Low-coherence interferometry measurement of capillary filling in porous silicon

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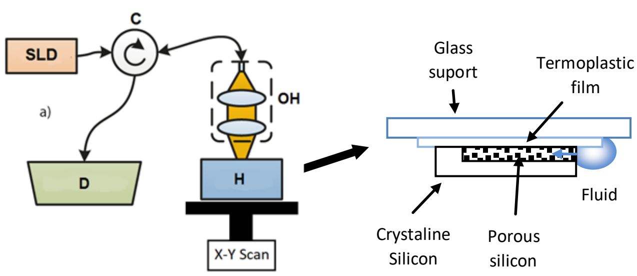
Abstract: *The determination of capillary filling dynamics in nanoporous structures and, in particular, the analysis of the filling fraction profile in the advancing wet front have been proposed as possible methods for characterizing the pore distribution of these structures. Furthermore, the filling dynamics in nanoporous structures of known morphology allows studying fluid properties under conditions of strong spatial confinement. In this work we determine the capillary filling dynamics of porous silicon structures using low-coherence interferometry. When the liquid enters the porous structure there is an increase in the optical thickness of the layer. The determination of optical thickness as a function of position and time allows monitoring capillary filling dynamics. The high spatial resolution of this technique allows to analyze the wet front broadening, which can be used to obtain information about the pore distribution in the sample.*

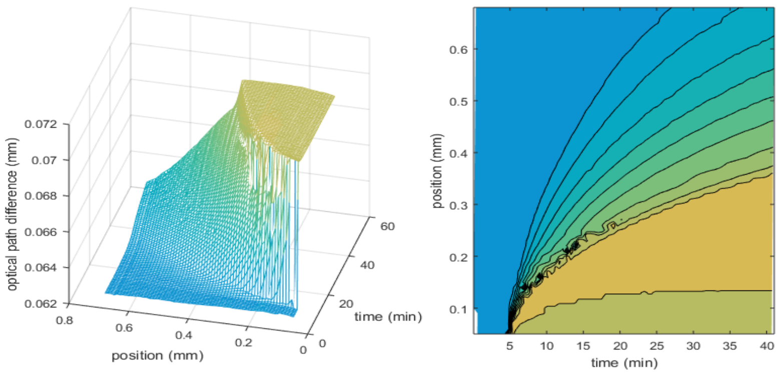
Key-Words: *low-coherence interferometry; porous silicon capillary filling; wet front broadening porosimetry*

Introduction: The imbibition of fluids in structures with nanoscale dimensions provides an elegant and effective way to propel nano-flows. It can also be exploited to explore the rheology of liquids in spatial confinement and under very high shear rates [1] or characteristics of the imbibition geometry at the nanometer scale [2]. Moreover, it is now frequently employed for the synthesis of novel hybrid materials [3]. In many applications it is important that the nanoporous medium infiltrates homogeneously, without empty pore segments created during the imbibition process. However, many nonporous media have a complex geometry that results in variations of the local bulk hydraulic permeability and in the capillary pressure at the moving interface, giving a broadening of the imbibition front and thus the coexistence of empty and filled pore segments during the imbibition process. Extensive simulations of spontaneous imbibition in networks of elongated pores with random radii show that the scaling relations for the front broadening result proportional to the position [4]. This demonstrates also that, analogous to the analysis of the pure front propagation [5], an analysis of the broadening of the imbibition front can yield important, otherwise hardly accessible, information on the pore geometry of the considered porous medium. Creating a measurement technique that allows the precise determination of the shape of the liquid advancing front would allow for a better understanding of these aspects.

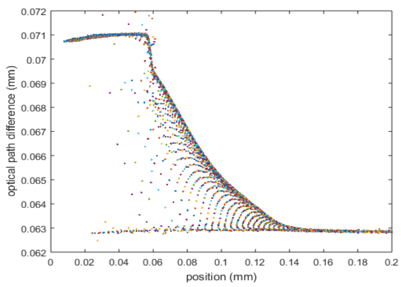
Experimental: The experimental setup consists in a single-branch interferometer that uses a wide-spectrum laser (~100 nm, centered at 800 nm) as a light source, a fiber optic system and an UV-VIS-NIR spectrometer (Ocean Optics HR4000) as a detection system; a schematic representation is shown in the figure below. The interference signal is generated by the superposition of the reflections in the different interfaces of the sample and a reference reflection. From the analysis of this signal it is possible to measure the optical path difference traveled by the beam through the sample. The porous silicon (PS) membranes were obtained by electrochemical anodization of crystalline silicon, p-type [100], 1-5 mOhm.cm in a solution of hydrofluoric acid and ethanol (1 HF (50%):2 EtOH). We prepare 30 µm-thick layers with porosities between 50% and 90%. The sample was sealed at the top with a film of ethyl-vinyl acetate (EVA) by controlled heating of the thermoplastic, as can be observed in the figure. The working fluid in the experiments was ethanol.



Results and discussion: The interference pattern acquired by the spectrometer was analyzed by means of a Fourier treatment and a reflectivity profile of the sample was reconstructed. This resulted in information on the optical path difference that could be used to obtain the thicknesses of the sample interfaces [6]. These values were processed with the help of specially developed software that allowed the generation of the corresponding image of the topography and tomography of the studied sample. Successive measurements were taken in a single line perpendicular to the edge of the sample as liquid fills laterally (i.e. in the direction perpendicular to the pores) the porous layer by capillary action. The entrance of liquid was evidenced as an increase in the optical thickness of the PS membrane. Points were taken every 10 microns along a total length of about 800 microns. The time for each sweep was approximately 30 s. From these profiles we built a 2D graph to represent the liquid front position as a function of time and position in the PS layer (see figure below, at left and center). The figure shows a liquid saturated region that advances at a decreasing rate over time. This zone is preceded by an intermediate filling region that widens as the liquid advances. These results indicate that the dynamics follows a Washburn type behavior ($x \propto t^{1/2}$) characteristic of the capillary filling of homogeneous structures. A pronounced widening of the advancing fluid front was also observed, which is due to the highly interconnected pore morphology in the PS structure.



If the optical profiles are normalized to the root of the evolution time all measurements collapse to a single master curve (see figure below) indicating that the liquid front broadening is proportional to the front position. This information can be useful to determine the porous distribution of the PS layer.



Conclusion: The low coherence interferometry technique presented here offers the possibility of studying time resolved capillary filling phenomena with high spatial resolution. The results indicate that the filling dynamics in nanoporous silicon follows a typical Washburn behavior ($x \propto t^{1/2}$). A pronounced widening of the advancing front is condensed into a master curve that only depends on position and could provide valuable information about the morphology of the PS structure.

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