Spectroscopic Ellipsometric Porosimetry (EP) in the low pressure regime: how pressure and temperature stability control enhances measurement's accuracy

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Ellipsometric porosimetry (EP) based on the measurement of the refractive index variation as a function of solvent sorption is a technique employed to control porosity and pore size distribution in porous thin films. Adsorption isotherms (adsorbed amount of material as function of the partial pressure) can be deduced from changes in the optical indices which are detected through spectroscopic ellipsometry measurements. This technique raises growing interest in the microelectronics industry as a powerful metrology tool in the low-k dielectric developments. An automatic home-built adsorption/desorption EP spectroscopic ellipsometer equipment has been designed (Fig. 1). It uses the basic detection system of a rotating polarizer spectroscopic ellipsometer in the 300-900 nm wavelength range, with an entirely reconsidered software. The solvent partial pressure in the vessel is controlled owing to an automatic and dynamical PID computer-remote system. The motorized inlet mass flow provides repetitive commands of pre-selected apertures which are then adjusted by the throttle. It covers the different pre-chosen pressure steps while ensuring an highly in-time stability. Such a system is particularly well adapted in the low pressure range (10^{-4} to 10^{-1} Torr) where adsorption phenomena in micropores are present. Since both solvent vessel and sample handler temperatures are rigorously controlled, it leads to a clear enhancement of the accuracy of isotherms (Fig. 2).

Most of the samples studied exhibit mesopores with diameters of the order of 1 to 4 nm and also micropores as this is the case for PECVD dielectrics. During the adsorption process, changes in the optical indices are detected through spectroscopic ellipsometry measurements. This change in optical index, gives rise to adsorption isotherms as function of the partial pressure P/Ps (Ps is the saturation pressure), in the measurement cell (Fig. 3).

Main EP features in porous materials are :
-Adsorption on plane surfaces and determination of "t-curves" for organic vapors.
-PSD (pore size distribution) determination in very thin porous films
-Adsorption in micropores
-Simultaneous determination of thin film thickness and refractive index which can lead to an innovative method for stress measurements.

Adsorption isotherms are usually determined by adsorption of gas such as N_2 at low temperature (77K) and expressed in terms of percentage of adsorbed solvent inside a adsorbent porous matrix. This technique cannot be used in the case of thin films but only for bulk materials. The volume fraction of solvent inside a thin layer is directly related to the optical index through classical Effective Medium Approximation models (EMA).

A quasi- linear relation exists between the refractive index and the void filling fraction (Fig. 5). Therefore a simple derivative of the optical index respect to the pore radius describes very well the pore size distribution (Fig. 4).

The system such as described enables to enhance the accuracy of data by choosing the right temperature which modifies the saturation pressure value Ps : this value can indeed vary from more than one decade (for example for ethanol, Ps varies from 10 to 50 torr, when the temperature increases from 10 to 30 degrees Celsius, a typical range which is accessible in our environment. More generally the evolution of the equilibrium vapor pressure for ethanol adsorptive is given by:

$\log(P_s)=a-b/(T+C)$

with A=8.1629, B=1623.22 and C=228.98, Ps (saturation vapor pressure), and T temperature .

Study of microporous thin films

In the case of microporosity, the BET model is no longer valid. The Dubinin-Radushkevitch (DR) model based on the Polanyi adsorption potential has been proposed for evaluating the filled fraction of micropores. Assuming a Gaussian pore size distribution, the filled volume fraction W/W_0 can be expressed as :
$W = W_0 \exp[-(A/\beta E_0)^2]$, with A = -RT $\log_e$ (P/Ps) where W_0 is the total microporous volume, and W is the filled volume. E_0 is a characteristic adsorption energy and β is the affinity coefficient of the solvent. A is the Polanyi adsorption potential of the solvent.

A plot of $\log_e$ (W/W$_0$) versus A^2 in a linear regime, enables to provide the slope p (p = (1/βE$_0$)^2) and then to deduce a value for βE0. This behavior is generally observed during the micropores filling in a range of P/Ps<0.1 The corresponding figures 7 and 8 below show a definitively different behaviour. The DR plot let appear clearly two linear regimes which have not be yet reported in the literature and could be attributed to micropore and supermicropore regimes in this material. This behaviour should be correlated to DFT Montecarlo simulations which are extensively developped presently in the literature.
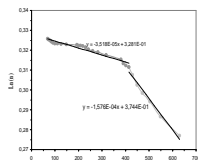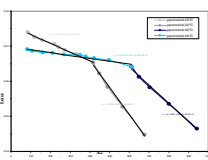
Since βE0 is the inverse square root of the slope, one can deduce the micropore mean radius r by :

r = K/βE0   with K ≈ 13 kJ.nm.mol^{-1}. The only proposed value for β ~1 has been given in the case of benzene molecule. Literature values do refer only to βr since the β coefficient is not known for ethanol

Fig. 1: Schematic of the EP equipment and of the measurement cell showing the input and output windows

Fig 2: Parameters (pressure control, signal intensity and tanΨ, cos Δ values versus wavelengths(nm) shown on the computer display during the measurements

Adsorption isotherms (Fig.3) can be exploited to establish the pore size distribution (PSD) as shown on Fig 4 when considering the refractive index derivative versus the pore radius given by the Kelvin equation at each P/P$_s$ values.

Fig. 3: Isotherm d'adsorption

Fig. 4: PSD corresponding to Fig. 3
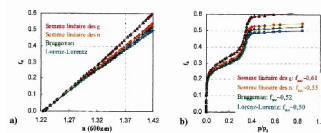
Fig.5 : Relation between the adsorbed volume fraction and the optical index (a), between the adsorbed volume fraction and the relative pressure P/P$_S$ acording the Lorentz, Bruggeman and linear approximations (b).

Porosimetry experiments can be deeply affected without control of pressure and temperature. Moreover, the choice of the right temperature enhances and optimizes the data accuracy's. This effect is demonstrated here in two applications of the technique.

Fig. 6 : Isotherms for two temperatures 28 °C and 52 °C (a) versus P, (b) versus P/P$_S$: the two isotherms are identical

Surface adsorption of ethanol on Si substrates
The BET equation (Fig. 9) is not adapted for reproducing the measurements.
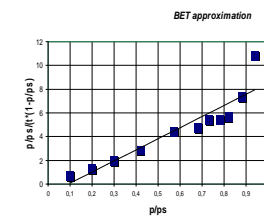
Fig. 9: BET plot of experimental results of Fig.10
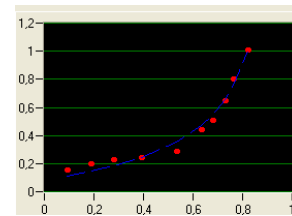
Fig. 10: Thickness of ethanol adsorbed on a Si substrate versus P/PS

The experimental t-curves of ethanol adsorbed on a silicon wafer are reported on figures 10 and 11 with a fit using the Halsey general form of the surface energy potential. It traduces the difference in chemical potential between the film and the bulk liquid in term of   the Van der Waals dispersion energies. Adsorption at two temperatures are reported, figure 11, showing that only a 5 °C temperature difference affects considerably the t-curve behaviour.   The reproductibility of the experimental data is reported on figure 12.
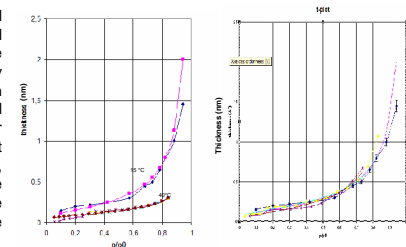
Fig. 11: Thickness of ethanol adsorbed on a Si substrate at two temperatures

Fig. 12: Reproducibility of experimental results

Fig. 7: DR plot for a microporous sample in the low pressure regime

Fig. 8: Same as Fig. 7 at two temperatures

In the case of the theory of surface adsorption, recent developpments demonstrate the powerness of EP: Adsorption has been reconsidered in term of fractal properties since then the number of molecules of size *a* in the range required to cover the surface with a monolayer is

N=C a^{-D}

where D is the surface fractal dimension (2<D<3) and C the Hausdorf measure of the surface. Data can be then analyzed through the fractal generalisation of the FHH isotherm.
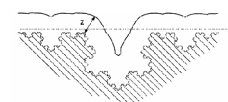
Fig. 13: Equipotential surface generated by a fractal substrate.It represents the film vapor interface in absence of surface tension

Conclusions

We emphasized the important role of the monitoring of the temperature during these experiments. The pressure stability realized in our system enables accurate measurement for pressure steps as low as 10^{-3} Torr in the cell as shown in the screen display here in (on the right).

We have shown also that the analysis of surface adsorption on a substrate is the reference to calibrate the equipment (beside the choice of a specific porous reference material which is difficult to consider as an intrinsic invariant material.)

Surface adsorption characterized by EP is also a powerful tool to study the surface fractal dimension of any material which can then be co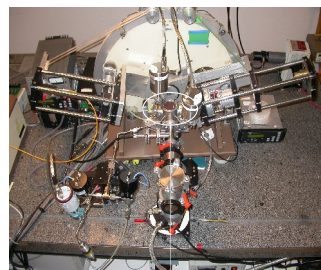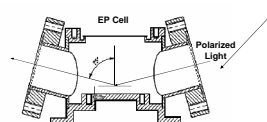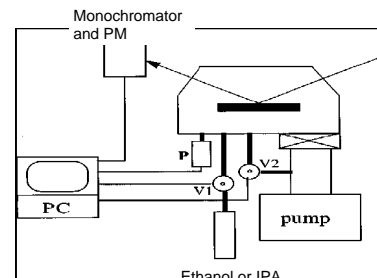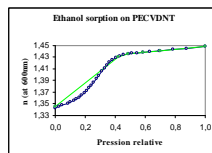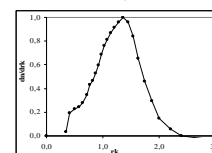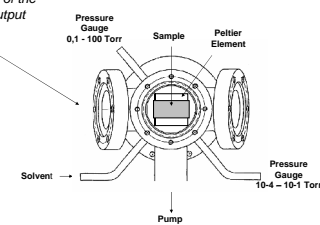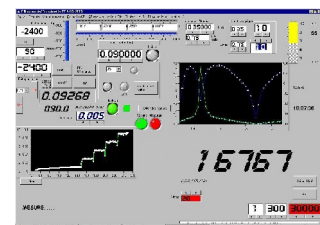rrelated to roughness and will be a future endeavour.