

Comparative evaluation of porous PMO materials by PAS and EP

A. G. Attallah^{1,*}, A. S. Vishnevskiy², M. O. Liedke¹, E. Hirschmann¹, M. Butterling¹, D. S. Seregin², A. A. Rezvanov², K. A. Vorotilov², M. R. Baklanov^{2,3} and A. Wagner¹

¹*Institute of Radiation Physics, Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstrasse 400, 01328 Dresden, Germany*

²*RTU MIREA—Russian Technological University, Prospect Vernadskog78, Moscow 119454, Russian Federation*

³*Molecular Electronics Research Institute, Akademika Valieva 6/1, Zelenograd, Moscow 124460, Russian Federation*

⁴*North China University of Technology, No. 5 Jinyuanzhuang Road, Shijingshan, Beijing 100144, Beijing, China*

*email: a.elsherif@hzdr.de

In this work we explored the effect of varying the molar ratio of terminal methyl (M) to bridging organic (1,4-benzene) (B) groups on the porosity and critical properties of periodic mesoporous organosilicates (PMO)-based low dielectric constant thin films. The porosity was introduced to the system by adding 30% sacrificial porogen. Positron annihilation spectroscopy (PAS), Ellipsometric Porosimetry (EP), and Fourier Transform Infrared spectroscopy (FTIR) have been used to characterize the porosity and chemical composition of the investigated films.

Positronium (Ps) lifetime showed that the matrix free volumes are negligibly affected but there is a dependence of the mesoporosity on the ratio of M/B. When M/B=100/0 (no benzene group), the size of the created mesopores approaches ~ 8nm. The $3\gamma/2\gamma$ ratio of Doppler broadening spectroscopy indicated that the pores are interconnected due to porogen clustering during curing in the low mechanically stable structure. Such an interconnectivity disappeared when 25% B (M/B=75/25) was added as the Ps lifetime probed ~ 2nm only. This 2nm-pores have increased to and stabilized at 2.3nm for M/B=55/45, 40/60, and 0/100. In comparison with a 0% porogen sample, possibly the mesopores in the 30% porogen samples are created by micropore collapse. The Ps intensity grows from 10% to 25% when B increases from 0 to 60% representing an increase in the porosity as we detected no *o*-Ps migration between pores. The Ps intensity dropped to ~15% at M/B=0/100 which means that the porosity is expected to be lower as compared to samples with smaller amounts of B.

EP data showed that the films deposited without porogen have intrinsic porosity related to large size of terminal methyl and benzene bridging groups. The measured porosity was equal to 10% (B) and 8% (M). The B films have very narrow pore size distribution with size about 0.7 nm. The M film has wide pore size distribution from 2 to 5 nm. The porogen (30%) increases porosity up to 25-30%. The pore size gradually increases with M concentration in the hybrid film (B+M). The data generated by PAS and EP are reasonably consistent and complementary.

FTIR analysis clearly shows higher hydrophilicity of benzene bridge rich films. Although the benzene bridged films had better mechanical properties, they have higher dielectric constant because of their hydrophilicity (presence of adsorbed moisture) and also higher polarizability of benzene groups.

In conclusion, it can also be noted that PAS and EP confirm their effectiveness for studying the porous structure of thin layers, and their combination allows a better understanding of the nature of these materials.