UNIVERSITAT ROVIRA I VIRGILI
DESIGN, FABRICATION AND CHARACTERIZATION OF POROUS SILICON MULTILAYER OPTICAL DEVICES
Elisabet Xifré Pérez
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Chapter 6

Ellipsometric study of porous silicon layers

The ellipsometric study of porous silicon monolayers and multilayers is presented in this chapter. The objective of this study is to determine the main physical characteristics of these layers: porosity (and therefore refractive index) and thickness. These characteristics have been previously calculated with other methods and the comparison between those results and the results obtained with ellipsometry is also presented. In addition, spectroscopic ellipsometry allows the analysis of the anisotropy of the porous layers. This characteristic can not be analyzed by any of the previous characterization methods used, so ellipsometry provides this additional data for the knowledge of the fabricated porous silicon layers.

First, in this chapter, we briefly explain the theoretical concepts of spectroscopic ellipsometry. Next, we describe the equipment used for the ellipsometric measurements, the ellipsometer. The different steps followed for the characterization of the porous silicon layers are also explained. After that, we show the most relevant results obtained from ellipsometry, firstly the

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ellipsometric study of fabricated porous silicon monolayers, and secondly the study of porous silicon multilayers consisting of a periodic repetition of two layers with different degrees of porosity. Finally, we present the conclusions obtained from our experiments.

6.1. Introduction to Spectroscopic Ellipsometry

Ellipsometry is an optical characterization technique based on the measurement of the polarization transformation that occurs after the reflection (or the transmission) of a polarized beam by a given sample [209]. Ellipsometry is a well known technique that has been currently practiced since the second half of nineteenth century and it is supported by a complete theoretical description [209].

When a beam of linearly polarized light of a known orientation is reflected at oblique incidence from a surface then the reflected light is elliptically polarized, for this reason the term ellipsometer was chosen. The shape and orientation of the ellipse depend on the angle of incidence, the direction of the polarization of the incident light, and the reflection properties of the surface.

Nowadays ellipsometry has many interesting applications. In particular, it is mainly used in semiconductor research and fabrication to measure the optical properties as well as the physical dimensions of complex systems such as multilayer stacks of thin films and the interfaces between those layers [210-214]. However, ellipsometry is also becoming more interesting to researchers in other disciplines such as biology and medicine [215,216]. These areas pose new challenges to the technique, such as measurements on unstable liquid surfaces and microscopic imaging [217-219].

Ellipsometry is sensitive to several material characteristics, such as layer thickness, optical constants (refractive index and extinction coefficient), surface roughness, composition, optical anisotropy; and is used to characterize both single layers and multilayer stacks [218,220,221].

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6.1.1. Fundamentals of ellipsometry

All the expressions that will be mentioned from now on will be related to reflection ellipsometry. Anyway, broad information can be found in the literature [222,223] about the instrumentation and the mathematical formalism of transmission ellipsometry.

In both reflection and transmission ellipsometry, the direction of the incident and reflected beams determine the plane of incidence. To easily introduce the basic ellipsometric magnitudes and to generalize them, we will first consider the case of a plane wave whose electric field vector can be decomposed into two components, one parallel (subscript p) and another perpendicular (subscript s) to the incidence plane. Fig. 6.1 shows the schematic representation of the incident $\vec{E}^i$ and reflected $\vec{E}^r$ fields, and their corresponding components $E^i{}_p$, $E^i{}_s$, $E^r{}_p$, and $E^r{}_s$.

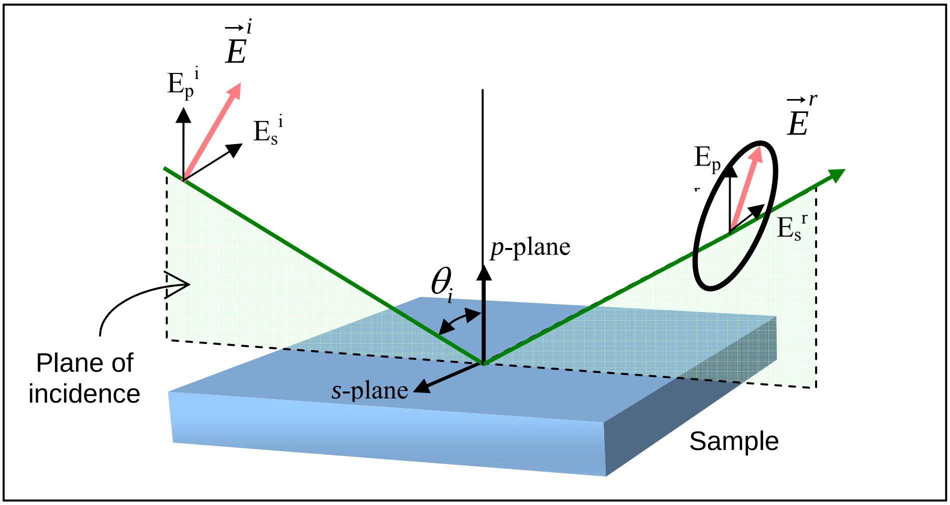

Fig. 6.1. Schematic of the incident electric field ($\vec{E}^i$) and the reflected electric field ($\vec{E}^r$).

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These components are usually expressed in complex notation:

$$\vec{E}^{i,r} = \begin{pmatrix} E_p^{i,r} \\ E_s^{i,r} \end{pmatrix} = e^{j(\omega t - \vec{k}_0 \vec{z})} \begin{pmatrix} A_p^{i,r} \\ A_s^{i,r} \end{pmatrix} = e^{j(\omega t - \vec{k}_0 \vec{z})} \begin{pmatrix} \alpha_p^{i,r} e^{j\beta_p^{i,r}} \\ \alpha_s^{i,r} e^{j\beta_s^{i,r}} \end{pmatrix} \tag{6.1}$$

where ω is the angular frequency, $\vec{k}_0$ is the wavenumber vector in the vacuum, $A^{i,r}{}_p$ and $A^{i,r}{}_s$ are the complex amplitudes of the field components, $\alpha^{i,r}{}_p$ and $\alpha^{i,r}{}_s$ are their modulus and $\beta^{i,r}{}_p$ and $\beta^{i,r}{}_s$ are their relative phases for t=0 and z=0. As the physical magnitude actually detected by ellipsometers is the radiation intensity, the general phase, $e^{j(\omega t - \vec{k}_0 \vec{z})}$, is not considered because it does not affect the magnitude value. On the contrary, the relative phases are very important for the intensity value determination.

The p and s components of the incident and reflected electric fields are related to each other with the reflection coefficient in parallel polarization r_p and the reflection coefficient in perpendicular polarization r_s, respectively. The expressions of these two relations are:

$$\begin{aligned} A_p^r &= r_p A_p^i \\ A_s^r &= r_s A_s^i \end{aligned} \tag{6.2}$$

Ellipsometry measures the modulus and phase of the quotient between the reflection factor in parallel polarization and the reflection factor in perpendicular polarization. This quotient is named complex relation, ρ, and is expressed as:

$$\rho = \frac{r_p}{r_s} \tag{6.3}$$

From this relation the ellipsometric angles Ψ and Δ are defined as:

$$\rho = \tan\Psi \, e^{j\Delta} \tag{6.4}$$

where Ψ is the angle whose tangent is the quotient of the modulus of the reflection factors r_p and r_s and Δ is the phase change difference that the p and the s components undergo in the reflection.

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Although the most used ellipsometric parameters are Ψ and Δ, for the study of the porous silicon layers we will study *Is* and *Ic*, because these are the magnitudes actually measured in the setup we have used [224] The relation of these values with Ψ and Δ are

$$I_S = \sin(2\Psi)\sin(\Delta)$$
$$I_C = \sin(2\Psi)\cos(\Delta) \qquad (6.5)$$

Because ellipsometry measures the ratio of two values, it can be highly accurate and very reproducible.

The most important application of ellipsometry is to study thin films. In the context of ellipsometry a thin film is one that ranges from essentially zero thickness to several thousand Angstroms, although this range can be extended in some cases. If a film is thin enough that it shows a colored interference pattern then it will probably be a good ellipsometric sample. The sensitivity of an ellipsometer is such that a change is film thickness of a few Angstroms is usually easy to detect.

The use of spectroscopic ellipsometry has many advantages. The most important one is that ellipsometry measures a ratio of two values which permits highly accurate and reproducible (even in low light levels) results. No reference sample is necessary and it is not as susceptible to scatter, lamp or purge fluctuations as other measurement techniques.

Ellipsometry provides two values at each wavelength so we obtain more information about sample and therefore more film properties. Some ellipsometers allow the variation of the incidence angle, being called Variable Angle Spectroscopic Ellipsometry (VASE) that report new information optimizing the sensitivity.

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6.1.2. Equipments for ellipsometric measurements. Ellipsometers

There are many different ways of determining the polarisation of a beam of light. In the first ellipsometers, the operator observed the light beam that was reflected off the sample through an eyepiece. The polarisers and retarders were rotated by hand until the effect of the polarisation was inverted and no light would pass through the instrument. This is called the nulling technique. Many instruments are still based on the nulling technique although today's null ellipsometers are somewhat more sophisticated. The light sources used in these instruments were often fixed to a single wavelength.

Modern nulling ellipsometers use computers to rotate the elements and to automatically calculate the ellipsometry signal very quickly. However, the nulling technique is not ideal for automated instruments because it is based on measuring a zero signal. This was an advantage in the early ellipsometers because the human eye is very sensitive to small changes in the signal around the 'null'.

In recent years, the advent of computer control and multichannel detectors has made it possible to develop fast spectroscopic ellipsometers. A technique that is more suited to modern-day instrumentation is Phase Modulated Ellipsometry. The phase modulated ellipsometer (PME) is that in which the state of the radiation beam polarization in a certain point of its trajectory is modulated, obtaining information of the measured system with an analysis of the harmonics of the detected signal.

The most relevant advantages of the PME are the absence of mechanical vibrations of the optical elements and the high modulation frequency that allows the fast data acquisition, that makes possible the monitoring of processes of preparation and treatment of samples in real time.

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6.2. Ellipsometric characterization process

The characterization of porous silicon layers using spectroscopic ellipsometry has been realized during my stage at the École polytechnique in Palaiseau (France), under the supervision of Dr. Enric García-Caurel. Part of the ellipsometric measurements were also realized at Horiba Jobin Yvon in Longjumeau (France). During this stage many porous silicon monolayers and multilayers where measured and characterized. In this section, the equipment and the process for the measurement and characterization of the layers are detailed.

6.2.1. UVISEL Ellipsometer

All the fabricated porous silicon layers have been measured using the UVISEL NIR Spectroscopic Phase Modulated Ellipsometer commercialized by HORIBA-Jobin Yvon. The ellipsometric data were acquired at an incident angle of 70° (some measurements for 55º) for the wavelength range 0.9-1.8 μm with a step of 10 nm.

Fig. 6.2a shows the photograph of the UVISEL ellipsometer used for the realization of the measurements. In Fig. 6.2b we can observe the different parts of this equipment [225].

Fig. 6.2b shows a schematic representation of the optical setup of the phase-modulated ellipsometer. The light source is a xenon lamp, which emits unpolarized light. The beam is focused on the entry of an optical fiber and then passes through a polarizer. After reflection on the sample, the beam is analyzed by a Photoelastic Modulator (PEM) with a 50 kHz modulation frequency, and a second polarizer called analyzer. The light intensity is then introduced to a spectrograph to process the data acquired.

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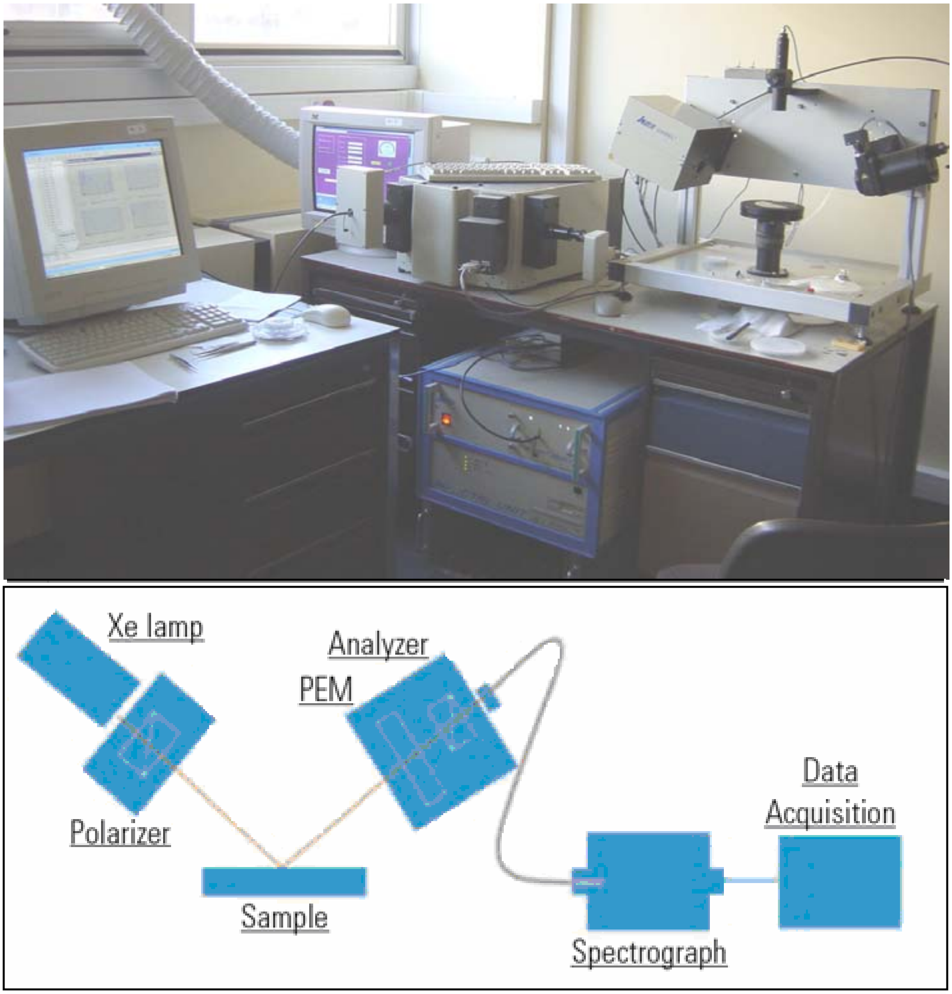

Fig. 6.2. a) UVISEL ellipsometer (École polytechnique) b) Schematic of the UVISEL ellipsometer elements [After 225].

6.2.2. Influence of the spot size on the ellipsometric measurements

Two different sets of samples have been characterized by ellipsometry. Each set has been fabricated using a different electrochemical cell: one set was fabricated with the lateral-wafer cell and the other with the bottom-wafer cell.

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In section 5.1.1, we have concluded that the porous silicon layers obtained with the lateral wafer cell where very inhomogeneous, being the bottom-wafer cell the most appropriate for the fabrication of homogeneous porous silicon layers.

The inhomogeneity of the porous layers obtained with the lateral cell can be also observed from the ellipsometric measurements of the porous silicon layers. The spot size of the beam for the ellipsometric measurement can be adjusted in the UVISEL ellipsometer. Three different spot sizes can be selected: macrospot (1 x 2 mm), mesospot (0.1 mm x 0.2 mm) and microspot (0.01 mm x 0.02 mm). The ellipsometric measurement is an average of the measurement in the spot area. If the refractive index and/or the thickness across the spot area are different the resulting ellipsometric measurement will lead to an averaged result which cannot be fitted because averaging is not taken into account by our ellipsometry software. In consequence, it is very important to choose the appropriate spot size for each type of layer. For inhomogeneous layers the smallest spot size, the microspot is the most suitable whereas the homogeneous layers can be measured with a better signal-to-noise ratio with the meso or the macrospot.

Our porous silicon monolayers, obtained with both electrochemical cell types, have been measured with the three spot sizes. Fig. 6.3 shows the ellipsometric measurements realized to a porous silicon monolayer obtained with the lateral-wafer cell for two different spot sizes. We can observe that the results obtained are very different for the macrospot and for the mesospot. With the mesospot all the maxima and minima of I_S and I_C can be observed whereas with the macrospot these variations are attenuated and some of them are lost. This effect of aliasing is explained by the inhomogeneity of the samples, which corroborates the conclusions obtained in section 5.1.1 that the wafers obtained with the lateral-wafer cell are inhomogeneous.

Fig. 6.4 shows the ellipsometric measurements of a monolayer fabricated with the bottom-wafer cell. We can observe that I_S and I_C do not vary with the spot size, which indicates that the porous silicon monolayer is very homogeneous. The little variations of I_C at the maxima of the mesospot

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measurements are not relevant, they are produced by the low signal-to-noise ratio of the instrument due to the small size of the spot.

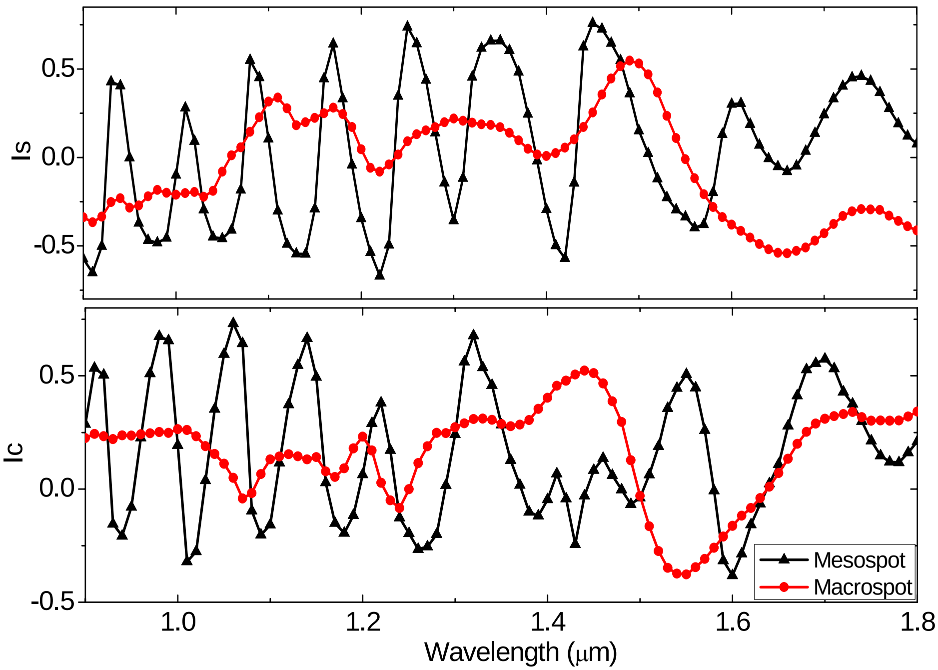

Fig. 6.3. Ellipsometric measurements of a porous silicon monolayer, fabricated with the lateral-wafer cell, for two different spot sizes.

The ellipsometric study has been realized for layers fabricated with both lateral and bottom-wafer cells. The results obtained with the latter cell are more accurate due to the homogeneity of the fabricated porous silicon layers. For this reason, in the next sections we only present the ellipsometric study realized for the bottom-wafer cell layers and the conclusions obtained from this study. The same conclusions have also been obtained for the lateral-wafer cell layers although the possible errors introduced in the characterization are slightly higher due to inhomogeneity.