to be larger than expected, is mainly due to a non-homogenous wavelength distribution inside the infrared beam (Chapter 2). However, the calibration procedure enables an accurate determination of the induced phase shift for each wavelength and thus a correction of the variations during the measurements.

- Polarizers, built on the principle of transmission of light at the Brewster angle, show high performance over a large spectral range. The measured extinction coefficient is up to two orders of magnitude higher than obtained in classical broad band polarizers, e.g. a wire grid polarizer (Chapter 2).

- A calibration procedure has been established and an estimation of the errors due to potential misalignment of the different optical elements has been made. It appears that the polarizer is the most critical element of the ellipsometer concerning the alignment (Chapter 3).

The ellipsometer has been used to investigate various materials. Contrary to other ellipsometry techniques, rotating compensator ellipsometry allows the analysis of metals, semiconductors and insulating transparent films (Chapter 3 & 4). This allowed the study of silicon sub-oxide films obtained by sputtering:

- The behavior of the dielectric function and the complex refractive index as a function of the stoichiometry of the SiO\(_x\) film has been investigated over a large spectral range. This study shows the transition of the optical properties of the film from a semiconductor to an insulator form (Chapter 4).

- A model of the distribution of the oxygen atoms in the silicon tetrahedra has been successfully applied to show the stoichiometry dependent drift of the characteristic absorption peak of SiO\(_x\) (Chapter 4).

The ellipsometer has also been used to investigate the effect of non-thermal plasma over the surface of bone tissue.

- It has been shown that ellipsometry is particularly suited for the analysis of bone surface. In particular, chemical changes occurring in the first 500 nm beneath the surface of the tissue can be observed. The difficulties due to the high transparency of bone tissue can be overcome.

- An interpretation of the plasma etching processes of bone has been made using combined results of ellipsometry and ion beam analysis measurements (RBS and ERDA). It is shown that an oxygen plasma reacts chemically with organic material of the tissue and plasmas with noble gases as feed gas privilege physical etching by ion bombardment. It is possible, by controlling parameters such as discharge power or gas mixture, to modify the etching selectivity of the tissue (Chapter 6).
7.2 Further improvements

Some possible improvements on the ellipsometer should also be mentioned. The main problem that is actually general to any infrared technique, is the intensity of the source and its stability. Until now, a globar was used. This particular source suffers from having large dimension, typically 1 cm². This generates a strong divergence of the beam. Furthermore the intensity of the globar is weak. A possible alternative would be the cascaded arc. Its stability has been demonstrated better than that of the globar and its intensity is a factor 2 to 5 higher. However, the emission spectrum is complicated by the presence of narrow spectral lines that can be a source of instability. More intense infrared sources are synchrotron sources but their sizes obviously limit their use. Technically, these sources present the advantage of being intense enough to allow ellipsometry measurements with a spatial resolution of few µm [1]. The consequences of a higher intensity of the infrared source would be:

- In-situ measurements with the ellipsometer. Presently, the absorption losses of the window of a reactor are prohibitive.
- Significant decreasing of the measurement time (less than 1 minute against presently more than 10 minutes for transparent or strongly absorbing material).
- Better spatial resolution by a reduction of the beam size.
- A reduced angle spread. This phenomenon is a source of errors in the interpretation of the spectra, if not correctly modelled (Chapter 4).

References

Appendix A

RBS and ERDA formulae

A.1 Rutherford backscattering spectrometry (RBS)

Rutherford backscattering spectrometry [1, 2] is a widely used technique which allows not only a determination of the stoichiometry, but also some quantitative measurements and depth profiling of the sample. The principle is based on the backscattering of energetic light ions (typically He ions at 1-2 MeV). The geometry of the setup is such that the incident ions come in perpendicular to the target surface (\(\theta_{in} = 0^\circ\)) and the scattered ions are detected by a semiconductor PIPS detector at a scattering angle of 170° (\(\theta_{s} = 170^\circ\)). Alternative configurations are however possible. The theoretical part will be established considering non specific incident and scattered angles. The experimental geometry is described in figure A.1.

Let us consider a He ion from the incident beam, with an initial energy \(E_o\) and an angle \(\theta_{in}\) with the sample normal and penetrating the sample through a depth \(x\), where it collides with a heavier atom. Because of mass difference, the incident ion can be scattered back and leave the sample material with an angle \(\theta_{out}\) with the sample normal, with energy \(E\), and reach a detector. The energy lost by the He ion during the whole process originates from 3 factors:
• The energy loss due to the stopping of the ion in the inward direction in the material ($\Delta E_{\text{in}}$)

• The energy lost during the collision with material’s atom.

• The energy loss due to the stopping of the ion in the outward direction in the material ($\Delta E_{\text{out}}$)

The stopping of the ion in the material is defined by the stopping power:

$$S(E) = \frac{dE}{dx} \quad (A.1)$$

It is thus defined by the energy loss per length unit. In some cases, the definition of stopping cross-section is used:

$$\epsilon = \frac{1}{N} \frac{dE}{dx} \quad (A.2)$$

The stopping is considered as a quasi-continuous process generated mainly by Coulomb (occurring at long range) interactions with electrons. Several attempts have been done on a theoretical treatment of the stopping power. For high velocity limit, corresponding to incident ions fully stripped of their electrons, Bethe [3] derived a formula using quantum mechanics principles:

$$\frac{dE}{dx} = \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 4\pi Z_1^2 N Z_2 \left[ \ln \left(\frac{2m_e v_{\text{ion}}^2}{I}\right) - \ln \left(1 - \frac{v_{\text{ion}}^2}{c^2}\right) - \frac{v_{\text{ion}}^2}{c^2} \right] \quad (A.3)$$

where $Z_1$ and $Z_2$ are the atomic numbers of the incident ion and target atom respectively, $v_{\text{ion}}$ is the velocity of the incident ion, $N$ is the atomic density of the target, $m_e$ the mass of the electron, and $c$ the speed of light. The term $I$ can be derived from quantum mechanics representing the mean ionization energy of the target atoms. From this formula, we can observe a dependence of the stopping power proportional to the square of the atomic number of the incident ion, and proportional to the charge of the the atomic number of the target atoms. This must be moderated by the presence of the quantum term $I$, as demonstrated in [2], illustrating the differences in electron configuration between target atoms of consecutive atomic numbers. In our particular case, the projectile ions are $^4\text{He}^+$, thus non fully stripped. The Bethe formula can be however applied, introducing the concept of an effective charge [4]. These corrections apply to effective charge but are refinements.

So far only mono-elemental targets in terms of atoms have been considered. In case of the presence of compound materials, the use’s of Bragg’s rules is required. The rules state that the contribution of all elements can be added linearly.

Based on the theoretical treatments of the experimental data, Ziegler et al. [5] derived a semi-empirical model which describe the stopping powers for He in all elements. These data are available for computer simulations, tabulated in literature and commonly used for the interpretation of ion beam analysis experiments.

The energy loss due to stopping on the inward path is given by:

$$\Delta E_{\text{in}} = \frac{x}{\cos \theta_{\text{in}}} \left(\frac{dE}{dx}\right)_{\text{in}} \quad (A.4)$$
and for the outward energy loss:

$$\Delta E_{\text{out}} = \frac{x}{\cos \theta_{\text{out}}} \left( \frac{dE}{dx} \right)_{\text{out}}$$  \hspace{1cm} (A.5)$$

where $x$, $\theta_1$, and $\theta_2$ are defined in figure A.1. The collision of the incident ion with the target atom can be described with non relativistic mechanics. Only elastic collisions are considered. By using conservation of energy and momentum, it can be demonstrated that the energy transfer process during the collisions is given by:

$$E_a = KE_b$$  \hspace{1cm} (A.6)$$

where $E_b$ and $E_a$ are the energies of the projectile before and after the collision, respectively, $K$ is the kinematic factor, and its expression is:

$$K = \frac{E_a}{E_b} = \left( \frac{\sqrt{(M_2^2 - M_1^2 \sin^2 \theta_s) + M_1 \cos \theta_s}}{M_1 + M_2} \right)^2$$  \hspace{1cm} (A.7)$$

$\theta_s$ is the scattering angle defined in figure A.1, $M_1$ and $M_2$ are the masses of the projectile and the target particle respectively. $M_1$, $E_b$, and $\theta_s$ are known by the experimental conditions and if the energy $E_a$ can be measured, the target element (via $M_2$) can be identified.

Thus, the energy of the ion, $E$ detected by the detector after the interaction with the material and by taking into account of the stopping effect is:

$$E = E_a - \Delta E_{\text{out}} = K(E_o - \Delta E_{\text{in}}) - \Delta E_{\text{out}}$$ \hspace{1cm} (A.8)$$

and by substituting the equations A.4 and A.5

$$E = KE_o - \frac{K}{\cos \theta_{\text{in}}} \left( \frac{dE}{dx} \right)_{\text{in}} + \frac{1}{\cos \theta_{\text{out}}} \left( \frac{dE}{dx} \right)_{\text{out}} x = KE_o - [S]x$$ \hspace{1cm} (A.9)$$

where $[S]$ is the energy loss factor.

If we consider impurities at the surface of the sample, ($x=0$), the energy of the scattered ion can be directly related to the target atom mass $M_2$ with the expression of the kinematic factor $K$ in relation A.7. Applying the surface approximation, i.e.

$$\left( \frac{dE}{dx} \right)_{\text{in}} \approx \left( \frac{dE}{dx} \right)_{E_0}$$ \hspace{1cm} (A.10)$$

and

$$\left( \frac{dE}{dx} \right)_{\text{out}} \approx \left( \frac{dE}{dx} \right)_{KE_0},$$ \hspace{1cm} (A.11)$$

the term $[S]x$ of equation A.9, shows a relation between the energy loss and the path of the ion in the material. In principle, this relation is not linear, but in practice, it is, because of the surface approximation. Thus, a depth profile of the material is possible as the energy scale is converted to a depth scale. The energy-depth relation is obtained by considering the quantity $\Delta E = KE_o - E$. $\Delta E$ is the difference in energy at the detector of a particle scattered at the surface and a particle scattered at a depth $x$.

$$\Delta E = [S]x$$  \hspace{1cm} (A.12)$$
From equation A.9 one can observe that the energy-depth relation depends on the target atom, and a new depth scale has to be redefined for each element. Figure A.2 shows a typical RBS measurement on a thick bone sample.

The energy \( E_{Ca} \) in figure A.2 corresponds to ions scattered of a Ca atom at the surface of the sample. These scattered ions did not experience any stopping in the sample and only lost a characteristic amount of energy due to the collision. The plateau on the low-energy side of the Ca step is due to collisions with Ca atoms at a certain depth in the sample. These scattered ions not only lost energy due to the collision, but they also lost energy due to stopping. Because of the thickness of the sample (\( \approx 2 \) mm), the Ca plateau runs all the way from the surface Ca step down to low energies. Superimposed on this Ca plateau similar step-plateau features for P and O are observed. The near surface concentrations of the different elements that can be detected in the sample can be determined from the step heights \( H_i \), as defined in figure A.2.

The measured signal height of the step for element \( i \), \( H_i \), can be expressed as [2]:

\[
H_i = Q \left( \frac{d\sigma}{d\Omega} \right)_i \Omega N_i \frac{\partial E}{[S]_i} \frac{1}{\cos \theta_{in}} \tag{A.13}
\]

where \( Q \) is the total number of incident ions, \( \Omega \) the detector solid angle, \( \partial E \) is the energy width per channel, \( \left( \frac{d\sigma}{d\Omega} \right)_i \) the differential scattering cross section for element \( i \), \([S]_i \) the energy loss factor of the target and \( N_i \) the atomic concentration of element \( i \) at the sample surface. \( \Omega \), \( \theta_{in} \) and \( \partial E \) are properties of the setup, which can be determined before the experiments. \([S]_i \), can be calculated from equation A.9. In the energy range used in our experiments, the scattering can be described by pure Coulomb scattering, also known as Rutherford scattering. The expression for the differential scattering cross section, \( \frac{d\sigma}{d\Omega} \), is given by [2]:

\[
\frac{d\sigma}{d\Omega} = \left( \frac{Z_1 Z_2 e^4}{4E_0} \right)^2 4 \left( \frac{\sqrt{M_2^2 - M_1^2 \sin^2 \theta_s} + M_2 \cos \theta_s}{\sqrt{M_2^2 - M_1^2 \sin^2 \theta_s}} \right)^2 \quad \tag{A.14}
\]
A.2 Elastic recoil detection analysis (ERDA)

Note the dependence of the cross differential cross section on \(1/E^2\) which is the continuous increase of the signal for decreasing energies in figure A.2. Rutherford scattering regime must actually be corrected for low and high energies.

By measuring \(Q\) and \(H_i\) and with equation A.13, the absolute atomic concentration at the surface can be calculated. In practice the quantities \(Q\) is difficult to measure on insulating sample, which means that it is difficult to obtain accurate absolute atomic concentrations. In that case one can choose to determine the stoichiometric ratios for different elements in the sample. The stoichiometric ratio between element \(n\) and \(m\) in the sample is given by

\[
\frac{N_n}{N_m} = \frac{\left(\frac{d\sigma}{d\Omega}\right)_m [S_n]}{\left(\frac{d\sigma}{d\Omega}\right)_n [S_m]} \frac{H_n}{H_m}
\]

(A.15)

in which the quantities \(Q\) and \(\Omega\) are divided out.

From equation A.15 it is clear that the composition near the surface can be calculated by measuring the step heights \(H_i\). The absolute concentrations at different depths can be calculated in a similar way by measuring the signal \(H_i\) for different energies. With equation A.13 the atomic concentration for this energy can be calculated. The energy to depth conversion is then done with equation A.9. This procedure only unambiguous when no peak overlap from the signals of the different elements occurs. If this is not the case computer simulation is required. The energy spectrum of backscattered ions, using experimental conditions and a specified target composition, is calculated and compared to the measured spectrum. The procedure is to iteratively change the target composition and recalculate the simulated spectrum until it is best matched with the measured spectrum. Several simulation programs are available, we used the RUMP [6, 7] program for our analysis. This software allows several options for depth profiling, considering stacks of elemental films, compound layers, or even layers with concentration gradients. The RUMP program correctly evaluates the energy dependence of both the scattering cross-section and the stopping power.

A.2 Elastic recoil detection analysis (ERDA)

Elastic Recoil Detection Analysis (ERDA) is a very useful ion beam analysis technique for depth profiling of light elements [8]. In ERDA a high-energy (\(\approx 1\) MeV/amu) heavy-ion beam (in our case Cl\(^{7+}\)) is used to probe the target. In contrast to RBS, not the scattered incident ions, but the recoiled target particles are detected.

From the law of conservation of momentum it is clear that recoils can only scatter over scattering angles from 0 to 90°. This implies that in order to detect part of the recoils, the incident beam should come in at a grazing angle with respect to the target. In this way, a part of the recoiled atoms will be scattered out of the target and can be detected. The ERDA measurement principle is schematically drawn in figure A.3.

The incident ion comes in with an energy \(E_0\), under an angle \(\theta_{in}\). On its inward path, the ion loses energy, \(\Delta E_{in}\), due to stopping. The incident ion is scattered over an angle \(\theta_s\), while the recoil is scattered at an angle \(\phi_r\) out of the sample. On its outward path, the recoil loses energy
\[ \Delta E_{\text{out}} \] due to stopping. Finally the recoil leaves the sample at angle \( \theta_{\text{out}} \), with an energy \( E \) after which it is detected by a detector.

From the laws of conservation of momentum in a two-body collision, one finds that the recoil will have an energy \( E_2 = K_2 E_c \) after the collision with \( K_2 \), the kinematic factor, given by:

\[
K_2 = \frac{4 M_1 M_2 \cos^2 \phi_r}{(M_1 + M_2)^2} \tag{A.16}
\]

in which \( M_1 \) and \( M_2 \) are the masses of the incident ion and recoil atom respectively.

The energy loss due to stopping on both the inward and outward path is described by

\[
\Delta E = \Delta E_{\text{in}} + \Delta E_{\text{out}} = \left[ \frac{K_2}{\cos \theta_{\text{in}}} \left( \frac{dE}{dx} \right)_{\text{in}} + \frac{1}{\cos \theta_{\text{out}}} \left( \frac{dE}{dx} \right)_{\text{recoil,out}} \right] x = [S] x \tag{A.17}
\]

where \( K_2 \) is the kinematic factor for the recoil, defined in equation A.16. The angles \( \theta_{\text{in}} \) and \( \theta_{\text{out}} \) are defined in figure A.3. Note that \( \left( \frac{dE}{dx} \right)_{\text{in}} \) and \( \left( \frac{dE}{dx} \right)_{\text{recoil,out}} \) are the stopping powers of the target material for the incident ion and recoil respectively. The energy loss due to the collision described by the kinematic factor, \( K_2 \) in equation A.16 is used to identify the different elements at the sample surface from the measured ERDA spectrum, similar to the element identification in RBS. The energy loss due to stopping, described in equation A.17 is used in the energy to depth conversion in the ERDA spectrum, similar to the energy to depth conversion in RBS.

One of the difficulty with ERDA is the discrimination of the scattered recoils in terms of mass. A solely energy sensitive detector is not able to discriminate between scattered projectiles and recoils. The ERDA beam line at the Rossendorf Institute is equipped with a semiconductor
A.2 Elastic recoil detection analysis (ERDA)

detector with Aluminium range foil for hydrogen detection and a Bragg Ionization Chamber for detection of other elements [9]. The H detection is based on the principle that heavy atoms experience more stopping in a material than light ions. From equation A.3 it is clear that the stopping \( \frac{dE}{dx} \) is proportional to \( Z^2 \), the square of the atomic number of the ion. The H detector consists of a simple semiconductor detector with an Al foil in front of the detector entrance window. The thickness of the Al foil is chosen in such a way that only the light H ions will pass the foil and all the ions heavier than H will be stopped in the foil. The H ions that pass the foil are detected energy resolved by a semiconductor detector. Because the thickness of the range foil is known, the stopping of the H atoms in the foil can be calculated and the original H energy spectrum before the foil can be reconstructed. The measured energy versus intensity profile for H ions can be converted to a depth profile of the absolute atomic concentration with the help of computer simulation.

In a Bragg Ionization Chamber one uses also the characteristic stopping power of the different atoms in a material, in this case a gas chamber. The energy deposition as function of depth in the chamber for two ions with different atomic numbers, calculated using equation A.3, is shown in figure A.4.

![Energy deposition as a function of depth for different ions, the characteristic Bragg ionization curve.](image)

Equation A.3 is valid in the high velocity limit. It breaks down, only at the end of the path when the incident ion has slowed down sufficiently to get neutralized. The stopping power is proportional to \( Z^2 \) and \( \frac{1}{v_{\text{ion}}} \). This means that ions with a higher atomic number will have a higher stopping at the same entrance energy. The higher stopping leads to a higher velocity loss and so consequently to an even higher stopping. This explains the different depths of the energy deposition peaks for different elements. The area under the curves in figure A.4 is the total energy loss in the target, which is equal to the initial energy of the ions. If the initial energy is the same for both ions, it is clear that the peak height of the heavy ion will be higher than the peak height of the light ion. The Bragg Ionization Chamber (BIC) is based on this principle. It measures both the total energy lost in the chamber and the energy loss peak height. In this way it is possible to discriminate between ions with the same energy but different atomic number. A schematic of the Bragg Ionization Chamber is given in figure A.5.

The BIC consists of a cylindrical vessel filled with 99.95 % isobutane gas at a pressure between 50 and 200 mbar. The recoils and scattered incident ions enter the BIC through a
Figure A.5: Bragg ionization chamber in the ERDA set-up.

entrance window, which consists of a 670 nm grid-supported mylar foil. When the fast moving ion passes through the gas of the detector, atoms will be ionized and electron-ion pairs are produced. By applying an electric field the produced charge can be collected at the electrodes. The entrance window grid is kept at a potential of -3000 V. On the other end of the chamber there is a anode plate at a potential of 600 V. In order to be able to separate the electron signal from the ion signal a fine-meshed Frisch grid (FG) at ground potential is placed a few mm in front of the anode. The electron drift velocities are of the order of cm/sec and much smaller than the velocity of the ion creating the electron-ion pairs. This implies that the electrons created closest to the anode, will reach the anode first. Therefore the anode current pulse corresponds to the energy deposition curve of figure A.4. A typical anode current versus time measurement is shown in figure A.5. From this current measurement, signals proportional to both the energy loss peak height and the total energy loss can be derived. This is done by means of the electronic arrangement shown in figure A.5. The anode current pulse is divided after the preamplifier (PA). One part goes to a main amplifier with a long shaping time (3 µs) providing the total energy signal. The other part goes to a main amplifier with a short shaping time (100 ns). This signal will only contain information about the peak height (Bragg-peak). This Bragg-peak is proportional to the atomic number Z.

In an ERDA measurement both the Bragg peak intensity and the total energy are measured and plotted in a graph. An example of an ERDA measurement is shown in figure A.6. The different branches in figure A.6 can be identified, from the Bragg-peak heights, as different elements. Especially the light elements C, N and O are well resolved. For heavier elements the mass separation becomes more problematic. The largest signal is the Cl signal from scattered projectile ion beam. However, the signal from Ca recoils can just be distinguished from the Cl signal. The P signal is overlapping with the Cl signal and can not be resolved. The distribution of the number of counts over a branch corresponds to the depth profile of the concentration of this element. To obtain the depth profiles for the different elements, each branch is selected from the measurements and the measured intensities for this branch is projected on the total energy axis. This gives a total energy versus intensity graph for each selected element. Depth profiles of the absolute atomic concentration for each element are obtained using a special computer code described in [10] using the stopping power data from Ziegler et al. [5].

The ERDA setup at the Rossendorf institute uses 35 MeV Cl²⁺ ions from a 5 MV tandem accelerator. The geometry is such that the incident ions come in at an angle θ_{in} of 15° with
Figure A.6: Typical ERDA measurement on a thick bone sample. Ion beam 35 MeV Cl\textsuperscript{7+}, $\theta_{in}=15^\circ$, $\theta_{out}=15^\circ$, $\phi_s = 30^\circ$, $Q = 3.4 \mu$C.

respect to the sample surface. The BIC detector is placed at a scattering angle of $30^\circ$ and the H detector at a scattering angle of $38^\circ$.

**References**


Ellipsometry is a popular technique for surface and near surface analysis. Its main advantage is its non-intrusive nature and its high accuracy. Furthermore, with a suitable model applied, one can determine various parameters of the material such as the refractive index, the thickness of layered systems or the roughness.

Infrared spectroscopic ellipsometry provides even more information, specially on the chemical composition of oxides and organic elements. However, application of this technique in the infrared became of interest only later, because of the lack of efficient sources or optical devices like polarizers or retarders. In this thesis, the development of a rotating compensator ellipsometer (RCE) working in the mid-infrared (2.5 to 12 µm) is described. The ellipsometer is associated to a fourier transform spectrometer. Compared to other ellipsometers, RCE offers several advantages that are highlighted in this study. The instrumentation, particularly the design of high-performance and broad band linear polarizers and retarders is detailed.

Because of its high sensitivity, the calibration of the ellipsometer requires a lot of attention. The different sources of imperfection have been identified and a calibration procedure is proposed. We have demonstrated that the main cause of misalignment and imperfection is the source, a globar. Its weak intensity prevents it from being used as a point source and an intrinsic divergence of the beam can strongly alter the performance of the other optical devices.

The ellipsometer has been used first for the analysis of silicon oxides and sub-oxides. In particular, the variation of the apparent transverse and longitudinal vibrational modes of the Si-O chemical bond groups with the thickness of the oxide has been monitored. The behavior of the dielectric function and the refractive index of the silicon sub-oxide as a function of the oxygen content has been investigated. We were able to demonstrate the transition from a semiconductor to a dielectric material. A model involving non-oxygen-saturated silicon tetrahedra has been successfully applied to explain the frequency shift of the main absorption peak of silicon sub-oxide towards higher frequencies.

In parallel, a study has been carried out on the effect of non-thermal plasma on biological tissues. We exposed bone to a low pressure inductively coupled plasma. The modification and the etching have been observed with infrared spectroscopic ellipsometry as well as with ion beam analysis techniques (Rutherford backscattering spectrometry and elastic recoil detection analysis). Ellipsometry proved to be a suitable technique for biological tissues, by identifying mineral (hydroxyapatite) and organic (collagen amide groups) constituents. It has been shown that the selectivity of the plasma etching and modification processes can be monitored. The most important plasma parameters are the gas mixture and the discharge power. two different models of etching have been described involving either ion bombardment (argon plasma) or chemical etching (oxygen). These results could lead to further applications such as the treatment of dental cavities or the removal of tumorous cells on tissues.
Samenvatting

Ellipsometrie is een populaire techniek voor de analyse van oppervlakken en de zones direct onder het oppervlak. De grootste voordelen van ellipsometrie zijn de niet-invasiviteit en de grote nauwkeurigheid. Met een adequaat model van het substraat kan men diverse materiaalparameters bepalen, zoals de brekingsindex, de diktes van diverse aanwezige lagen en de ruwheid. Als ellipsometrie in het infrarode deel van het spectrum wordt bedreven, kan men informatie verkrijgen over de chemische samenstelling van bijvoorbeeld oxides en organische bestanddelen.

De toepassing van ellipsometrie in het infrarood is echter pas recentelijk goed op gang gekomen. Dit werd veroorzaakt door een gebrek aan efficiënte lichtbronnen en optische componenten zoals polarisatoren en fasevertragers. In dit proefschrift wordt de werking van een zogenaamde "rotating compensator ellipsometer" beschreven die actief is in het midden-infrarood (2.5-12 micrometer). De ellipsometer maakt gebruik van een Fourier Transform Spectrometer. De diverse voordelen van het gebruik van de Rotating Compensator geometrie worden bediscussieerd. De instrumentatie, in het bijzonder de concepten voor nieuwe polarisatoren en fasevertragers, wordt uitgebreid besproken.

Vanwege de grote gevoeligheid van het instrument verdient de calibratie van de ellipsometer grote aandacht. De diverse foutenbronnen worden besproken en de algehele calibratieprocedure wordt toegelicht. De lichtbron, een globar, blijkt de grootste foutenbron te zijn. Door de zwakke lichtsterkte moet een groot oppervlak van deze lichtbron worden gebruikt, hetgeen leidt tot een slechte definitie van de lichtbundel en depolariserende effecten.

De eerste series experimenten betreffen siliciumoxides en -sub-oxides. In het bijzonder zijn de veranderingen in de absorpties van de transversale en longitudinale vibraties van de Si-O bindingen met de dikte van het (sub-)oxide bestudeerd, alsmede het gedrag van de diëlectrische constante en de brekingsindex. De overgang van een halfgeleider naar een diëlectricum kon worden aangetoond. De verschuiving van de grootste absorptiepiek naar hogere frequenties kon worden verklaard met een model van niet-verzadigde silicium-tetrahedra.

Tegelijkertijd is een studie uitgevoerd naar het effect van de behandeling van biologische weefsels met een niet-evenwichts-plasma. Botweefsel is blootgesteld aan een inductief gekoppelde plasma. De modificatie en het etsen van dit weefsel door de plasma-behandeling werd geanalyseerd met infrarood-ellipsometrie, alsmede met ionenbundeltechnieken als RBS (Rutherford Back Scattering) en ERDA (Elastic Recoil Detection Analysis). Het bleek dat ellipsometrie een betrouwbare techniek is voor het karakteriseren van biologische weefsels, omdat minerale (calcium hydroxy-apatiet) en organische (amide-groepen in collageen) componenten goed kunnen worden geïdentificeerd. De selectiviteit van de ets- en modificatie-processen kon worden gedemonstreerd. Het bleek dat de gassamenstelling en het elektrische vermogen de meest relevante makroscoopische plasma-parameters zijn. Twee modellen voor de plasma-weefsel-interactie werden voorgesteld: de n gebaseerd op de invloed van het ionen-bombardement (ar-
gonplasma) en de ander gebaseerd op chemisch etsen (zuurstofplasma). De resultaten kunnen wellicht bijdragen aan het ontwikkelen van medische toepassingen van plasmas bij bijvoorbeeld het bestrijden van kanker in diverse weefsels, restenose en tand-cariës.
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