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Ellipsometry porosimetry (EP): thin film porosimetry by coupling an adsorption setting with an optical measurement, highlights on additional adsorption results

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Abstract Ellipsometry porosimetry (EP) is an emerging technique that is well adapted to porous thin films[1] analysis; it is non contact and non destructive. EP tools developed at SOPRA, allows us to obtain adsorption isotherms with many different adsorptives at an ambient temperature. EP leads to the same results as classical adsorption experiments (e.g. porosity, pore size distribution …), but it also has some particular features leading to new information. For instance, our optical setup (Spectroscopic Ellipsometry) allows us to determine the variation of the thickness of the samples during the adsorption experiment. It is also very sensitive to interfaces; it is thus possible to detect a porosity gradient or to study a bi-layer sample and plot the two corresponding adsorption isotherms at the same time (Bourgeois et al. 2004). For porous thin films with a non porous barrier layer deposited on top, it is also possible to study the lateral diffusion phenomenon in the film (see figure below). In this paper, we will demonstrate a part of the different features of EP for adsorption on porous thin films.

Keywords Gas phase adsorption · Diffusion

1 Introduction

Spectroscopic ellipsometry is a reference technique for thin films characterization. This optical technique is particularly suited for the determination of the thickness and refractive indices of thin films. To facilitate the study of porous thin films, SOPRA has developed measurement devices that couple the classic spectroscopic ellipsometry measurement with an adsorption tool. As the Ellipsometric porosimeter (EP) is inspired by the traditional adsorption setups (BET, BJH apparatus), the true revolution is that the amount adsorbed during the experiment is not obtained by a weighing process or the measurement of a differential of pressure anymore, but through the evolution of the optical properties (refractive indices) of the porous material. In this configuration, the accuracy of the measurement remains excellent even for very few quantities of matter; layers with a thickness as low as 100 nm can then be characterized, which combined with the size of the optical beam (approximately 1 mm^2) corresponds to a volume of material of approximately 10^{-7} cm^3. This original measurement device, allows a non-destructive and direct characterization of thin films in the range of thickness going from 60 nm to few micrometers, whatever the substrate used for the deposition; it does not require any preparation or scratch of the film.

To avoid experimental complications associated with low-temperature experiments, we choose adsorptives that perform well at ambient temperatures. In this paper, we will present results obtained with two different adsorption tools where water and toluene have been used as the adsorptives.

After a quick presentation of the measurement tools, we will focus on three different particular features of EP. First, we will present its ability to give a direct and accurate measurement of the thickness adsorbed on the plane surface of an adsorbent as a function of the relative pressure (t-curve).

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[1] We have to underline that in optical studies, thin films are defined as thin layers of material deposited on top of a non-porous solid (substrate). It does not refer to a layer of the adsorptive which has been adsorbed on the adsorbent surface.

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Measurement of this thickness is of particular interest for the porosity analysis (for instance for t-plot or accurate determination of the pore size distribution using the Kelvin equation). Then, we will focus on adsorption results obtained from porous thin films. We will describe how ellipsometric measurements lead to the obtention of the adsorption isotherm and the thickness variation of the film during adsorption. Change of the volume of the adsorbent is not obtained through classical adsorption experiments, and is usually neglected in adsorption models. As a third illustration of the technique, we will present an innovative experiment to characterize the diffusion of the adsorptive within the porous layer.

2 Tools

Two different tools have been used to perform the experiments presented in the following sections. Both tools are a combination of an adsorption setup and an in situ optical measurement. A concise description is given in this section.

The first one (EP-A) uses water as the adsorptive and allows measurements at atmospheric pressure and ambient temperature through a flow process (Boissière et al. 2005). Control of the relative humidity in the measurement cell is obtained by controlling the mixing proportions of the two different flows; the first one is a dry flow of nitrogen (no nitrogen adsorption occurs at ambient temperature), the second flow goes through a column of water and is saturated in humidity. For the EP-A tool, the optical measurement is performed with a SOPRA spectroscopic ellipsometer (GES5E model with a CCD spectrograph allowing fast and accurate measurements in the range 1.37 to 4.96 eV). The variable angle goniometer allows precise ellipsometric measurements to be performed from 60 to 90° range for the angle of incidence.

The second one (EP 12) is presented on Fig. 1. It allows the use of many different adsorptives and requires a low pressure experiment (Baklanov et al. 2000). The adsorption setup is piped on a high vacuum chamber especially designed to allow the optical measurements. The setup is equipped with a turbomolecular dry pumping system, which allows pressure below 10^{-5} torr to be reached. The adsorptive can be progressively introduced into the chamber through a special controllable valve on a bypass line; it can be progressively removed through the pumping system using the same procedure.

On EP 12 tool, the optical measurement setup consists on a SONY CCD camera (SSC-DC80P) and a SOPRA spectroscopic ellipsometer (GES5E model with a CCD spectrograph allowing measurements in the range 1.37 to 4.96 eV) at a fixed angle of incidence of 60°. The camera allows images of the sample surface to be recorded for selected steps during the entire adsorption process. Evolution of the sample during the experiments can be directly seen that way. Ellipsometric spectra can be measured the same time, and allows the determination of the amount of adsorptive adsorbed during the experiment. EP 12 tool possess mapping capabilities to allow the sample to be measured on its whole area.

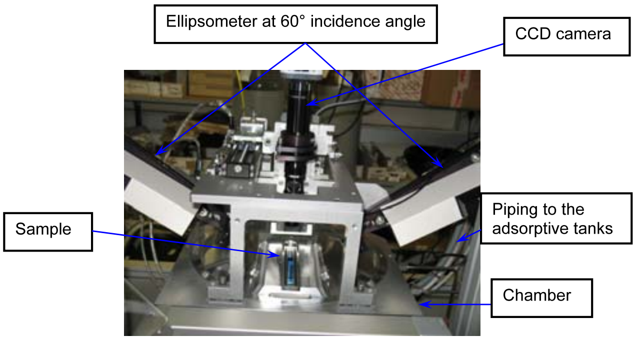


Fig. 1 View of the measurement part of the EP 12 tool

Using both EP-A and EP 12 tool, every parameter of the experiment can be tailored in order to adapt optimally with the sample being measured, and the measurement is automated.

3 Spectroscopic ellipsometry

As ellipsometry is a novel technique in the adsorption field, we will detail it a little further in this section.

Ellipsometry is an optical technique, which is based on measuring the change of the polarization state of light after reflection on a plane surface. It is a non-destructive technique, capable of being used for any transparent and semitransparent medium. It should be emphasized that ellipsometry is particularly adapted to measure a wide range of thickness for each layer, extending from a fraction of a mono-atomic layer to several micrometers. Ellipsometry also allows the determination of the properties (thickness and optical characteristics) of single layer and multi-layer stack samples. In addition, ellipsometry allows the absolute characterization of a materials optical properties by extraction of the refractive index (n) and optical absorption (k) data.

3.1 Principle

Spectroscopic Ellipsometry (SE) consists in sending a linearly polarized white light on the surface of a sample at a non-normal incidence, and analyzing the new (elliptical) state of polarization after reflection on the sample. Thanks to the penetration depth of light- being a function of the optical properties of the deposited materials—SE enables the analysis of each independent layer of a stack.

The measured ellipsometric parameters ($\tan\psi$ and $\cos\Delta$) are defined by the fundamental formula:

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

r_p: reflectivity coefficient for P polarization (parallel to the plane of incidence); r_s: reflectivity coefficient for S polarization (perpendicular to the plane of incidence); $\tan\psi$ amplitude ratio of the P and S components of the reflected light; Δ Phase ratio of the P and S components of the reflected light.

Each measurement gives both $\tan\psi$ and $\cos\Delta$ for a number of wavelengths distributed over a wide spectral range (which can go from Deep UV to the far infrared depending on the ellipsometer configuration).

Refer to SOPRA web site, www.sopra-sa.com, for definition and basic tutorial on Spectroscopic Ellipsometry.

During the adsorption experiments, in-situ ellipsometric measurements provide access to the evolution of ellipsometric spectra $\tan\psi$ and $\cos\Delta$ of the samples. Analysis of these spectra allows to be determined the sample characteristics (optical indices and physical thickness). The link between the optical measurement and the amount adsorbed in the pores will be described in the results section using the case of a porous layer as an illustration.

3.2 Analysis of the ellipsometric measurements

The different steps of the analysis are the following. A model is defined to describe the sample structure. Fitting the experimental data with the model, a regression program leads to the determination of the thickness t, the refractive index n, and the extinction coefficient k on the whole spectral range of measurement. In this study, as the samples are transparent porous layers ($k = 0$), we will deduce their thickness and refractive index only. As we will see in the section concerning the adsorption results, the amount adsorbed in the pores is obtained from the refractive index and requires very few hypotheses.

4 Results and discussion

4.1 Adsorption on a plane surface/non porous sample

Classic adsorption techniques require a hypothesis to determine the thickness of adsorptive adsorbed on a non porous material (including the specific surface area of the porous material). Ellipsometry, on the other hand provides direct and precise measurement of this forementioned thickness. To optimise the measurement with respect to the sensibility, an angle of incidence in the neighbourhood of the Brewster angle substrate should be utilized. For this purpose, we used the SOPRA EP-A tool designed to perform water adsorption at ambient conditions. This tool includes a variable angle goniometer bench capable of performing measurements for incident angles ranging from 60 to 90° with outstanding repeatability and precision.

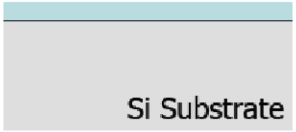


Fig. 2 Schematic representation of the sample: native oxide layer (SiO_2) on silicon substrate

In the following study, we will present results of water adsorption performed at 21 °C on a flat silicon wafer with an angle of incidence of 75°; this angle corresponds to the Brewster angle for the silicon substrate.

As can be seen in Fig. 3, $\cos\Delta$ undergoes a significant variation around 1.7 eV. Silicon wafers are covered with a native oxide layer (silica) due to an oxidation process at the silicon surface (see Fig. 2). The slope of the $\cos\Delta$ curve is related to the thickness of the superficial layer.

Ellipsometric parameters are fitted on the first measurement performed under a flow of dry nitrogen before any adsorption occurs, considering the sample as a thin layer of silica on a silicon wafer. A thickness of 3.4 nm for the silica layer is thus obtained.

Water adsorption takes place over the native oxide layer, were the oxide has the same kind of chemical properties than silica.

Ellipsometric spectra variations during adsorption are presented on Fig. 3. We notice that the slope of $\cos\Delta$ increases as the thickness of the adsorbed layer increases.

The results are interpreted by supposing that refractive index of water is the one of the liquid state (1.33 at 633 nm). At each relative pressure, the thickness of water is the only parameter that varies. Results are presented on Fig. 4.

Uncertainty on the thickness value is about 0.4 angströms. It is estimated from the fit on ellipsometric parameters and remains practically constant during adsorption.

The shape of the experimental isotherm (type III in the IUPAC classification) is characteristic of a weak interaction between the substrate and the adsorbate fluid. Surface covering of the silica layer remains incomplete until high relative pressure.

The multilayer regime is only reached for relative pressure above 0.8, at which point the adsorbed thickness increases rapidly. The effective thickness of water adsorbed on the silica surface remains inferior to the dimension of the water molecule for the first part of the isotherm. This effective thickness is obtained because the size of the measurement spot includes the contribution of areas covered with water molecules as well as areas non-covered by the adsorptive.

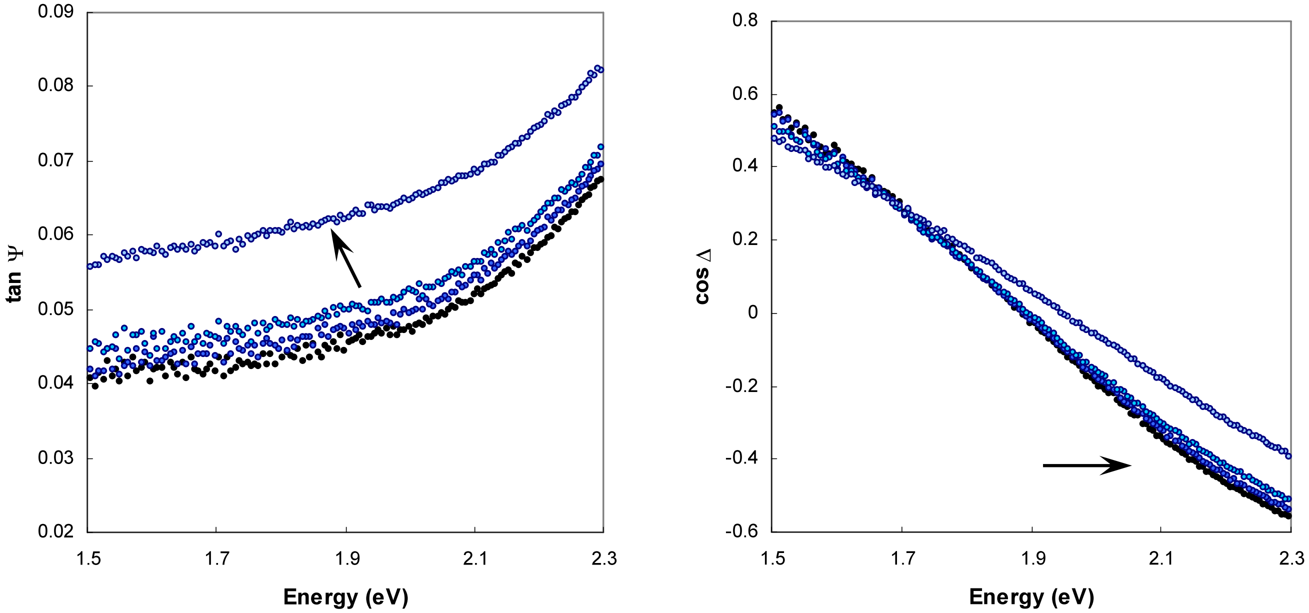


Fig. 3 Variation of the ellipsometric parameters during water adsorption on a silicon wafer

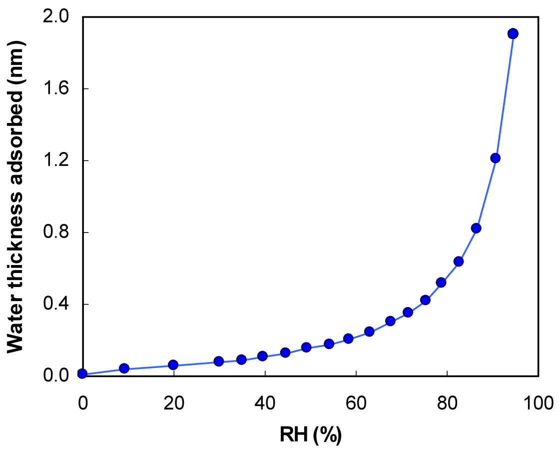


Fig. 4 Water thickness adsorbed at 21 °C on a flat silica surface as a function of the relative pressure

4.2 Adsorption experiment on porous sample (thickness variation and adsorption isotherm)

Results presented in the following sections concern a low-*k* porous sample with disordered porosity. Low-*k* samples are developed in the microelectronic industry to be used as the insulator part of electronic devices. They are usually obtained by CVD or spin-coating techniques. As considerable economic interests are invested in this field of research very little information is disclosed about these samples. However, low-*k* porous thin films still remain of particular interest for us, because their properties (and particularly their porosity and mechanical properties) can be managed at wish.

Using the EP 12 tool, toluene adsorption has been performed on low-*k* sample 1 at room temperature (25 °C).

4.2.1 Model and spectra analysis

Sample 1 is modeled as a layer of dielectric material deposited on a silicon substrate (see Fig. 8a).

The thickness and the refractive index of the porous layer are initially determined for the first measurement performed under vacuum conditions, before any adsorption process occurs. Thickness of 164.7 nm and refractive index of 1.285 at wavelength 633 nm are obtained for this low-*k* porous layer.

These values are then inserted into the model as starting values for the regression sequence on all the ellipsometric spectra that have been recorded for each relative pressure. In this way, we can plot the two adsorption isotherms of Fig. 5: thickness and refractive index variation as a function of the relative pressure for the porous layer.

As we can see in Fig. 5a, the refractive index isotherm ressembles the classic adsorption isotherm (isotherm of the amount adsorbed). In fact, the relation between the change in refractive index and the fractional volume of adsorptive adsorbed in the pores of the porous layer is quasi linear (Bourgeois 2005).

Spectroscopic ellipsometry measurement also gives access to the thickness variation of the porous layer during the adsorption. Considering the thickness isotherm (Fig. 5b), we can see that the porous layer first undergoes a contraction until the mesopores are filled with the adsorptive (bellow 0.2 relative pressure), then a swelling over the entire domain of relative pressures greater than 0.2. Note that this domain

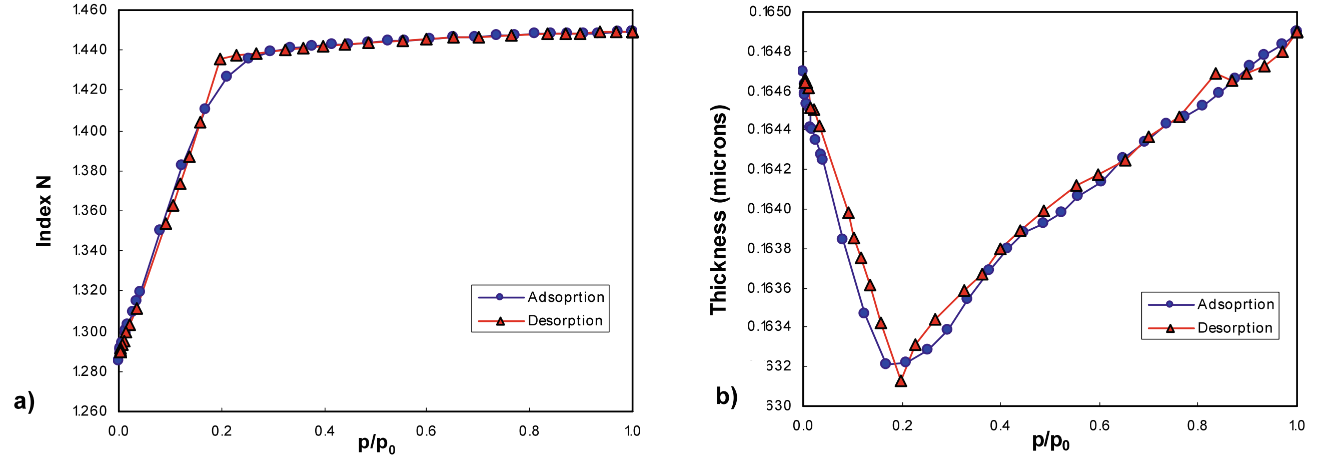


Fig. 5 (**a**) Refractive index variation during the adsorption experiment (Refractive Index Isotherm). (**b**) Thickness variation during the adsorption experiment (Thickness Isotherm)

corresponds to the quasi horizontal plateau reached on the refractive index isotherm.

It must be underlined that in most of adsorption theory, volume change of the porous samples is usually neglected. In the example given here, the thickness variation is about 1% and can reasonably be neglected. However, in other cases the thickness variation is often greater and therefore should not be disregarded.

4.2.2 *Young Modulus determination*

This thickness variation is interpreted as an effect of capillary forces on the skeleton of the porous material. In the case of thin films, the deformation only occurs in a direction perpendicular to the surface:

$$t\,(p/p_0) = s \cdot \ln\,(p/p_0) + t\,(p_0)$$

where: p/p_0 is the relative pressure, p_0 being the saturated pressure of the adsorptive; $t\,(p_0)$ (µm) is the thickness without capillary forces; s is the slope of the curve.

This deformation has been related to the Young's Modulus of the porous layers (Baklanov and Mogilnikov 2002). The Fig. 6 shows the fit used for Young's Modulus calculation.

The Young Modulus is defined as follows:

$$E = (\mathrm{As} * t\,(p_0))/s$$

where: $\mathrm{As} = (RT)/v_{\mathrm{L}}$, R is gas constant, T is temperature (K) and v_L is molar volume of the liquid adsorptive ($\mathrm{As} = 23$ for toluene); t_0 (µm) is the thickness without capillary forces ($t_0 = 0.1648$ µm in this case); s is the slope of the curve ($s = 0.0011$ in this case). For this sample, we determine a Young Modulus $E = 3.5$ GPa.

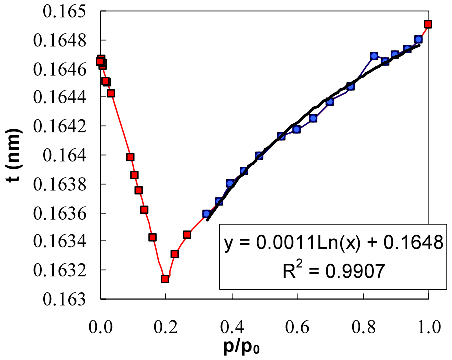


Fig. 6 Fit on the thickness isotherm in order to determine the Young Modulus

4.2.3 *Adsorption isotherm*

The adsorption isotherm (amount adsorbed as a function of the relative pressure) can be directly calculated from the change of refractive index occurring during the adsorption using the Lorentz-Lorenz formula (Baklanov et al. 2000).

Lorentz-Lorenz effective medium approximation (EMA) is widely used in optics. It consists of a relationship between the fractional volume, the refractive indices of the different compounds of a mixed material and the effective index of the resulting material. The Lorentz-Lorenz formula gives the fractional volume of adsorptive in the porous material (f_a) at each step of the adsorption:

$$f_a(p/p_0) = \frac{L(n_{\mathit{eff}}(p/p_0)) - L(n^i_{\mathit{eff}})}{L(n_a) - L(n_v)}$$

where $L(n) = \frac{(n^2-1)}{(n^2+2)}$ for a transparent material, $n_a, n_v, n_{\mathit{eff}}$ and n^i_{eff} are respectively the refractive indices of the adsorptive (in liquid phase), of void (i.e. 1), of the effective material (mixing) at each step of the adsorption experiment, and of the effective material at the first step of the experiment (before any adsorption occurs).

An important result of the use of ellipsometry to determine the amount adsorbed must be underlined at this stage. As can be seen from the Lorentz-Lorenz formula, no assumption has to be made on the refractive index of the skeleton (or in other words on its density) to obtain the adsorption isotherm using ellipsometry.

This adsorption isotherm corresponds to the fractional volume of the porous material filled by the adsorptive during the adsorption experiment. Refractive index of the adsorptive is that of the liquid phase (1.492 at 633 nm for toluene).

This is a type IV isotherm; it is characteristic of adsorption in mesoporous materials. There is a small hysteresis loop between the adsorption and desorption branch of the isotherm.

The final point on the adsorption branch of the isotherm yields the value of the open porosity filled by the adsorptive. Accessible porosity for this film is 31.1%. The presence of a near horizontal plateau at high relative pressures (in this case from 0.3 to 1 relative pressure) suggests that the whole porosity of the film has been filled.

This adsorption isotherm can then be analysed as "classic" adsorption isotherm. In this case, pore size distribution has been calculated using a modified Kelvin model, and a mean pore size of 2.6 nm has been determined.

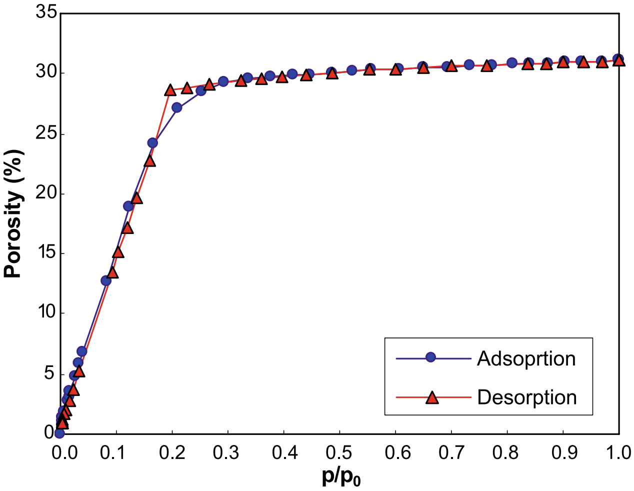


Fig. 7 Adsorption isotherm: fractional volume of the layer filled with toluene

4.3 Lateral diffusion in a porous film

4.3.1 Principle

These experiments have been performed for samples that consists of a non porous barrier layer deposited on top of the porous sample 1 previously studied (Fig. 8b). The porous layer is thus protected from any adsorption or diffusion of the adsorptive through the porous network. However, diffusion in the porous layer could occur if defects are present in the barrier layer (pore killers), or from an unprotected edge of the sample. In this paper we will focus on the second case: lateral diffusion of the adsorptive through the sample porosity by one of its edge.

In order to perform this experiment, sample 2 (shown above) has been cleaved at its edge, which has then been positioned in front of the acquisition camera (Fig. 9a).

During this diffusion experiment sample 2 is placed under saturated pressure of a given adsorptive and the evolution is recorded by measuring the two following quantities as a function of time. Images recorded on the sample surface (Fig. 9a) with the camera leads to the measurement of the distance travelled by the adsorptive from the edge of the sample. Ellipsometric spectra (Fig. 9b) are measured near the edge of the sample (see the spot position in Fig. 9a) in order to get the adsorbed volume during the experiment. Indeed, comparison of the ellipsometric measurement obtained before any adsorption occurs with one for which equilibrium has been reached at saturated pressure, allows the determination of the accessible porosity of the porous layer.

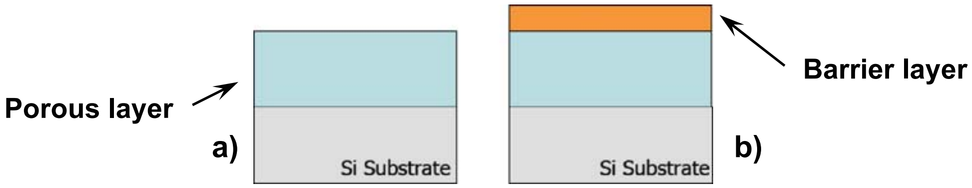
Lateral diffusion experiments have been performed on sample 2 using toluene as the adsorptive. As a reminder, sample 2 corresponds to the first porous low-*k* layer capped with a non porous barrier.

4.3.2 Model and spectra analysis

This sample is modeled as a stack of two layers of dielectric materials deposited on a silicon substrate (see Fig. 8b).

Analysis of the initial measurement performed under vacuum conditions, before any adsorption process occurs, gives a thickness 66.5 nm with refractive index 1.428 at wavelength 633 nm for the cap layer, and a thickness 159.1 nm with refractive index 1.265 at wavelength 633 nm for the low-*k* porous layer.

Fig. 8 Schematic representation of (**a**) porous sample 1. (**b**) Sample 2 obtained by deposition of a non porous layer on porous sample 1



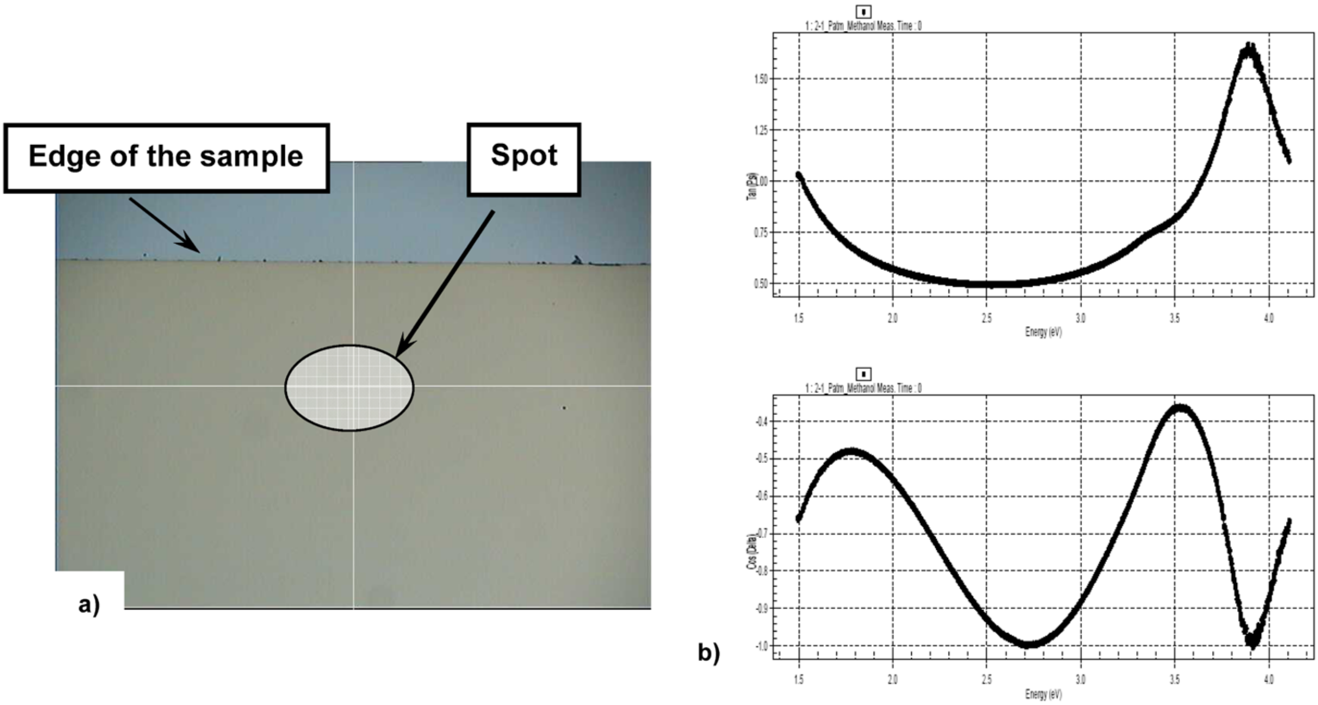


Fig. 9 Lateral diffusion experiment: (**a**) Image of the sample surface, (**b**) ellipsometric spectra measured on the centre of the cross. The spot size of about 1 mm^2 has been determined on a diffusive sample

4.3.3 *Results*

Figure 10 shows the different steps of the diffusion of the adsorptive form the edge of the sample during the experiment.

A change of colour with a lateral front can be clearly observed as the toluene penetrates inside the porous layer from its edge.

During the lateral diffusion experiment, the adsorptive penetrates inside the low-k layer through its edge. The diffusion length (l) of the adsorptive from the edge is directly obtained by analysis of the sample pictures showing the adsorptive diffusion in the porous layer as a function of time. It has been suggested (Shamiryan and Maex 2003) to express the results by the lateral diffusion coefficient D.

The diffusion coefficient (D) is calculated using the following diffusion law:

$$l = 2(Dt/\pi)^{1/2},$$

where t is the time.

The adsorptive covers 1171 µm in 1230 seconds, giving a toluene diffusion coefficient of 876 μm^2/sec.

Porosity of the low-k film can be obtained by the ellipsometric spectra measured during the same diffusion experiment.

To get the porosity of the layer, the first ellipsometric measurement performed under vacuum before any adsorption occurs is compared with another measurement performed under saturated pressure of toluene when all the porosity is filled with the adsorptive. Comparison of the refractive index of the porous layer obtained under vacuum with the one obtained when the layer is filled with adsorptive allows us to estimate the porous fractional volume of the low-k layer filled with toluene using the Lorentz-Lorenz effective medium approximation as the mixing model. This accessible porosity is estimated at 30.2%.

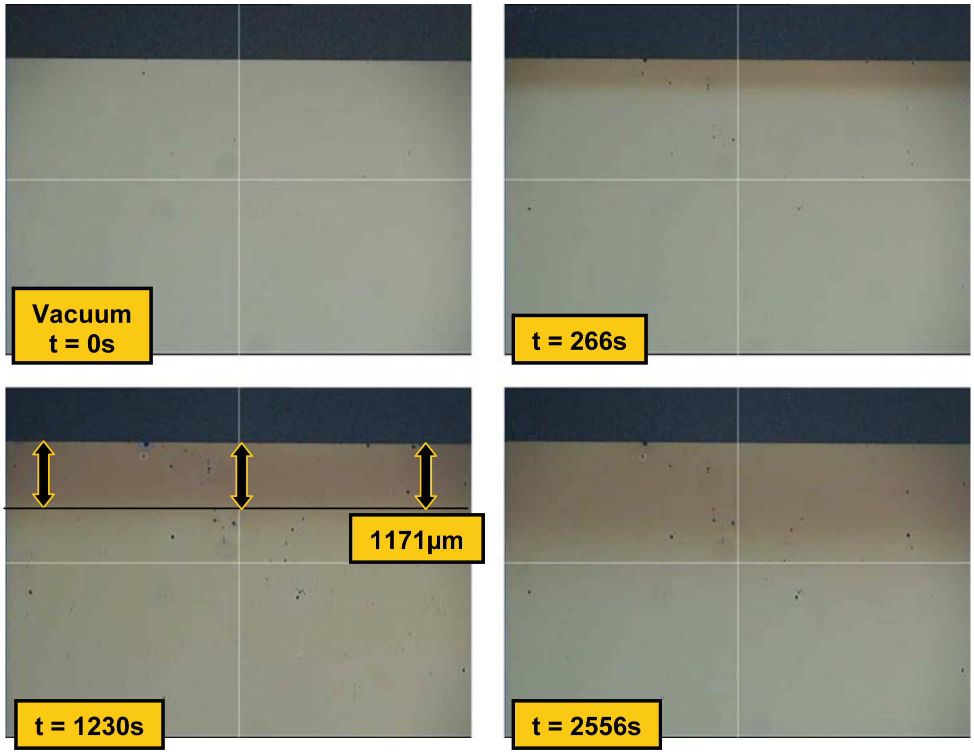
Another way to determine the porosity of the low-k layer can be obtained using the mapping capabilities of the EP-12 tool. As the optical setup can be translated over an area of the sample (see Fig. 11a), it is thereby possible to obtain the ellipsometric spectra on a line extending from the edge of the sample to its centre. A mapping of the amount adsorbed on a line perpendicular to the edge of the sample can thus be obtained (Fig. 11b).

This method allows the determination of an adsorption profile in the porous layer, on the measurement line at a given time (Fig. 11b). The shape of the adsorption profile can be thus obtained.

5 Conclusion

In this paper we presented the main features of ellipsometric porosimetry for porous thin films analysis. We first demonstrate the tool sensitivity for the analysis of adsorption on

Fig. 10 Lateral diffusion experiment: Diffusion of the adsorptive in the porous layer as a function of time



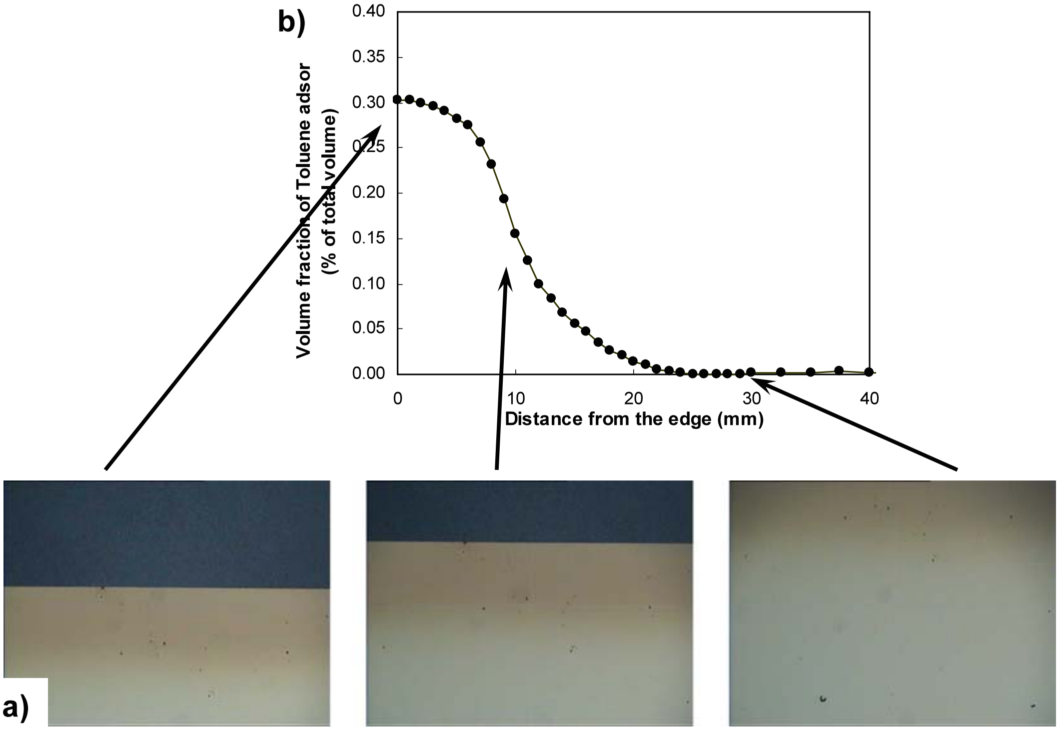


Fig. 11 (**a**) Pictures of the sample showing different steps of the adsorptive diffusion in the porous layer. (**b**) Mapping of the amount adsorbed in the porous layer obtained after 45 minutes since the beginning of the lateral diffusion experiment

non porous samples. We have thus highlighted that a direct measurement of the thickness adsorbed was obtained.

Then we showed the capabilities of EP systems for porous samples studies. We showed that ellipsometric measurements provide an easy and accurate way to obtain adsorption isotherms. Moreover we underlined that no hypothesis on the skeleton characteristics (like for instance its density or its optical index) was needed to get the amount adsorbed in the sample pores. Finally, we presented results of lateral diffusion experiments which constitute an original and elegant procedure to get information on diffusion phenomenon in the porous layers. We obtained thanks to the mapping capabilities of the EP 12 system, the shape of the adsorption profile of the adsorptive in the porous sample.

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