

Gemini-templated PMO low-k films

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The application of self-assembling chemistries is considered as the most promising porosity scaling strategy for low-k films for sub 10 nm technology nodes. [1] Periodic mesoporous organosilicas (PMO) are materials that are synthesized through the sol-gel method in which a hydrolysable bis-silane (e.g. R'OSi-R-SiOR') polycondensates around sacrificial self-assembled surfactant molecules. Consequently, PMOs have chemical composition similar to the currently employed low-k materials with the distinct feature of bridging organic (Si-R-Si, R=(CH₂)_n, Ph, etc.) groups. As a result, they have been shown to possess superior chemical and mechanical stability. [1] [2] Therefore, their attractiveness for low-k application has grown in the recent years.

We report the synthesis of PMO films containing Si-CH₂-CH₂-Si (ethylene) bridging group and templated by Gemini 16-12-16. The surfactant was synthesized according to the procedure described in [3]. The films were prepared through the evaporation induced self-assembly (EISA) mechanism [4] by spin-coating the solution at a rate of 5000 rpm onto a Si coupon. After drying for 120 h in ambient conditions, the films were heated to 400°C with a heating rate of 1°/min and kept at this temperature for 2 hours under N₂ to remove the template. The characterization was performed by toluene ellipsometric porosimetry (EP), Fourier-transform infra-red (FTIR) spectroscopy, nanoindentation (NI), symmetric and asymmetric x-ray diffraction (XRD) and grazing-incidence small angle x-ray scattering (GISAXS) at the Austrian SAXS beamline of the storage ring ELETTRA (Trieste, Italy).

FTIR investigation (Fig. 1) reveals the presence of ethylene groups inferred from the peaks at 1419, 2895 and 2918 cm⁻¹. Additionally, existence of Si-OH groups is evident from a sharp peak at 3734 cm⁻¹. The obtained films are calculated to have a porosity of ~50% and a narrow pore size distribution centred around 2 nm (Fig. 2). Nevertheless, since the hydrophilicity due to the silanol groups is expected to have detrimental effect on the chemical and electrical performance the films were hydrophobized by a vapour-phase reaction with N,N-dimethylaminotrimethylsilane (DMATMS) at 250°C. The treatment successfully caps the Si-OH groups (Fig. 1) but it also leads to considerable reduction in open porosity resulting in ~42% porous films (Fig. 2). On the other hand, asymmetric XRD investigation results in a diffraction peak from planes spaced at 2.64 nm (Fig. 3) indicating the presence of ordered pores for some of the samples. The latter was confirmed by SAXS measurements which further indicate 2D hexagonal organization of the pores (Fig. 4). Nevertheless, for some of the films a halo rather than a diffraction peak is observed while SAXS experiments result in a Debye ring reflecting the narrow pore size distribution leading to the conclusion that the pores are organized in a so-called wormhole-like manner. [5] Notably, a comparison of the Young's modulus values obtained for the film with ordered pores and that of disordered pores supports the expectation [6] that ordered pores lead to improvement of Young's modulus (Fig. 5). The latter is not due to difference in density supported by FTIR, EP and SAXS. Therefore, a relative dielectric constant of 2.3 is calculated at 100 kHz for both films. Finally, the ambient humidity is shown to have an impact on the surfactant self-assembly. (Fig. 6)

References

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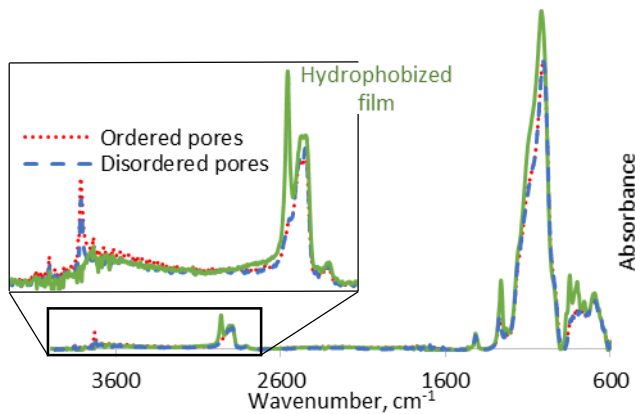


Fig. 1. There is no difference in the chemical composition of the films with ordered and disordered pores. Silylation is effective in capping the Si-OH groups

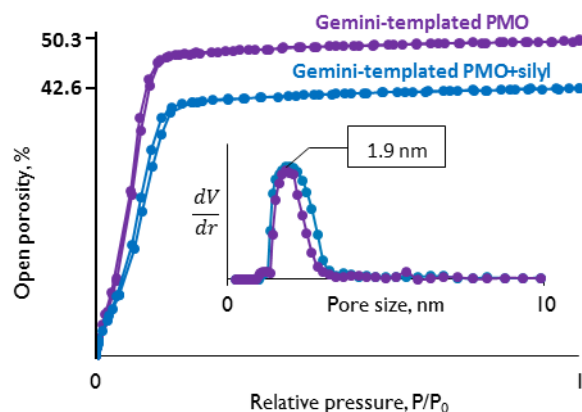


Fig. 2. Open porosity is reduced by the silylation with no effect on the pore size distribution

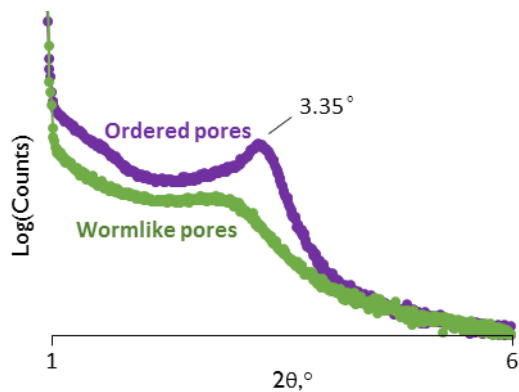


Fig. 3. One of the films produced sharper XRD peak indicating parallel planes spaced at 2.64 nm

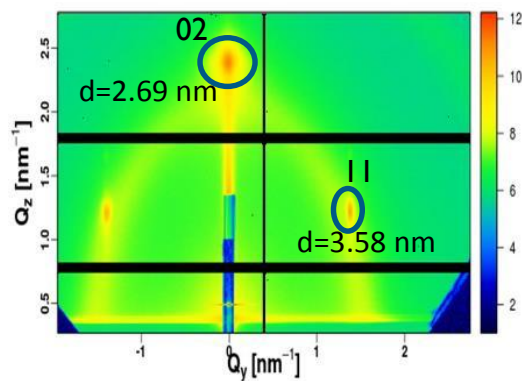


Fig. 4. SAXS investigation revealed 2-D hexagonal pore organization distorted in the z direction due to shrinkage

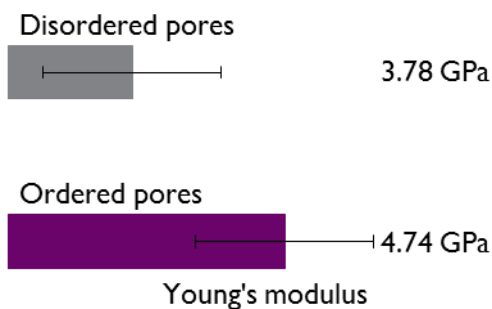


Fig. 5. The observed pore organization increases Young's modulus by ~ 1 GPa

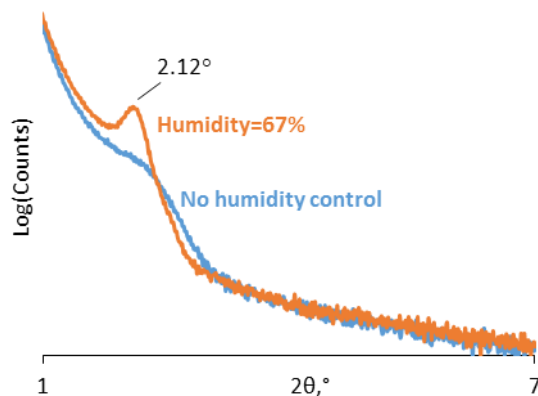


Fig. 6. Control of relative humidity allows for tuning of the template self-assembly