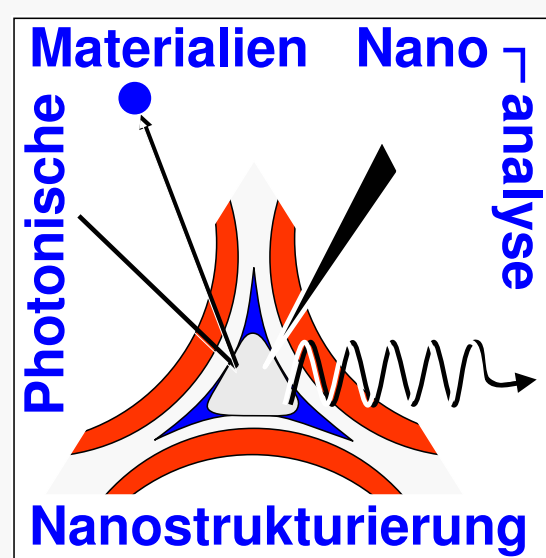


# Morphology investigation of nanopores by block copolymer lithography on different material surfaces



K. Brassat<sup>1,2,3</sup>, D. Kool<sup>1,2</sup>, A. Taube<sup>3,4</sup>, M. Schaper<sup>3,4</sup> and J. K. N. Lindner<sup>1,2,3</sup>

<sup>1</sup> Nanostructuring, Nanoanalysis and Photonic Materials group, Dept. of Physics, Paderborn University, Germany

<sup>2</sup> Center for Optoelectronics and Photonics CeOPP, Paderborn, Germany

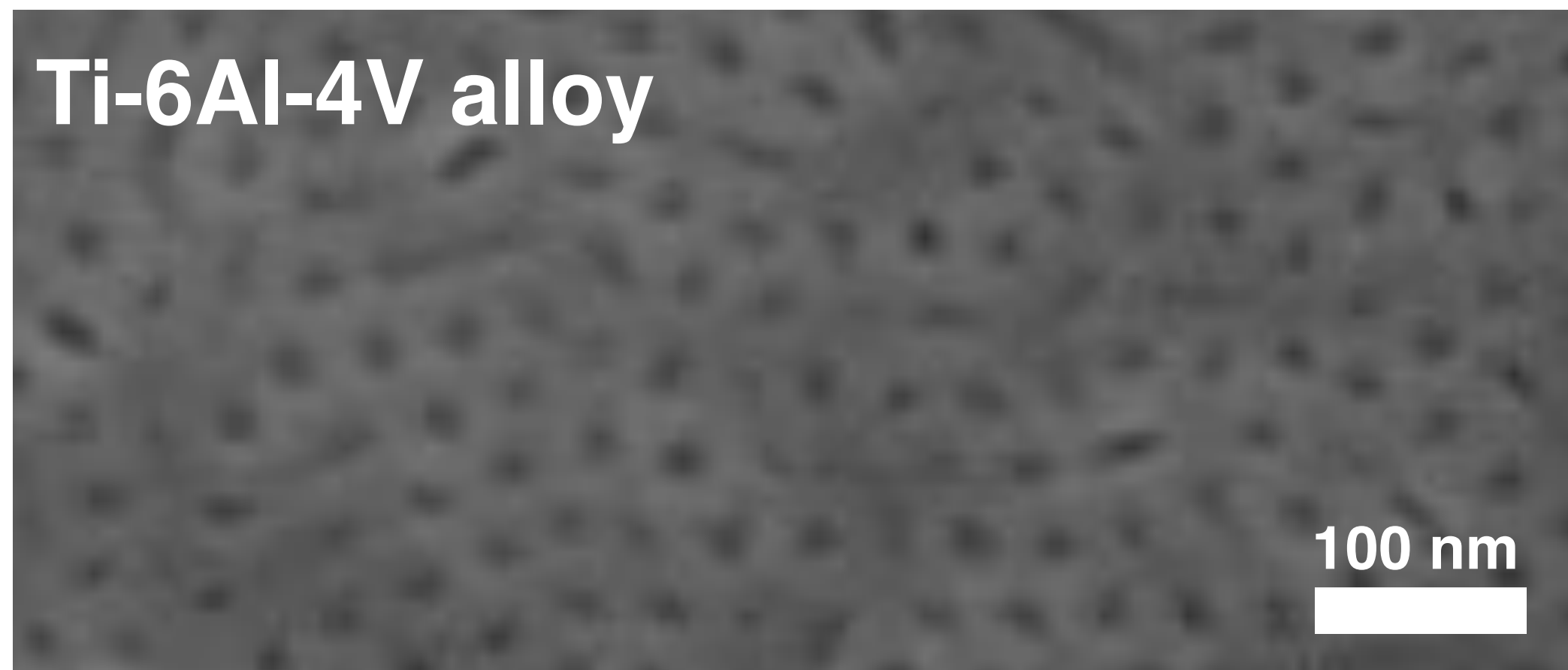
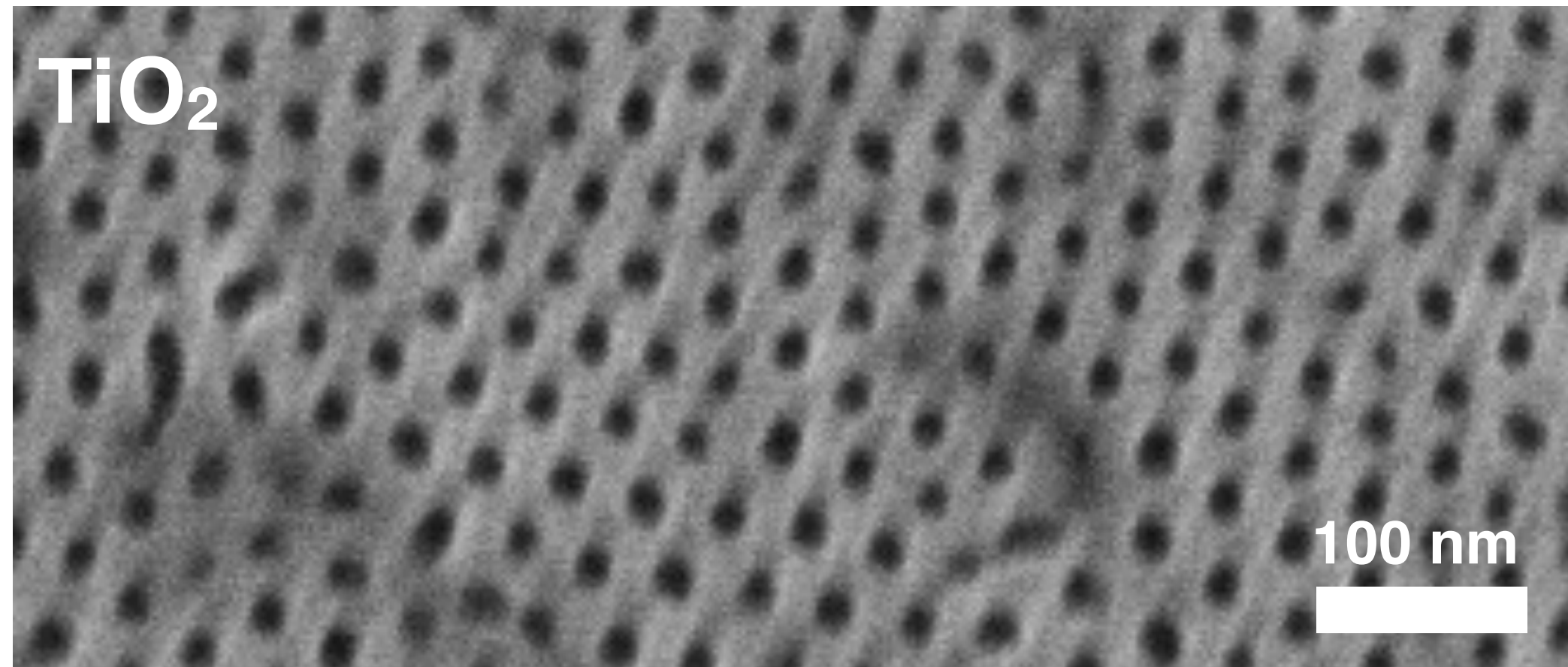
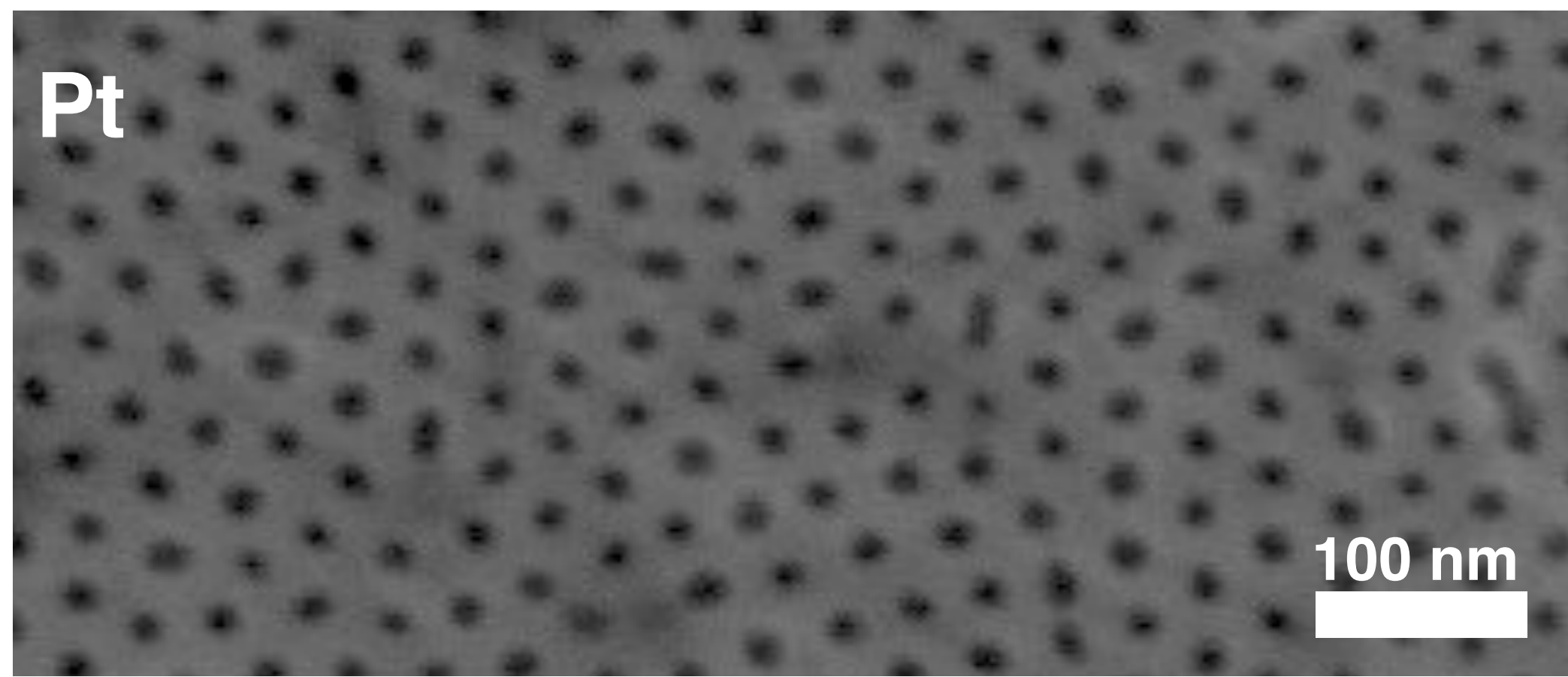
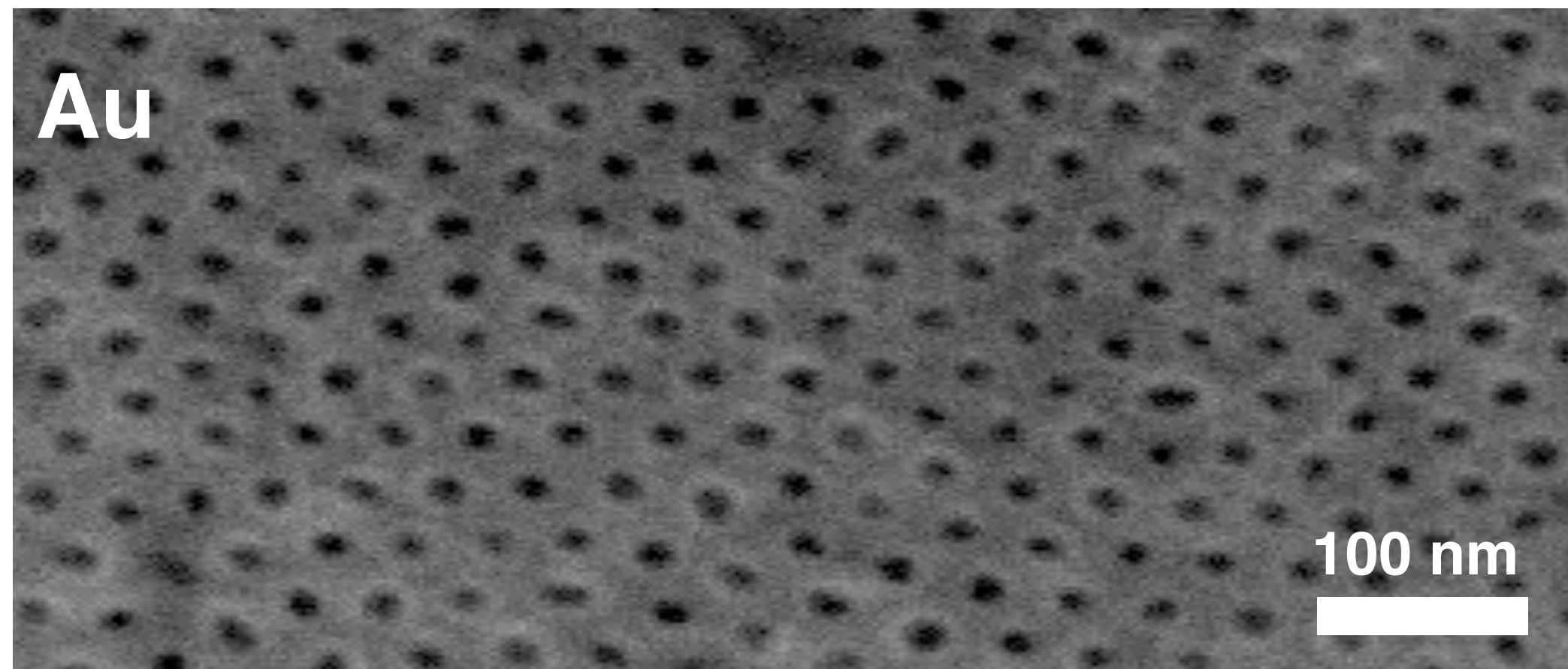
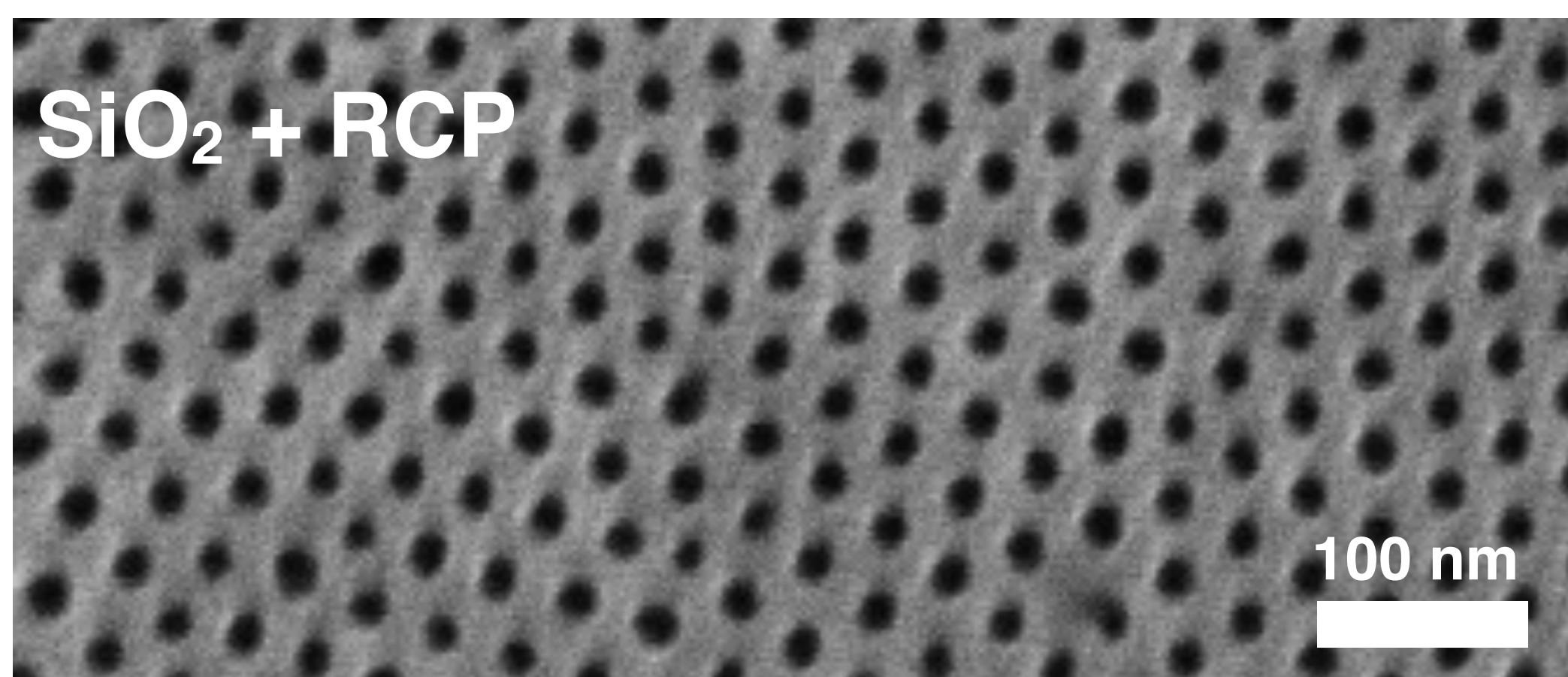
<sup>3</sup> Institute for lightweight design with hybrid systems, Paderborn, Germany

<sup>4</sup> Chair for materials science, Dept. of Mechan. Engineering, Paderborn University, Germany



## Motivation

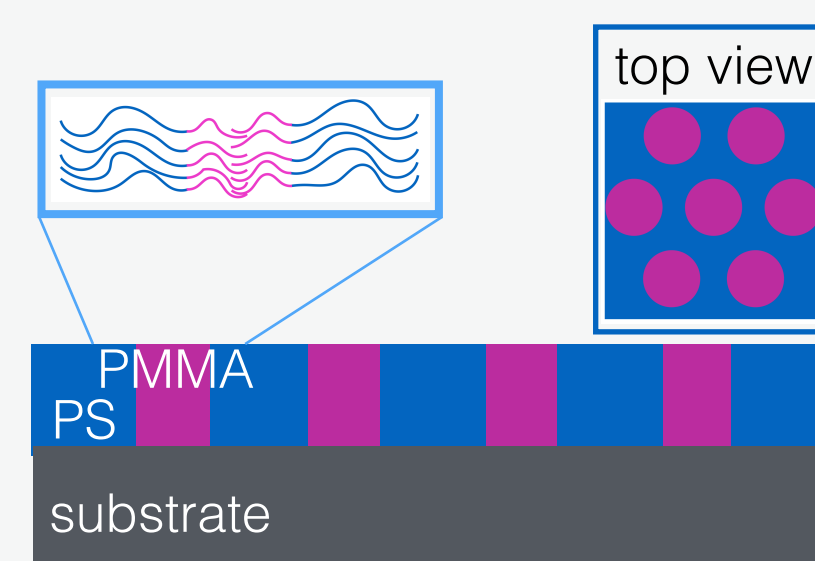
Block copolymer (BCP) lithography for self-assembled thin film nanopatterning is known to strongly depend on the interactions between the polymer species of the BCP and the substrate surface. The system of PS-b-PMMA on SiO<sub>2</sub> surfaces is investigated for promising applications in semiconductor technology. A SiO<sub>2</sub> surface can, however, only be patterned by BCP lithography if the surface is neutralized, e.g. by a RCP brush, which then allows for pattern orientation control. For many other applications of BCP lithography materials other than SiO<sub>2</sub> are of interest. In particular, nanopatterned TiO<sub>2</sub> on Ti-6Al-4V alloys can be exploited in biomedicine.



## Block copolymer lithography

Polymer thin films are patterned due to the microphase separation behavior of BCPs into self-assembled hexagonally arranged PMMA cylinders in a PS matrix.

Review: R. A. Puglisi, Hindawi J. Nanomaterials, Art. ID 586458 (2015).



The free energy of a polymer film on a substrate surface can be described by:

$$F = F_{\text{mix}} + F_{\text{elast}} + F_{\text{interface}}$$

$F_{\text{mix}}$  is the mixing Gibbs free energy of the BCP (Flory Huggins theory),  $F_{\text{elast}}$  the elastic energy, which changes with the chain conformation, and  $F_{\text{interface}}$  the interfacial energies of polymer species A and B with each other, the substrate interface and the interface towards air/ vacuum.

A. Andreozzi, E. Poliani, G. Seguíni, M. Perego, Nanotechnology 22, 185304 (2011)

## Influence of surface polarity

The interfacial energies  $\gamma$  between the polymer species A and B of the BCP and the substrate surface s are known to determine the orientation of nanopores formed during microphase separation. For equal interfacial energies between substrate and polymer A as well as polymer B, nanopores will be oriented perpendicularly to the surface. This is the desired orientation for most lithographical purposes. An interfacial energy with one polymer species much larger than with the other one, however, will result in preferential wetting of one polymer and thus a parallel orientation of nanostructures.

$$\gamma_{A-s} \approx \gamma_{B-s}$$



$$\gamma_{A-s} < \gamma_{B-s}$$

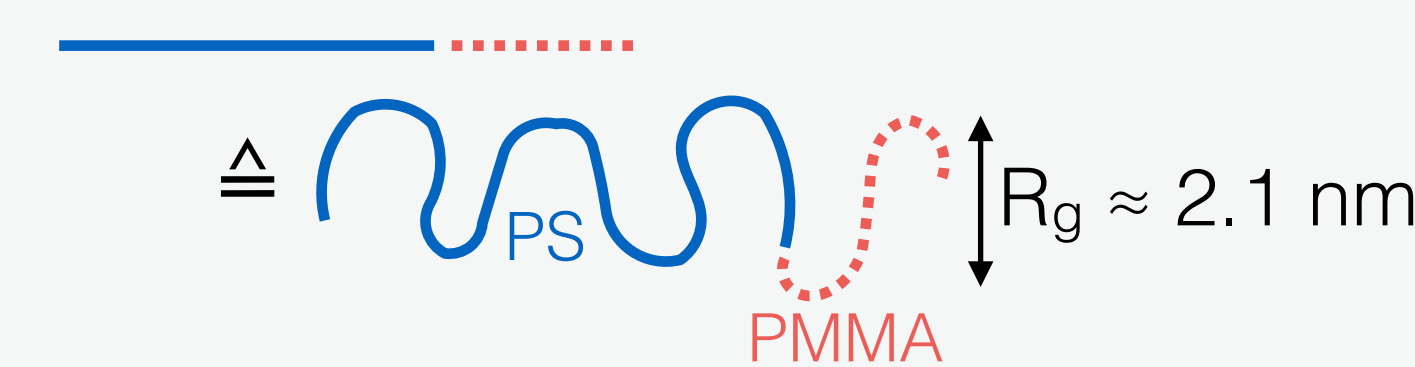
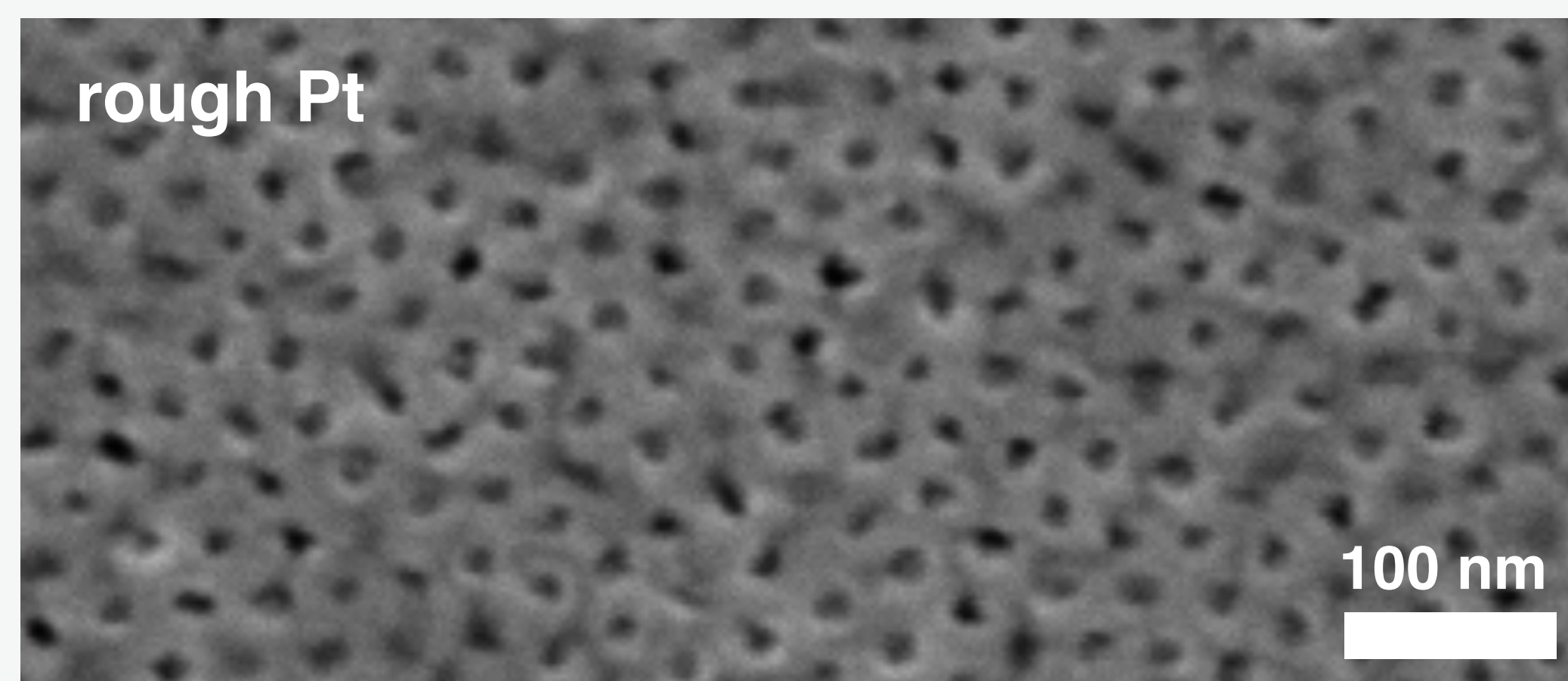


	SiO <sub>2</sub> + RCP	SiO <sub>2</sub>	Au	Pt	CrO <sub>x</sub>	TiO <sub>2</sub>
SFE [mN/m]	39	48	46	40	48	39
Polar	9 %	46 %	0.1 %	12 %	28 %	7 %

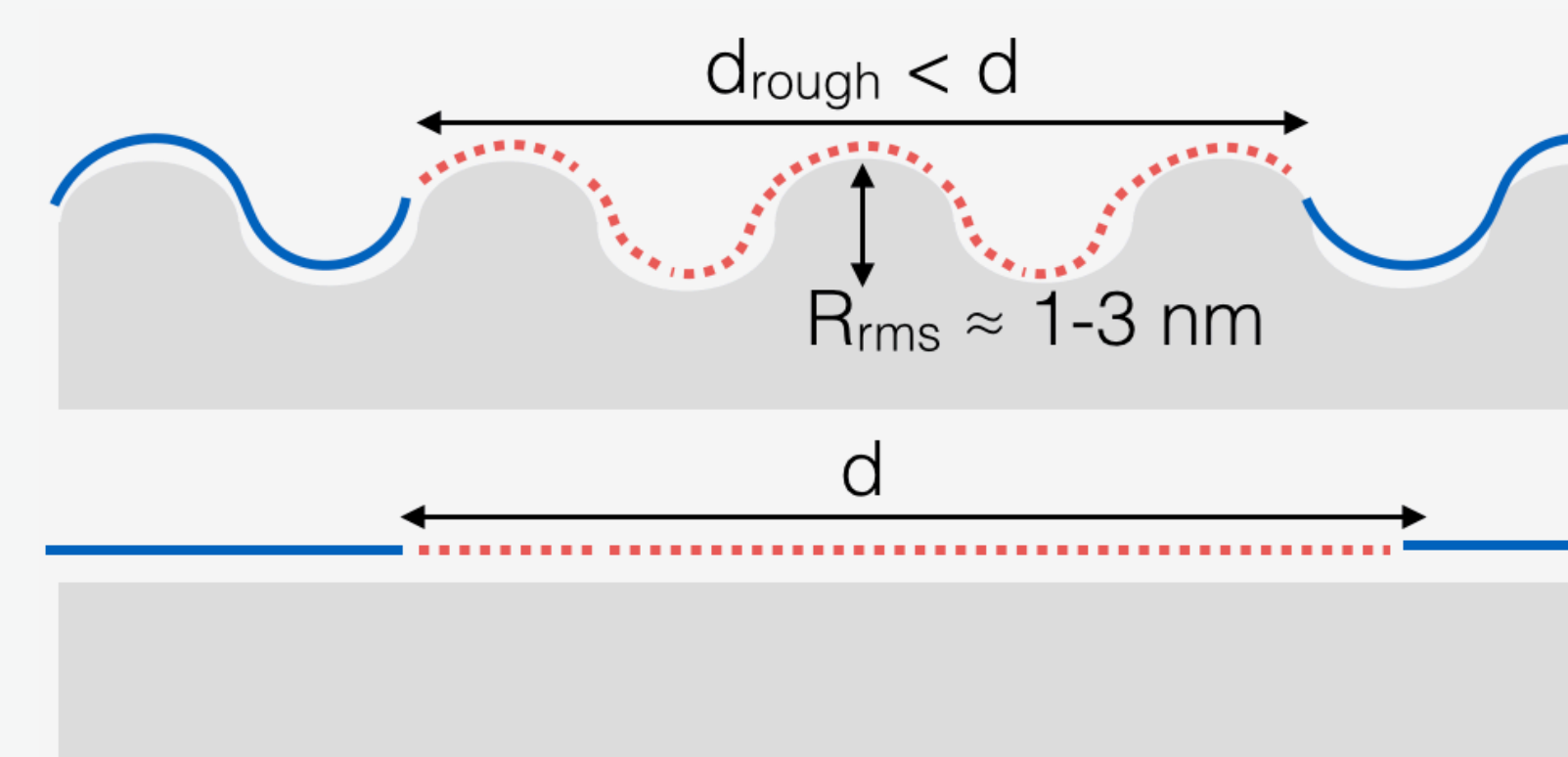
Our investigations show, that in particular the polar fraction of the substrate surface energy determines the nanopore orientation. Surfaces such as SiO<sub>2</sub> or CrO<sub>x</sub>, which have a partially polar character, are not neutral to PS and PMMA, thus parallel nanostructures are formed. On predominantly dispersive surfaces, perpendicular nano-pores form, e.g. on Au, TiO<sub>2</sub>, Pt, or RCP-functionalized substrates.

## Influence of surface roughness

The comparison of BCP nanopores formed on smooth surfaces (roughness  $R_{\text{rms}} < 1$  nm, all SEM images in left column) with those formed on rough surfaces ( $R_{\text{rms}} > 1$  nm, SEM image below) reveals that nanopore diameters decrease and their shape becomes less defined on rough surfaces. For Pt, the average diameters change from  $d = 17.4 \pm 3.2$  nm (at  $R_{\text{rms}} = 0.6$  nm) of to  $d_{\text{rough}} = 15.7 \pm 2.4$  nm (at  $R_{\text{rms}} = 1.6$  nm) as apparent in top view SEM.

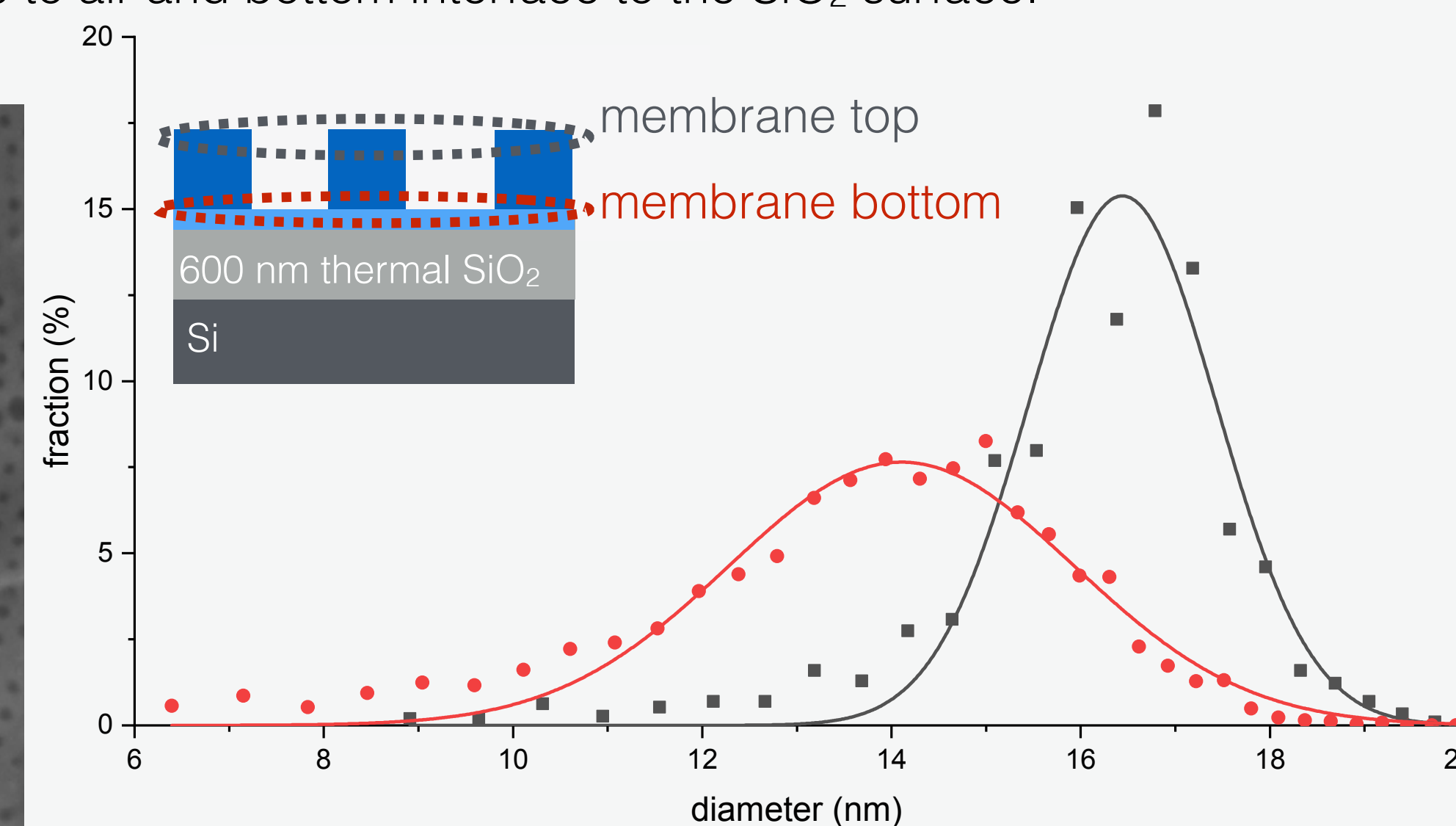
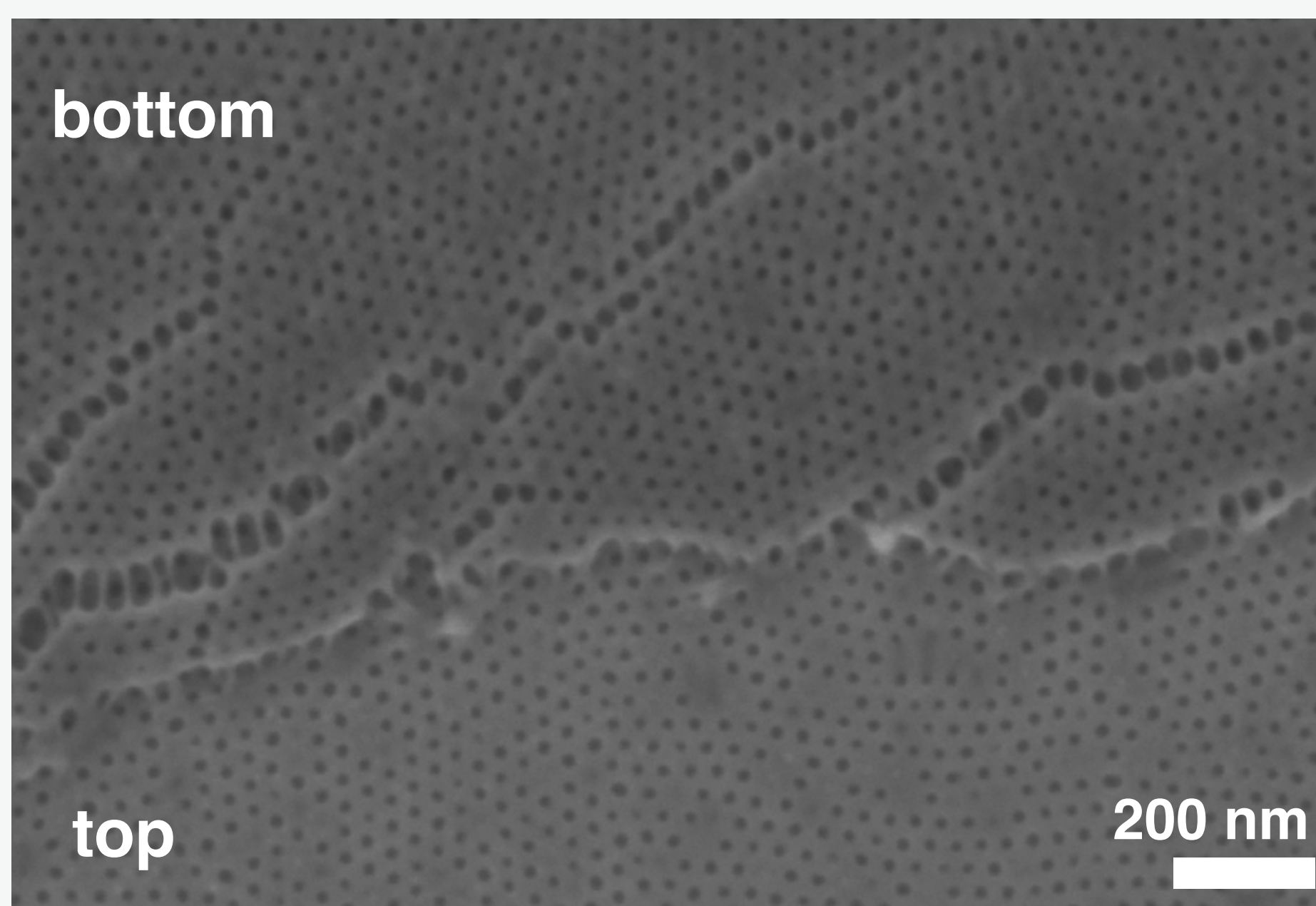


We believe that the decreased nanopore size  $d_{\text{rough}}$  results from an adjustment of the chain conformation according to surface roughness, if  $R_{\text{rms}}$  is in the size regime of the polymer radius of gyration  $R_g$ .



## BCP membrane - top and bottom

In order to investigate the nanopore morphology throughout the thin film, BCP lithography was performed on a 600 nm thick sacrificial thermal SiO<sub>2</sub> layer (functionalized with RCP). Etching of the SiO<sub>2</sub> with HF (5%, aq) results in the release of the nanopatterned PS film (25 nm thickness). The floating membrane was skimmed with a Si wafer. The SEM image below shows a folded part of the membrane, revealing its former top interface to air and bottom interface to the SiO<sub>2</sub> surface.



Nanopores at the top surface have a larger diameter and narrow size distribution, while nanopores at the bottom surface appear smaller with broad distribution. Besides possible RCP residuals, this is likely to result from the influence of the interfaces and could suggest a conical nanopore shape.

## For more information see our latest publication:

Hierarchical nanopores formed by block copolymer lithography on surfaces of different materials pre-patterned by nanosphere lithography

K. Brassat, D. Kool, J. Bürger, J. K. N. Lindner, Nanoscale 10, 10005 (2018) DOI: 10.1039/C8NR01397G

