ESRF	**Experiment title:** In-situ investigation of the foaming of nanoporous SiOCH thin films by GISAXS	**Experiment number**: MA-3031
Beamline: BM02	**Date of experiment**: from: June. 24th, 2016 to: June. 27th, 2010	**Date of report**: May 10th, 2017 *Received at ESRF:*
Shifts: 9	**Local contact(s)**: Mireille Maret*	

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Report:

Framework of the Project :

Ultra Low-κ films deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) have been introduced as dielectric in ULSI interconnects for 10 years. Generally, porous SiOCH films are deposited through a subtractive strategy. This approach is based on the co-deposition of an organosilicate precursor with an organic porogen molecule during the PECVD process. After deposition, the sacrificial porogen is removed during an appropriate thermal treatment, creating porosity. A maximum of 50% of porosity can be obtained by this method. Furthermore, the pore radius is difficult to vary (and is always close to 1 nm). Recently, we have discovered that porous SiOCH thin films can be obtained by covering a non-porous SiOCH thin film by a dense capping layer (as a crust, using for instance SiO_2). The stack is then annealed at high temperatures (typically between 400 and 600°C). When the temperature is high enough to slightly degrade the organic part of the skeleton, the gas cannot exhaust due to the crust and thus coalesce to produce bulk porosity in the thin film. This method (a foaming process) was demonstrated recently for SiOCH thin films leading to porosity up to 70% (i.e. considerably beyond the accepted limit (~50%) of actual porous SiOCH by PECVD). To characterize such huge porosity and understand its formation, further investigation in these new foams is required.

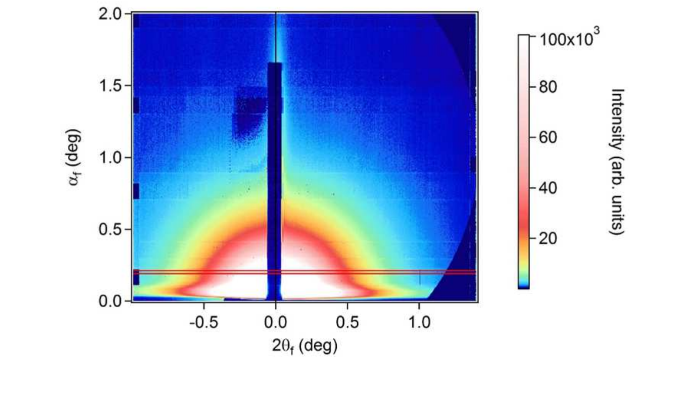
Experimental method and strategy :

Grazing Incidence Small Angle X-Ray Scattering (GISAXS) is certainly the best appropriated technique since it allows characterizing the internal structure of such porous films capped by a “crust” layer, while this is impossible by Ellipsometry-Porosimetry. However, to our knowledge, such characterization technique for studying porosity is seldom used because radiation synchrotron is mandatory. In this experiment, we have studied the porosity of SiOCH thin films (on Si substrate) fabricated using different approaches: porogen approach vs foaming, different pore diameters (from 1 nm to a dozen of nanometer), different porosity rates (from 5 to 70 %). Moreover, we have performed in-situ GISAXS measurements during the annealing process in order to better understand the porosity evolution during a foaming process. For it, measurements were performed between room temperature and 700°C under an inert atmosphere, using a thermal oven compatible with GISAXS measurements.

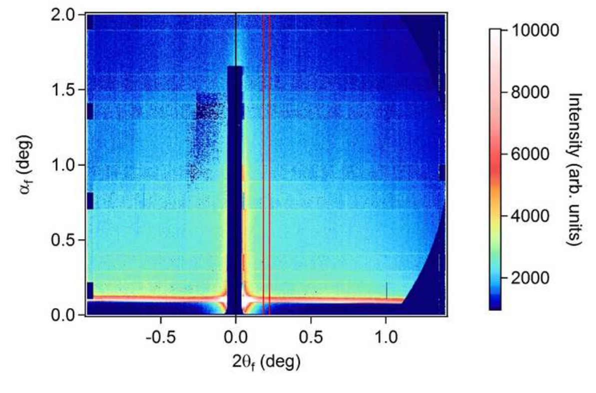
Results

<u>Ex-situ experiments:</u> Tests were performed on the BM02 beamline and ~ 30 different samples were measured. Fig. 1 shows examples of GISAXS pattern obtained for a foaming sample (figure 1a, 63 % porosity) and for a porous SiOCH deposited using a porogen approach (figure 1b, 25% porosity). Log-normal distributions of the lateral and vertical pore sizes are shown in Fig 2 (analyses performed using FitGISAXS software).

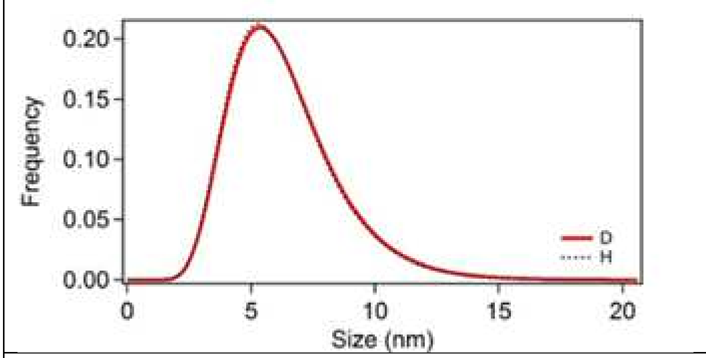
It's worth noting that the foaming samples are very difficult to measure using Ellipsometry-Porosimetry (EP, another common technique to probe porosity of porous thin films) because the film is swelling during the solvent adsorption isotherm, preventing an accurate use of the Kelvin model (giving access to the mean pore size and pore size distribution). Therefore GISAXS appears to be the unique method to accurately characterize the porosity of these thin films. In the case of SiOCH deposited using the porogen approach, the mean pore size is in good agreement with EP results. In this case, GISAXS gives access to information on the total porosity while EP only takes into account the "open" porosity accessible to the probe molecule used during the experiment (usually toluene).



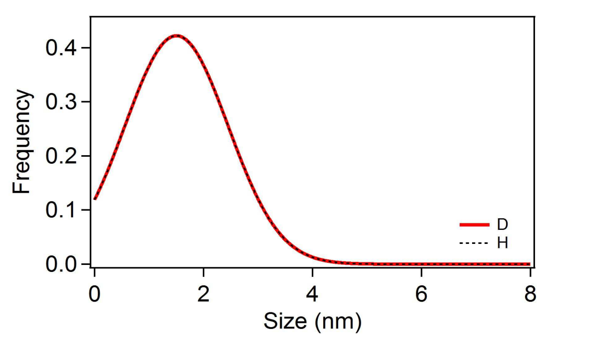
a) Scattering picture of a SiOCH thin film deposited from OMCTS and foamed for 9 minutes.



b) Scattering picture of a SiOCH thin film deposited using the porogen approach.



c) Mean pore size and pore size distribution for the foamed sample



d) Mean pore size and pore size distribution for the sample performed using a porogen approach

Fig 1. Experimental scattering pictures of porous SiOCH films and pore size distribution deduced from simulation.

<u>In-situ experiments</u>: Several experiments were performed from room temperature to 700°C to understand the evolution of the porosity during a thermal annealing and to characterize the foaming process when a crust is deposited on top of the SiOCH thin films. Unfortunately, the presence of the dome during the in-situ GISAXS experiments complicates (even prevents) the interpretation of the results. The dome signal is so broad (whatever the nature of the dome used (PEEK vs graphite) that the study of small variations of porosity in-situ during a thermal annealing remains very complicated.

Figure 2 shows examples of the GISAXS scattering pictures with or without the dome (PEEK).

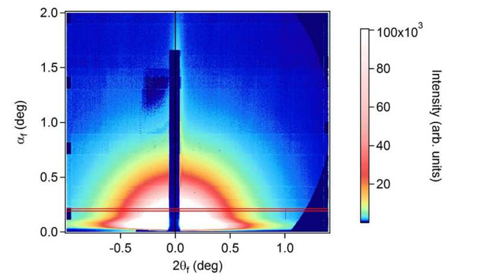
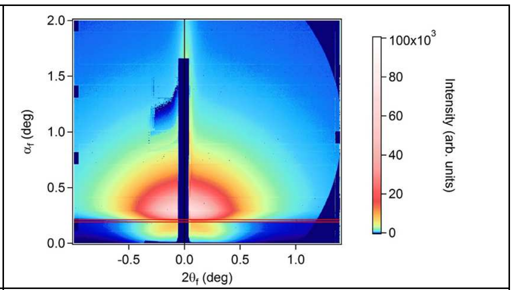
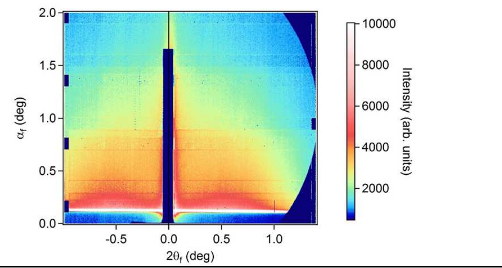
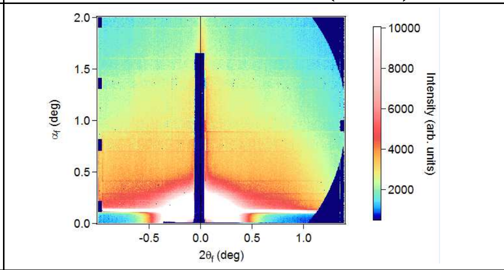
	
a) Scattering picture at room temperature of a foamed SiOCH without dome	b) Scattering picture at room temperature of a foamed SiOCH with dome (PEEK)
	
c) Scattering picture at room temperature of a porous SiOCH annealed at 700°C, without dome	d) Scattering picture at room temperature of a porous SiOCH annealed at 700°C, with dome (PEEK)

Fig 2. Experimental scattering pictures at room temperature of porous SiOCH films with or without the dome.

Finally, several experiments of in-situ annealing were performed on different SiOCH thin films, then GISAXS was performed at room temperature without dome. This allowed us to carefully study the variation/creation of porosity “quasi-in-situ”. Figure 3 shows an example of movie realized.

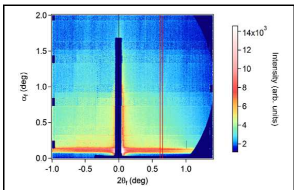
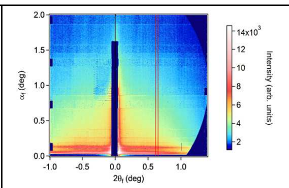
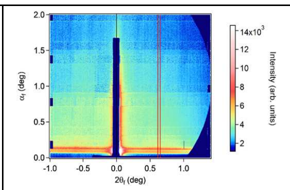
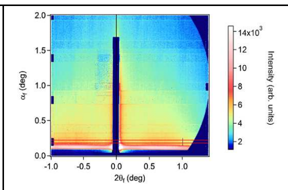
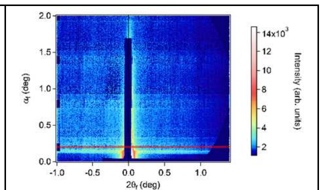
				
Annealed at 450°C	Annealed at 500°C	Annealed at 550°C	Annealed at 600°C	Annealed at 700°C

Fig 3. Experimental scattering pictures at room temperature of a porous SiOCH film after an in-situ annealing.

In this case, slight variations are observed in the evolution of the porosity and the use of a 2D detector allows the study of anisotropy in the pore network and pore shape that occur during the annealing (in this case, the pore shape evolves from sphere to flat spheroid upon annealing). Part of these results were presented at the 2017 MRS spring meeting (S. Beaurepaire et al., “Thermal Stability of low-k dielectrics for 3D Sequential Integration”).