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Positron Annihilation Lifetime Spectroscopy (PALS) on Advanced, Self-Assembled Porous Organosilicate Glasses

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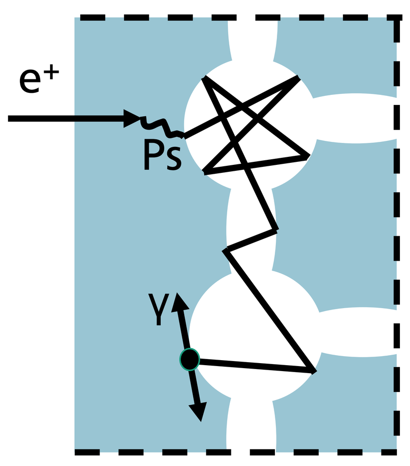
Motivation

The dielectric material, necessary for insulation and packaging of on-chip wiring in microelectronics, causes capacitances and signal delays, which ever increase with continuing minimization down to the nanoscale. The root cause for the capacitance is the permittivity, also called dielectric constant or k-value. The aim is to reduce the permittivity to a minimum in order to make further down-scaling possible and keep up the pace of structure integration. It seems that the only viable approach to decrease the k-value below 2.2 is to introduce a significant amount of porosity into the dielectric material. Porous organosilicate glasses (OSGs) are promising materials to serve these requests. Concurrent with the introduction of porosity, the mechanical properties substantially deteriorate and are a great concern for chip reliability. In this work, self-assembled organosilicate glasses with varying k-values down to 1.8 are investigated by positron annihilation lifetime spectroscopy (PALS) to assess the pore size. By self-assembly, the pore structure is ordered and allows higher mechanical strength at the same porosity level compared to non-ordered pores.

Method

The PALS measurements were performed at the positron laboratory EPOS at the electron linear accelerator with high brilliance and low emittance ELBE at the Helmholtz-Zentrum Dresden-Rossendorf. The monoenergetic positron beam is pulsed and has a high repetition rate and intensity. The positrons are created by pair-production at a tungsten target. During the monoenergetic positron spectroscopy (MEPS) measurements, the energy of the positrons was tuned between 0.5 and 12 keV with corresponding penetration depths up to 2 microns, ideal for the study of the thin films.

Below: Schematic of a positron forming positronium and annihilating in a pore



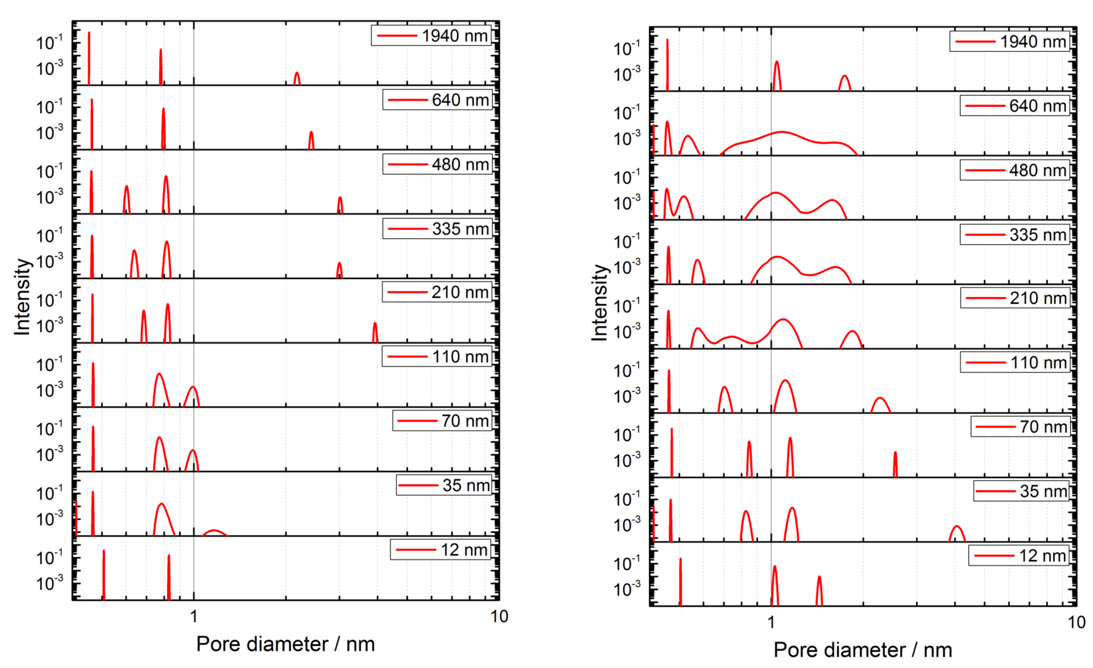
Material

The organosilicate glass is prepared by a sol-gel template synthesis [1]. Silane precursor sols are deposited by spin coating on a silicon substrate. The porogen consists of amphiphilic triblock copolymers which act as labile blocks and are evaporated upon thermal curing. The self-assembly process forms uniform nanopores with a narrow pore size distribution. Films with thickness of about 500 nm were produced with varying porogen loading, leading to varying porosity from upper limits of 25% to 50% and k-values from 2.4 to 1.8.

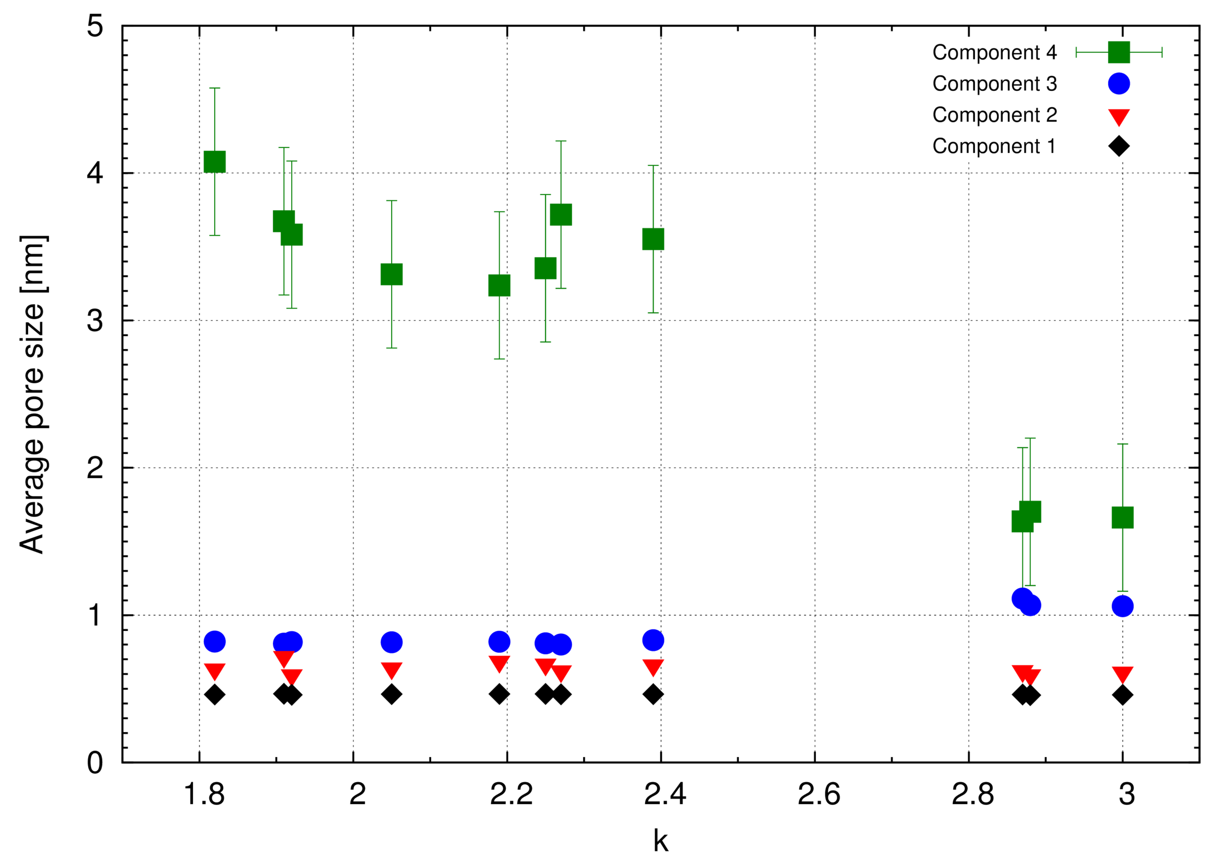
Dielectric constant k	Porosity
1.82	< 50%
1.91	< 42%
1.92	< 42%
2.05	< 42%
2.19	< 32%
2.25	< 32%
2.27	< 32%
2.39	< 25%
2.87	0%
2.88	0%
3.0	0%

Results

k = 2.05 (porous) k = 3.0 (nonporous)



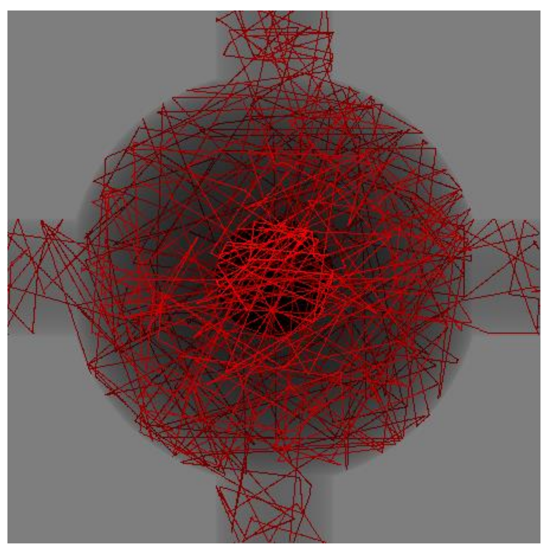
Left: Intensities of the pore components as derived from the PALS measurements, representative for the porous and nonporous OSG samples. The plots are stacked for different positron penetration depths. Pore components below 1 nm are attributed to matrix effects and open volume in the glass matrix and carry no information about the pore structure. The peaks between 2 and 4 nm correspond to the intentionally put in pores. The pore diameter was calculated from the lifetimes using the extended Tao-Eldrup model [2,3].



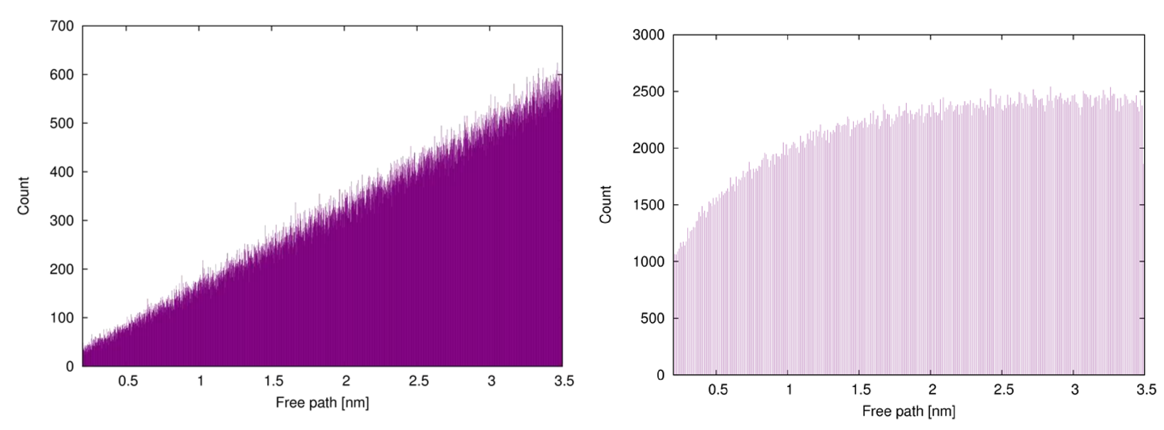
Left: Results of the pore size measurement. The average pore size (component 4) is between 3 and 4 nm for the porous samples. As reference, also dense OSG with k-values of 2.9 to 3.0 was measured. Here the component 4 is attributed to another open volume in the glass matrix. The average was taken over positron penetration depths from 200 nm to 500 nm.

Simulation of the Ps trace

Right: Modeled Ps trace in a single 3D pore with periodic boundary conditions and connections to the front, back, bottom, left and right. For practical reasons, only 500 reflections are shown. The pore diameter is 3.5 nm and the total connection length is 1 nm. The diameter of the connection is 1 nm.



Challenge in simulation



Further left: Theoretical distribution of free paths in a spherical 3.5 nm pore. Left: Corresponding distribution from the simulation with deviations from linearity due to discretization. Some paths are forbidden and the counts for allowed paths are higher. This effect needs to be well understood in order to derive conclusions about the mean free path from the simulation.

Conclusion

- 4 PALS lifetime components were measured for each sample (k = 1.8 – 3.0)
- Component 1 and 2: attributed to non-pore related effects
- Component 3: open volume in the glass matrix (0.8 – 1.1 nm)
- Component 4: porous: intentional pores (3 – 4 nm), nonporous: another open volume glass matrix component
- Component 3 densifies from nonporous (k ≥ 2.9) to porous (k < 2.4)
- The large pore diameter (component 4) remains relatively constant, indicating good process control in the porous films

References

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