

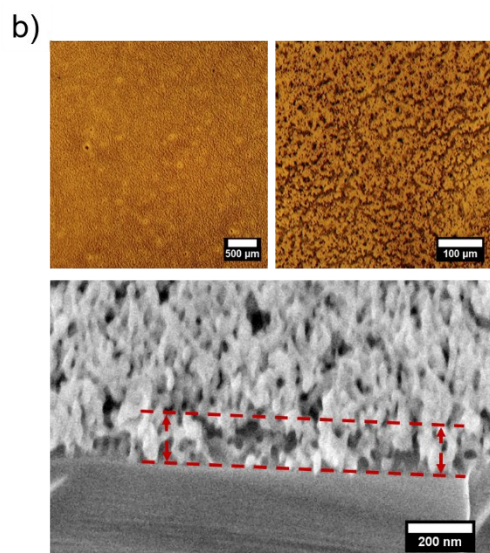
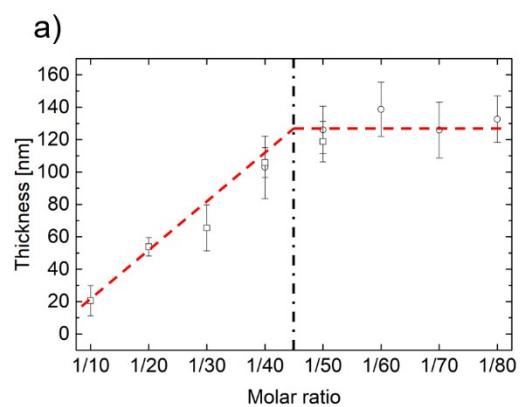
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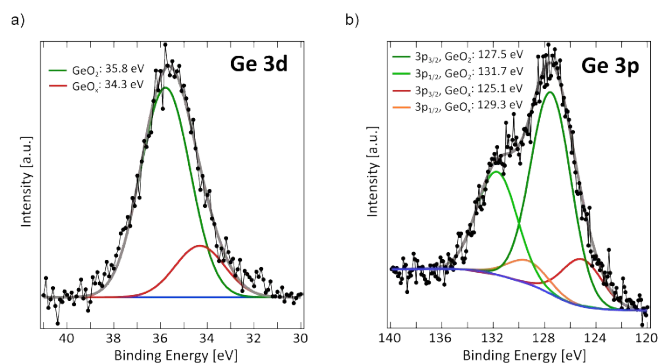


# Supporting information: Amphiphilic diblock copolymer-mediated structure control in nanoporous germanium-based thin films

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To probe the thickness of nanoporous Ge-based thin films, profilometry measurements with a DektakXT™ apparatus by Bruker are carried out on films prepared from precursor solutions with molar ratios in the range from 1/10 to 1/80. Corresponding results are depicted in **Figure S1a**. The red dashed line serves as a guide-to-the-eye. Accordingly, the thickness increases up to an approx. molar ratio of 1/45. An increase of the  $K_4Ge_9$  precursor content above this ratio leads to no further thickness increase as polymeric domains are over-saturated with the precursor  $K_4Ge_9$ .

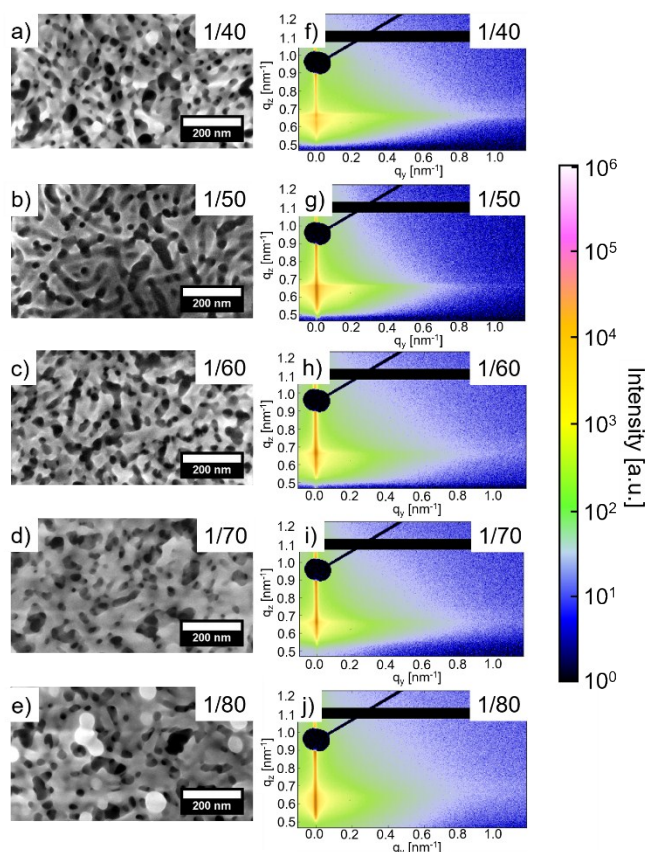
Surface characterization of fabricated nanoporous Ge-based thin films is carried out via an Axiolab A microscope by Carl Zeiss, which is coupled to a CCD camera. Respective images are shown in Figure S1b. At lower magnification a rather homogeneous film is observed with only few impurities. However, at higher magnification indications for a foam-like surface with high surface roughness can be seen. In order to prove that the observed foam-like structured is not only retained at the surface, cross-section SEM images are acquired. As observed for an exemplary molar ratio of 1/50, the whole film consists of nanoporous Ge-based material with a thickness of approximately 120 nm.



**Figure S2.** XPS spectra of the Ge 3d and Ge 3p core-level regions with a) two Gaussian curves and no spin-orbit split components and b) four Gaussian curves with spin-orbit doublets used for fitting and to account for the possible presence of  $\text{GeO}_x$  (red and orange lines) and  $\text{GeO}_2$  (dark and light green lines). For both fits a Shirley background is used (blue lines). Extracted positions of the respective Gaussian centroids are depicted in the legend.

The minimum estimated concentration ratio of O : Ge of 1.8 as determined from the intensity ratio  $I(\text{O } 1s):I(\text{Ge } 3d)$  of the survey scan in conjunction with the respective photoionization cross sections suggests the possible presence of incompletely oxidized Ge ( $\text{GeO}_x$ ). Therefore, an alternative XPS fitting with components for  $\text{GeO}_x$  and  $\text{GeO}_2$  can be found in **Figure S2**. Accordingly, for the Ge 3d core-level region two Gaussian curves with the same FWHM are fitted in Figure S2a. The fitting yields a FWHM of 2.5 eV, which is significantly larger than the neglected spin-orbit splitting of d levels (0.6 eV). Centroid positions of 34.3 eV and 35.8 eV are extracted for  $\text{GeO}_x$  and  $\text{GeO}_2$ , respectively. Positions of  $\text{GeO}_2$  match the expectation of 33.9 eV when accounting for the observed charging effects in the order of 2 eV.<sup>1-3</sup> A binding energy difference of 1.5 eV between  $\text{GeO}_x$  and  $\text{GeO}_2$  is determined, which is consistent with findings in literature.<sup>4-7</sup> An intensity ratio  $I(\text{GeO}_x) : I(\text{GeO}_2)$  of approximately 1 : 4 is determined, which indicates that mainly  $\text{GeO}_2$  is present as compared to  $\text{GeO}_x$ . This agrees with the estimation of concentration ratio from the survey scan. Ge 3p line analysis is performed using four Gaussian curves with the same FWHM (Figure S2b). A FWHM of 3.7 eV is determined, which is smaller than the fixed spin-orbit splitting of 4.2 eV. Therefore, spin-orbit doublets are accounted for through 2 additional Gaussian curves as compared to the Ge 3d analysis. Additionally, the intensity ratio of spin-orbit doublets is fixed to 2 : 1. For  $\text{GeO}_x$ , binding energies of 125.1 eV ( $3p_{3/2}$ ) and 129.3 eV ( $3p_{1/2}$ ) are extracted, which match theoretical values from literature (123.1 eV for Ge  $3p_{3/2}$ ) when considering the above mentioned charging effects ( $\sim 2$  eV). For  $\text{GeO}_2$ , binding energies of 127.5 eV ( $3p_{3/2}$ ) and 131.7 eV ( $3p_{1/2}$ ) are extracted, which again agrees with literature ( $>125.3$  eV for  $3p_{3/2}$ ).<sup>8</sup> In conclusion, XPS proves that the surface of the measured films primarily consists of  $\text{GeO}_2$ ; traces of incomplete oxidation

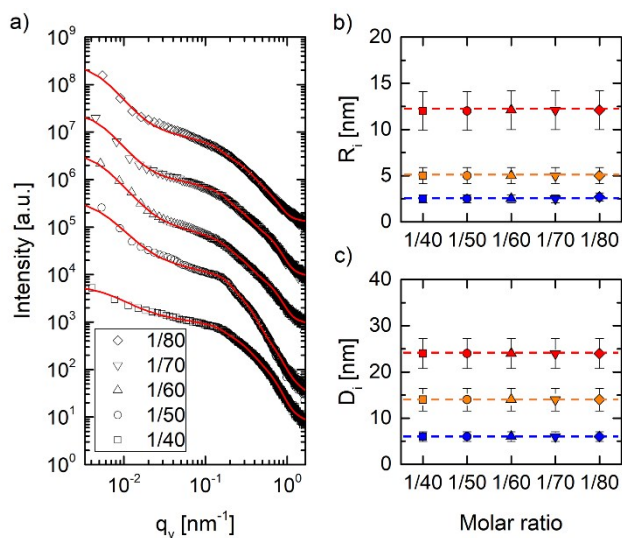
**Figure S1.** a) Thickness of nanoporous Ge-based thin films as obtained from profilometry measurements. Shown is the effect of different PS-*b*-PEO/ $\text{K}_4\text{Ge}_9$  molar mixing ratios on the final thickness of the thin film. Exemplary optical microscope images for a molar ratio of 1/50 are depicted in the top row of b). Cross-section SEM proves the existence of a fully nanoporous Ge-based thin film (from surface to substrate). An average thickness of approx. 120 nm is confirmed and is indicated by the red dashed rectangle.



**Figure S3.** a) – e) Scanning electron microscopy images of nanoporous Ge-based thin films with increasing molar mixing ratio from top to bottom as indicated in the inset. f) – j) Respective 2D GISAXS data as obtained at the MiNaXS beamline P03 at the PETRA III storage ring at DESY, Hamburg, is depicted on the right side showing no significant change for different molar ratios.

( $\text{GeO}_x$ ) appear possible as well, but cannot be confirmed with complete certainty due to insufficient resolution (1-1.3 eV). The observed large FWHM values might be additionally broadened by the rough morphology of nanoporous thin films. Surface characterization for an extended molar ratio range from 1/40 till 1/80 is additionally performed via SEM. Corresponding images are depicted in **Figure S3a** - e). The foam-like nanostructure is retained for all molar ratios. However, the formation of sphere-like aggregates can especially be observed for the highest molar ratio. As a possible explanation, the polymer domain is expected to be saturated with the precursor  $\text{K}_4\text{Ge}_9$ . Consequently, the polymer has no templating effect on the excess amount of precursor and an aggregate layer is formed on top of the nanostructured bottom layer.

For the same molar ratio range, samples are investigated via GISAXS at the MiNaXS beamline P03 of the PETRA III storage ring at DESY, Hamburg ( $\lambda = 0.94 \text{ \AA}$ , sample-detector distance = 4.377 m, incident angle =  $0.35^\circ$ , vertical beam size  $12 \mu\text{m}$ , horizontal beam size  $24 \mu\text{m}$ ). A Pilatus1M by Dectris Ltd. with a total of  $981 \times 1043$  pixels ( $172 \mu\text{m} \times 172 \mu\text{m}$ ) is used for data acquisition. Specular and direct beam are blocked by two beamstops to prevent oversaturation of the detector. Acquired 2D GISAXS images are shown in the right column for Figure S2.



**Figure S4.** a) Horizontal line cuts obtained from 2D GISAXS images of nanoporous Ge at the material specific Yoneda peak position for different molar ratios as indicated in the axis label. Through data modelling average predominant b) radii and c) distances of scattering centers are derived. The system appears precursor-saturated and no further indication for structural change is found.

At first sight, no apparent change in the 2D GISAXS images could be observed for different molar ratios.

For a quantitative analysis, horizontal line cuts are taken at the material specific Yoneda peak position of Ge (**Figure S4a**). As described in the main part, data modelling is performed and average radii and distances of scattering centers are extracted. In contrast to the low molar ratio regime in between 1/10 – 1/40, no indication for a significant change of radii and distances is found for the molar ratio range between 1/40 – 1/80 (**Figure S3b – c**). Consequently, the polymeric domain is assumed to be saturated with the precursor  $K_4Ge_9$  and additional precursor either leads to the formation of a spherical aggregate layer on top of the nanostructured bottom layer or is simply flung of the substrate during the spin-coating process, since there is no further thickness increase detected. Note that the horizontal line cut for the molar ratio of 1/50 exhibits a slightly more pronounced shoulder-like feature, which might be an indication for an improved periodic structure inside the thin film. Nevertheless, the  $q_y$  position is not significantly altered. A more detailed description of the employed model for horizontal line cut fitting has already been published.<sup>9</sup> In short, the differential cross-section for X-ray scattering is described as:

$$\frac{d\sigma}{d\Omega} = \frac{A\pi^2}{\lambda^4} (1 - n^2)^2 |T_i|^2 |T_f|^2 P_{diff}(\vec{q}) \sim P_{diff}(\vec{q})$$

with the illumination area  $A$ , wavelength  $\lambda$ , refractive index  $n$ , Fresnel transmission functions  $T_i$  and  $T_f$  and the diffuse scattering factor  $P_{diff}$ . The scattering factor is in turn described as:

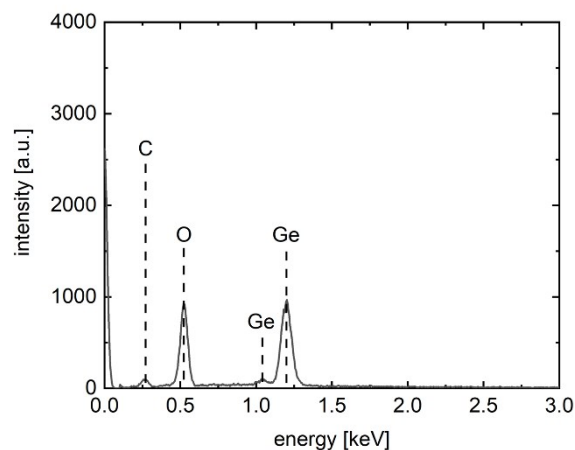
$$P_{diff}(\vec{q}) \sim N |F(\vec{q})|^2 |S(\vec{q})|$$

with the form factor  $F$ , the structure factor  $S$  and the number of scattering centers  $N$ . The form factor describes the form of the scattering object whereas the structure factor refers to the geometrical arrangement of scattering objects. A cylindrical form was used in the applied model as mostly cylindrical objects were observed via SEM.

Additional proof that the presented thin films are composed of the elements Ge, O and C remains is found via energy-dispersive X-ray spectroscopy measurements (EDX). **Figure S5** reports the respective results with Ge, O and C marked via dashed lines. The presence of a C-assigned peak is in agreement with the claim that unassigned peaks in XRD measurements might originate from germanium carbide phases. Note that the presented EDX results are measured on a drop-casted film with a molar ratio of 1/50 and a prolonged calcination protocol in air to be comparable to the results obtained via XRD.

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**Figure S5.** Energy-dispersive X-ray spectroscopy measurements on nanoporous Ge-based thin films calcined in air with peaks assigned to respective elements marked by dashed lines.