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# Nanoscale mapping of thermal and mechanical properties of bare and metal-covered self-assembled block copolymer thin films

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## ABSTRACT

We report on the structural, mechanical and thermal analysis of 40 nm thick polystyrene-block-poly (ethylene oxide) (PS-b-PEO) block copolymer (BCP) films coated with evaporated chromium layers of different thicknesses (1, 2 and 5 nm). Solvent annealing processes allow the structural control of the BCP films morphology by re-arranging the position of the PEO cylinders parallel to the substrate plane. High-vacuum scanning thermal microscopy and ultrasonic force microscopy measurements performed in ambient pressure revealed that the nanometer thick metal coated layers strongly influence the heat dissipation in the BCP films and the local surface stiffness of the individual BCP domains, respectively. The measured tip-sample effective thermal resistance decreases from  $6.1 \times 10^7$  to  $2.5 \times 10^7$  KW<sup>-1</sup> with increasing Cr film thickness. In addition, scanning probe microscopy measurements allow the thermal and mechanical mapping of the two segregated polymer domains (PEO-PS) of sub-50 nm characteristic sizes, with sub-15 nm thermal spatial resolution. The results revealed the effect of the surface morphology of the BCP and the incorporation of the metal film on the nanoscale thermal properties and volume self-assembly on the mechanical properties. The findings from this study provide insight in the formation of high aspect ratio BCP-metal structures with the more established applications in lithography. In addition, knowledge on the thermal and mechanical properties at the nanoscale is required in emergent applications, such as thermal management, where the BCP is part of the final structure or device.

## 1. Introduction

Block copolymers (BCPs) composed of two or more chemically distinct, incompatible blocks are well-known to regularly self-assemble into various ordered nanostructures over macroscopic areas. In thin films, the domain structure is dependent on the interfaces energies (for example, air-BCP and BCP-substrate) and the film thickness, in addition to the other known parameters like composition and molecular weight. The control of the orientation in BCP thin films can be achieved by different approaches including surface modification, solvent annealing, temperature gradient, mechanical and electrical fields, etc.<sup>1-4</sup>

BCPs are suitable for a number of nanotechnologies on account of the tunability of their size, shape, and composition.<sup>5</sup> Different etch contrast between blocks allows the selective removal of one block and the use of the remaining one as a mask for pattern transfer into a functional material.<sup>6</sup> Hard-mask approaches can be introduced into the nanofabrication process when high-aspect ratio structures have to be realized,<sup>7-11</sup> such as conductive nanowires and semiconductor nanopillars. Alternatively, the remaining pattern can be employed as a sacrificial soft template structure. Functional materials are then introduced into the pore spaces of sacrificial templates by deposition, followed by removal of the template and generating the desired nanostructure.<sup>12-14</sup> The patterning process can be repeated to produce a stack of 2D patterns, which can be constituted of the same or different materials, morphologies and orientations.<sup>15</sup> Such block copolymer self-assembly methods have been implemented to pattern microelectronic circuit elements on the nanometre length scale (e.g. high density hard drivers,<sup>16</sup> memory semiconductor capacitors<sup>17</sup> and magnetic films<sup>18</sup>). Furthermore, BCP (PS-*b*-PEO) films composed of selectively localized metal nanoparticles recently have been used as transparent patterned electrodes<sup>19</sup> in organic thin film transistors.

Beyond the generation of templates for lithography, the applications of BCPs are expanding to other fields exploiting their functional properties.<sup>20-21</sup> However, there is a need to find complementary properties available from inorganic materials in many cases to enhance existing properties or impart novel functionalities to BCPs.<sup>22-23</sup> Various applications require the deposition of the inorganic materials on the surface of the BCP, instead of incorporating the inorganic materials into the phases of the BCP.<sup>24</sup> The selective decoration of evaporated metals has been reported, where nanoparticles and continuous films form by aggregation in the polymer.<sup>10-11, 25-31</sup> This provides a route for the metallization of templates; however, it is required to get more insight on the factors and parameters involved in the process.

Metallization in the form of thin films can also be used to improve the heat dissipation in polymer containing active nanoelectronic and optoelectronic devices, where the high thermal resistance of these materials prevents an efficient extraction and may cause the degradation of the organic material.<sup>32</sup> The measurement of the thermal conductance of such polymer based structures is very important as the polymer layer, polymer-metal or polymer-semiconductor interface can act as a heat barrier in the nanostructure. In addition, the knowledge of heat resistance and thermal stability of self-assembled nanostructures is crucial to define an upper temperature limit for the use of polymers on devices (e.g. to avoid overheating).<sup>33</sup> The possibility given by nanostructuring polymers for further tuning its low thermal conductivity and combining them with efficient heat conductive materials, opens new prospects in the control of heat transport for applications in thermal management.

Contrary to homopolymers, however, thermal transport in such polymer based systems has been barely explored. George et al.<sup>34</sup> reported thermal transport measurements on BCP films containing PS and Poly (methyl methacrylate) (PMMA) polymers (PS-b-PMMA). They found

that neither the film thickness nor the **block's** phase separation influenced the effective thermal conductivity of the BCP, obtaining values consistent with the bulk homopolymer values. The authors, however, used an optical diffraction-limited spatial resolution ( $\sim 300$  nm) technique that is not sufficient to characterize individual BCP blocks only a few nanometres in size. At such highly localized length scales heat transport is affected by interfaces, boundaries and contacts, thus the thermal imaging of individual BCP blocks is of high importance.

Furthermore, the mechanical property is arguably the weakest (both figuratively and literally) point of the polymer in the nanostructure applications, essentially defining the stability of polymer nanostructure in contact with the nano-patterned metal, especially for polymers structures with high aspect ratios. For instance, in self-assembled structures the presence of a much stiffer block greatly affects microphase separation.<sup>35</sup> In addition, previous works predicted that as the stiffness of one of the blocks is significantly increased, new intermolecular interactions can be introduced,<sup>36-37</sup> influencing the macroscopic structure of the BCP film and thus the nature of thermodynamically stable microphases. In particular, in thin films, these effects can cause significant deviations from the predicted bulk BCP structure and needs to be investigated. Consequently, the nanomechanical mapping of individual phases of the BCP structures is essential to investigate such effects.

The characterization of such complex structures at the nanoscale is crucial for further understanding the morphology-property relationship and the connection between the properties of the constituent components and the structure in the mesoscale. Electron microscopies can simultaneously provide structure characterization and chemical composition. Moreover, Atomic Force Microscopy (AFM)-based techniques, such as Ultrasonic Force Microscopy (UFM) and Scanning Thermal Microscopy (SThM), allow the nanoscale characterization of materials

beyond their surface topography and provide surface nanomechanical<sup>38</sup> and thermal<sup>39</sup> properties imaging, respectively.

In this work, we investigated the effect of microphase separation in BCP films on the aggregation of an evaporated metal. Particularly, we studied two different morphologies of these films, which were used as templates for metal coating. The primary BCP morphology consists of vertically oriented PEO cylinders within a PS matrix, which can be transformed in a morphology with in-plane oriented PEO cylindrical domains embedded in a PS matrix by solvent exposure. Structural and chemical characterization was primarily performed in order to gain insight into the morphology of the heterogeneous structures. Then, we studied the thermal and mechanical properties of the resulting BCP films and the effect of the incorporation of evaporated metal films. The surface imaging and measurements of nanoscale physical properties of these structures, which also revealed sub-surface detection and imaging, were performed by SThM and UFM. The complexity and size scale of the samples represents a challenge to the performance of Scanning Probe Microscopy (SPM) for both spatial resolution and probe sensitivity. Moreover, the thermal and mechanical response of the heterogeneous structure reflects the complexity of their morphology, i.e., surfaces, interfaces and film thickness, along with the intrinsic properties of the forming materials.

## 2. Results and Discussion

**Fabrication and structural analysis of BCP templates.** A 1% (w/w) solution of PS-*b*-PEO diblock copolymer in toluene with molecular weights of  $M_{n, PS} = 102 \text{ kgmol}^{-1}$  and  $M_{n, PEO} = 34 \text{ kgmol}^{-1}$  was dispersed into a Si substrate, and spin-coated at 4000 RPM for 60 sec. The Si substrates were cleaned in ethanol, toluene and acetone prior to use. The microphase separation

of the BCP film by self-assembly resulted in the formation of vertically oriented PEO cylinders showing a hexagonal arrangement embedded in a PS matrix, as seen in previous works using similar methodology.<sup>27, 40-41</sup> Schematic of the morphology of the bare BCP film is shown in Figure 1a. Then, we proceeded to deposit Cr on a first set of as prepared BCP templates by using electron beam evaporation and targeting Cr layers with different nominal thicknesses (1, 2 and 5 nm).

Figures 1c-f show Scanning Electron Microscopy (SEM) images of the surface of the bare (0 nm Cr) and the three metal decorated BCP samples, respectively (1<sup>st</sup> set of samples). The surface of the bare BCP film shows the presence of cylindrical domains (dark color in SEM) with average radius and average spacing between them of  $r = 15 \pm 2$  nm and  $D = 25 \pm 2$  nm, respectively. The composition of the cylinders was further verified after performing the thermal and mechanical measurements, by selectively etching the PEO block of the bare BCP film with an oxygen plasma.<sup>40-41</sup> (see Figures S2a, b in the Electronic Supplementary Information (ESI)). The PS matrix is higher than the PEO cylinders by a difference of  $5 \pm 1$  nm in average. After the evaporation of Cr on the non-etched samples, the oriented polymer template is still distinguishable, indicating a preferential metal coverage. This observation will be further confirmed by transmission electron microscopy (TEM) measurements. The RMS surface roughness of the BCP films decreases from 3 to 2 nm with increasing Cr layer thickness as estimated from AFM topography images (Figure S3 in the ESI).

A second set of as prepared BCP templates was processed by solvent annealing in mixed chloroform and toluene atmosphere for 2 hours. The selective wetting of the minor block of the BCP (hydrophilic PEO) resulted in the alignment of the PEO cylinders parallel to the substrate

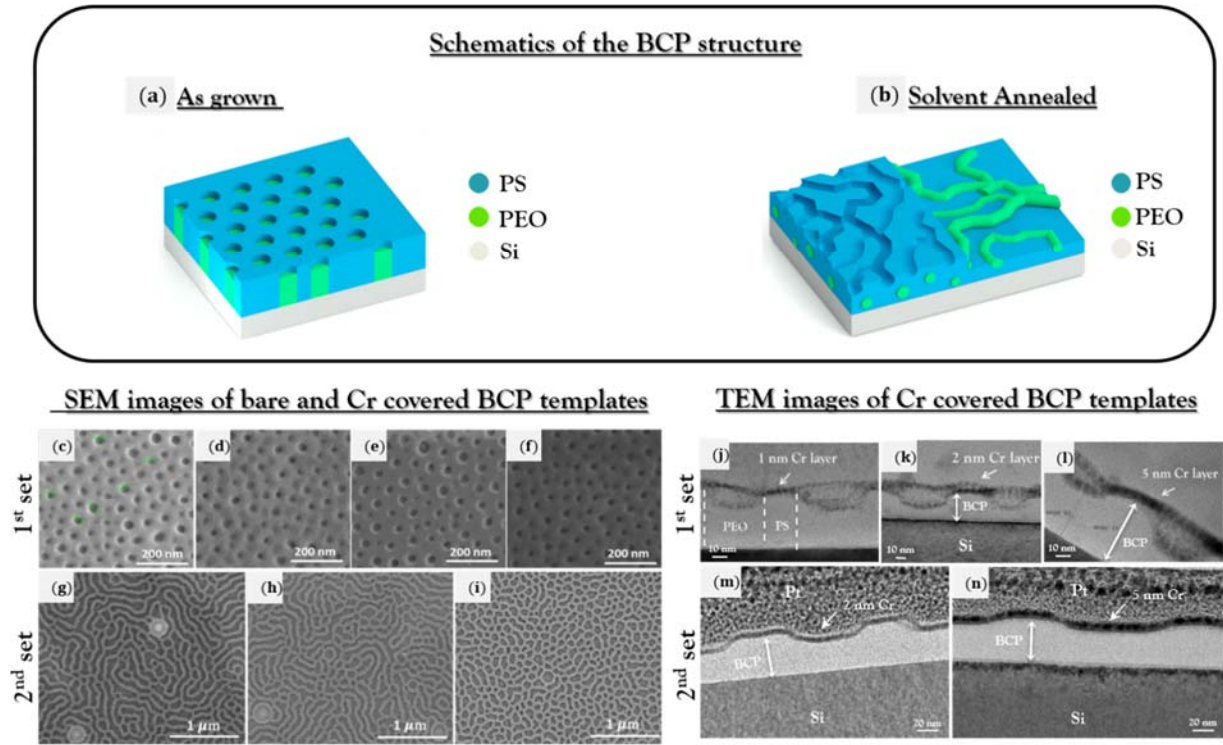


plane, as has been shown elsewhere.<sup>40</sup> Particularly, the local segregation of the different polymer blocks of PS-*b*-PEO thin films through a solvent annealing process has been studied in previous works.<sup>40-41</sup> A schematic illustration of the morphology of the resulting BCP template is shown in Figure 1b. The rate of the structural conversion is time and film thickness dependent and, since the PS and PEO blocks are highly immiscible, the microphase separation occurs at relatively high solvent concentrations.<sup>27, 41</sup> Figure 1g shows a SEM image of the solvent annealed BCP film. The brighter color in the SEM images corresponds to the PS matrix while the PEO cylindrical domains are expected to be rearranged horizontally to the film, and embedded in the PS matrix.<sup>40, 42</sup> Then, similarly to the previous set of samples, Cr layers with nominal thicknesses of 2 and 5 nm were evaporated on the surface of the BCP template by electron beam evaporation (see Figures 1h, i, 2<sup>nd</sup> set of samples).

To study the morphology and chemical composition of the BCP templates, we performed transmission electron microscopy (TEM), energy dispersive x-ray (EDX) and electron energy-loss spectroscopy (EELS) measurements. TEM measurements are shown in Figure 1 while EDX and EELS measurements are presented in the ESI (Figure S4). In Figures 1j, k, l we show cross-section TEM images of the BCP templates with nominal Cr coatings of 1, 2 and 5 nm, respectively (see 1<sup>st</sup> set of samples). The resulting BCP film thickness was measured  $39 \pm 2$  nm. The Cr film is seen to deposit preferentially on the PS matrix, forming islands that grow laterally as the evaporation time increases. The selectivity of Cr is not complete, but a slower kinetics of the growth-coalescence process on PEO cylinders than in the PS matrix results in a partial coverage of the PEO cylinders.<sup>43</sup> The different metal deposition on the two BCP blocks can be seen with higher resolution in STEM mode. In the ESI we show the BCP template with 2 nm thick Cr (1<sup>st</sup> set of samples) in STEM mode (Figure S4a) and, with higher magnification at the

framed area, in Figure S4b. From these images, we observe that the metal layer (see brighter regions in Figure S4b) is preferentially formed on the PS surface. However, the EDX spectrum taken along the line indicated in Figure S4b confirmed the presence of Cr atoms within the PEO domains as well (see Figure S4c).

High-resolution TEM images of the solvent annealed BCP templates (2<sup>nd</sup> set of samples) with nominal 2 and 5 nm thick Cr layers are shown in Figures 1m, n, respectively. From the TEM images we observe that there is no selectivity in the deposition of the Cr layer, i.e., a homogeneous Cr layer is evident all along the sample surface. Figure S4d shows the selected area for the composition analysis (orange box) in the BCP template with 2 nm Cr layer. Figures S4e, f show the EELS composition maps for chromium and oxygen elements, respectively. As already seen in the TEM images, Figure S4e shows that the Cr layer is homogeneously distributed on top of the BCP surface. Oxygen content (brighter regions in Figure S4f) is clearly detected at the substrate-BCP interface and at the Cr layer. The former is attributed to the native SiO<sub>2</sub> film formed on top of the Si substrate and the latter reveals the oxidized Cr.



**Figure 1.** (a), (b) Schematics of the BCP films morphology. (c) SEM image of the fabricated microphase separated BCP film on Si substrate, and (d), (e), (f) Top view SEM images of the BCP templates with nominal Cr coatings of 1, 2 and 5 nm (first set of samples), respectively. The darker regions are the PEO domains that were degraded while the lighter regions correspond to the PS matrix. (g) SEM image of the BCP film after the solvent annealing, showing the modified morphology; (h), (i) Solvent annealed BCP templates with 2 and 5 nm Cr layers, respectively. (j), (k), (l) cross-section TEM images of the BCP templates with nominal Cr coatings of 1, 2 and 5 nm, respectively; (m), (n) cross-section TEM images of the solvent annealed BCP templates with 2 and 5 nm Cr, respectively.

From the TEM measurements it is clear that the metal deposition in the two sets of samples has distinctive morphologies. While there is a weak preference of Cr for the matrix surface over cylinders in the 1<sup>st</sup> set of samples, in contrast, it fully covers the whole surface of the 2<sup>nd</sup> set of

samples. The uniform metal coverage in the 2<sup>nd</sup> set of samples suggests surface homogeneity and further supports the description of the parallel oriented cylinders embedded in a PS matrix. A full PS surface is favored as air-PS interface minimizes the energy of the system.<sup>44</sup> In addition, the surface of the 2<sup>nd</sup> set of samples was activated (solvent annealed) prior to metal deposition, thus expected to exhibit enhanced metal adhesion.<sup>45-47</sup> The presence of additional functional groups after the solvent annealing may interact with the evaporated Cr atoms creating the homogeneous Cr layer on the BCP surface with uniform thickness. Although the morphology of the metal deposition on the different BCP templates is a necessary information to interpret the thermal and mechanical measurements presented below, further investigation of the basic physical mechanisms of metal film formation on BCP surfaces is beyond the subject of this work. A better understanding of the wetting behavior of metal films on solid substrates and their growth kinetics can be found elsewhere.<sup>48-49</sup>

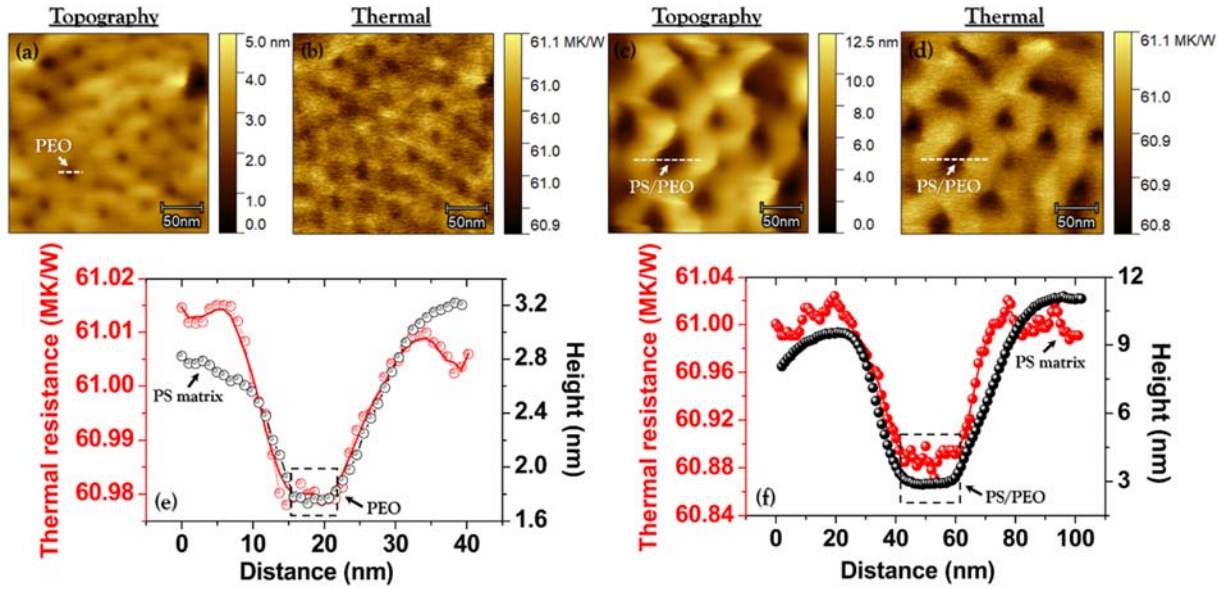
**Thermal analysis of the BCP templates.** Next, we study heat transport between a SThM microscope tip and the fabricated BCP films. Measurements were performed in specialized high vacuum SThM ( $10^{-7}$  mbar).<sup>50</sup> Using a doped-Si probe with an integrated resistive heater close to the tip (Figure 3b), operating in active mode (described in ESI), we measured variations of the tip-sample effective thermal resistance in all the BCP samples. More details about the experimental setup and the quantification of the thermal resistance can be found elsewhere.<sup>51</sup> First we study individual regions of the BCP films. In Figure 2 we present topography and thermal images of the bare BCP templates obtained by simultaneous mapping the local variations in height (Figures 2a, c) and tip-sample thermal resistance (Figures 2b, d). The high-resolution thermal image of the BCP template with the vertical cylinder morphology (Figure 2b) shows thermal contrast between the PS matrix and the PEO cylindrical domains, where the hexagonal

arrangement of the latter is visible. The PEO cylinders appears darker than the PS matrix in the thermal image, i.e. lower thermal resistance, indicating an increased tip-sample heat transfer when the tip is in contact with the PEO domains.

In particular, from the 40 nm long thermal resistance line profile (white dashed line in Figure 2b), we observe that as the tip is moving from the PS matrix towards the PEO cylinders, the thermal resistance decreases approximately 0.04 MK/W (see Figure 2e). The same trend has been observed in the full 1<sup>st</sup> set of samples, as shown in the ESI (Figure S5). Similarly, in the BCP film with the embedded horizontal cylinders (Figure 2d), the thermal map shows darker contrast in the depressions than the higher level PS matrix. From the 100 nm long thermal resistance line profile along the white dashed line of Figure 2d, we found that as the tip is moving from the higher level PS matrix towards the depressions, the thermal resistance decreases approximately 0.12 MK/W (see Figure 2f). Note that in this case the tip is continuously in contact with the PS matrix while the embedded PEO cylinders cannot be directly probed.

Since the two constituent polymers have similar intrinsic thermal conductivities, the origin of the thermal contrast between the PS matrix and PEO vertical cylinders (see Figure 2b), could be related to a topography artifact. However, by analysing the topography and thermal resistance profiles of Figures 2e,f we show that the thermal spatial resolution in our measurements (sub-15 nm range) is sufficient to resolve features with sizes similar to the PEO vertical cylinders. In particular, the thermal lateral resolution is extracted by comparing the slope of the acquired thermal resistance signal, when the tip is moving at the interface between the PS matrix and PEO cylinders, with the corresponding topography, taking the full width at half maximum as a resolution criterion (see line profiles in ESI), as has been applied in previous SThM

measurements<sup>52</sup>. Therefore, the change of the thermal resistance signal, when the tip is moving from the PS matrix to the PEO cylinders, is not related to the geometrical change of the contact area, mostly ruling out the effect of topography artifacts.



**Figure 2.** (a), (c) Topography and (b), (d) thermal resistance maps of the bare BCP films formed by vertical (1<sup>st</sup> set, Figures 2a, b) and horizontal cylinders (2<sup>nd</sup> set, Figures 2c, d). (e), (f) Topography (black data points) and thermal resistance profiles (red data points) along the white dashed lines of Figures 2a, c and Figures 2b, d, respectively. Open symbols in Figure 2e correspond to data points from Figures 2a, b and solid symbols in Figure 2f correspond to data points from Figures 2c, d.

Once topographic artifacts are discarded, a simple explanation of the thermal contrast in the images would be the small difference between the thermal conductivities of the PS and PEO constituent polymers. However, a complete interpretation needs to take into account the heat spreading into the substrate that, consequently, affects the tip-sample heat transfer. As the BCP

film shows a marked surface topography with the vertical PEO cylinders forming surface depressions, it introduces a film thickness modulation, which results, accordingly, in a thermal conductance and thermal contrast change because of different distance between the heater and substrate. The fact that we observe a larger thermal resistance decrease in the depressions in the 2<sup>nd</sup> set of samples, where larger changes in height are observed (see Figure 2e), further supports the interpretation of a thickness-dependent substrate effect causing the thermal contrast.

We have performed point contact measurements, where the SThM tip is brought in- and out-of contact with the sample at randomly chosen positions on the BCP samples surfaces in order to obtain more insightful and quantitative measurements of the effect of deposited Cr on the effective thermal resistance between the tip and the samples. Each point contact measurement gives us the heat flux variation caused by the difference in tip-sample temperature. Then, an averaged effective thermal resistance  $R_{ts}$  is obtained for each BCP sample by taking the mean value of the point measurements. In general, for a given sample,  $R_{ts}$  can be expressed as a sum of three different thermal resistances:

$$R_{ts} = R_t + R_c + R_{spr} \quad (1)$$

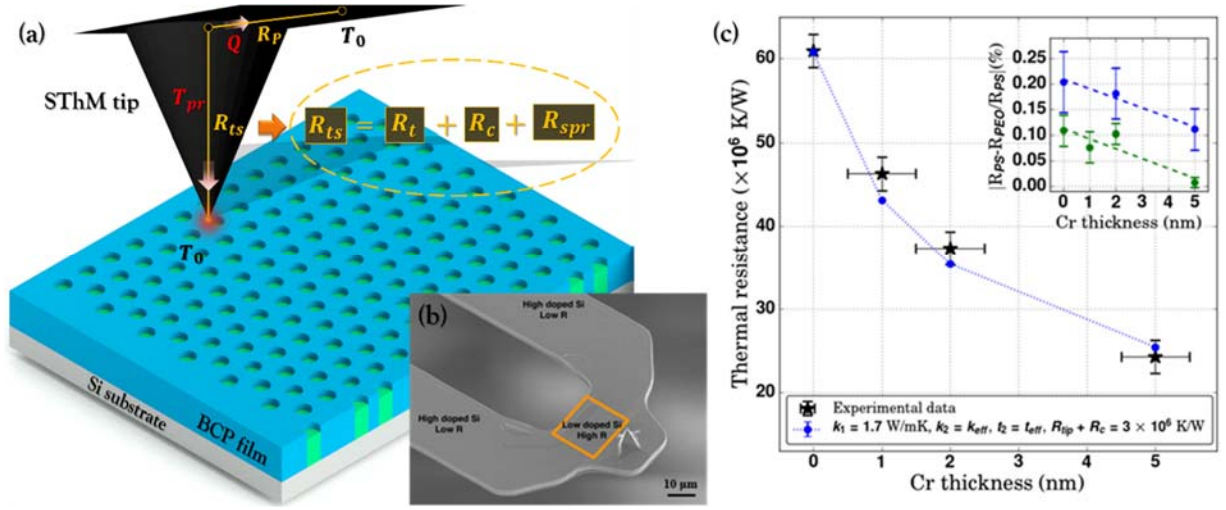
where  $R_t$  is the thermal resistance of the SThM conical tip,  $R_c$  the thermal interface resistance between tip and the sample in contact (thermal contact resistance) and  $R_{spr}$  the thermal spreading resistance within the sample (see schematic in Figure 3a). Particularly, when the probe is in contact with the sample, the heat generated in the SThM heater can only transfer to two heat sinks: the probe cantilever and the sample. By monitoring the change in probe excess temperature ( $\Delta T = T_{probe} - T_0$ ) out ( $\Delta T_{nc}$ ) and in contact ( $\Delta T_c$ ), we measure the effective thermal resistance  $R_{ts}$  between the tip and the sample.  $R_{ts}$  is given by the following equation:

$$R_{ts} = R_p \left( \frac{\Delta T_{nc}}{\Delta T_{nc} - \Delta T_c} - 1 \right) \quad (2)$$

where  $R_p$  is the probe thermal resistance, which is measured during the probe calibration procedure (see ESI) and was found  $R_p = 8.7 \times 10^4 \text{ KW}^{-1}$ .

In Figure 3c we show the effective thermal resistance as a function of the Cr thickness in the 1<sup>st</sup> set of BCP samples (black stars). It corresponds to the mean value  $R_{ts}$  of the measurements taken at each sample and the error bars the dispersion found in the measurements. Note that we measured negligible differences in  $R_{ts}$  between the 1<sup>st</sup> and the 2<sup>nd</sup> set of samples. The measurements show that by increasing the Cr layer thickness on the BCP films, the thermal resistance,  $R_{ts}$ , decreases, thus, the heat transfer from the tip to the sample increases. We have implemented a model to account for the previous point contact measurements and gain more quantitative information regarding the heat transport in the Cr/BCP/Si system. Provided that the point contact measurements were performed at random positions, we have assumed that we can model the BCP film as an equivalent homogeneous layer with effective properties, which can be modelled as the weighted average of the properties of each block. Details of the heat transport model can be found in the ESI. The blue dashed curve in Figure 3c shows the calculated thermal resistance values.





**Figure 3.** (a) Schematic of the probe-sample thermal resistance model and (b) SEM image of the Si-doped SThM probe. A tip of a nanoscopic radius curvature ((5–10) nm) with a pyramidal shape is mounted on top of the resistive element. (c) The tip-sample thermal resistance variations of the 1<sup>st</sup> set of samples as a function of the Cr thickness (black stars) and the two layers on substrate analytical model (blue spheres). The error for the Cr thickness is  $\pm 0.5$  nm. The inset graph in Figure 3c shows the percentage of the thermal resistance variations between PS and PEO in the BCP films with the vertical (green spheres) and horizontal (blue spheres) cylinders, respectively.

Furthermore, by analysing the thermal images and taking into account  $R_t$  and the power generated in the probe, we estimated the percentage of the thermal resistance variations when the tip is on a surface depression ( $R_{PEO}$ ) and on the top-most of the surface ( $R_{PS}$ ) (see inset graph in Figure 3c). Note that these values include the error derived by topography related changes of the tip-sample contact geometry and film thickness modulations. Although the percentage variation decreases for both sets of samples with increasing the Cr and giving a similar trend, the values are larger in the case of the 2<sup>nd</sup> set of samples. Considering the small tip apex of the thermal

probe, it is reasonable to assume that the tip-sample thermal exchange is localized at the point contact. Particularly, in high vacuum experimental conditions the heat transfer through the liquid meniscus and air is eliminated and, neglecting the conductance due to radiation, the dominant heat transfer mechanism is the conduction due to the mechanical contact of the probe with the sample. Here, the heat source size is comparable to the thickness of the Cr layer and the influence of the Cr layer, with a thermal conductivity one order of magnitude larger than the thermal conductivity of the block copolymers, dominates over the substrate. Therefore, the increase of the Cr layer enhances heat dissipation or conductance within the sample giving the trend seen in Figure 3c. In addition, the decrease of the thermal resistance seen in the measurement on the sample with 1 nm Cr layer compared to the measurement on the bare sample indicates that the heat spreading due to the presence of the metal dominates over the Cr-BCP interface thermal resistance.

Finally, the effect of the substrate can also be detected when the thermal resistance is measured in different positions of the same sample. This is the case of thermal resistance line profiles in Figure 2e where the variation of the thermal resistance from the top most of the sample surface to the surface depression is a factor of three larger in the case of the sample with horizontally orientated cylinders. It reflects a commensurate variation in the relative height between the top-most of the surface and the surface depression (as seen in the topographic line profile in Figure 2e), which translates to the relative distance between the top-most of the surface

60"o"Petersen, 1979#201" ADDINEN.CITE<EndNote><Cite><Author>Petersen</Author><Year>1979</Year><RecNum>201</RecNum><DisplayText><style face="superscript">60</style></DisplayText>covered samples and it is at the origin of the shift between the data in the inset to Figure 3c obtained from the two sets of samples.

**Mechanical analysis of the BCP templates.** To probe nanomechanical properties, UFM measurements were performed in all the samples. UFM uses the standard contact mode capabilities coupled with a high frequency ( $\sim 4$  MHz) vertical oscillation of the sample substrate (see Figure S6 in ESI).<sup>53</sup> In addition to the high frequency oscillation, a sawtooth shape waveform modulates the oscillation at low frequency ( $\sim 2.7$  kHz). As the cantilever (Budget Sensors ContAl-G,  $0.2 \text{ Nm}^{-1}$ ) resonant frequency lies around 13 kHz, the tip remains effectively stationary and indents the sample surface with the same amplitude as sample displacement.<sup>53</sup> Then, the tip-sample forces are modulated at high frequency creating an additional force. Using the intrinsic tip-sample forces vs distance non-linearity, this additional force, the UFM response, is detected at the low modulation frequency. Therefore, we record the effect of the ultrasonic amplitude on the friction force and the cantilever deflection. The surface stiffness's can then be mapped at the nanoscale as the UFM response increases with the material local stiffness.<sup>54</sup> This relationship was shown to hold for a wide range of materials from polymers to semiconductors.<sup>53, 55</sup> More details regarding the UFM working principle are shown in the ESI.

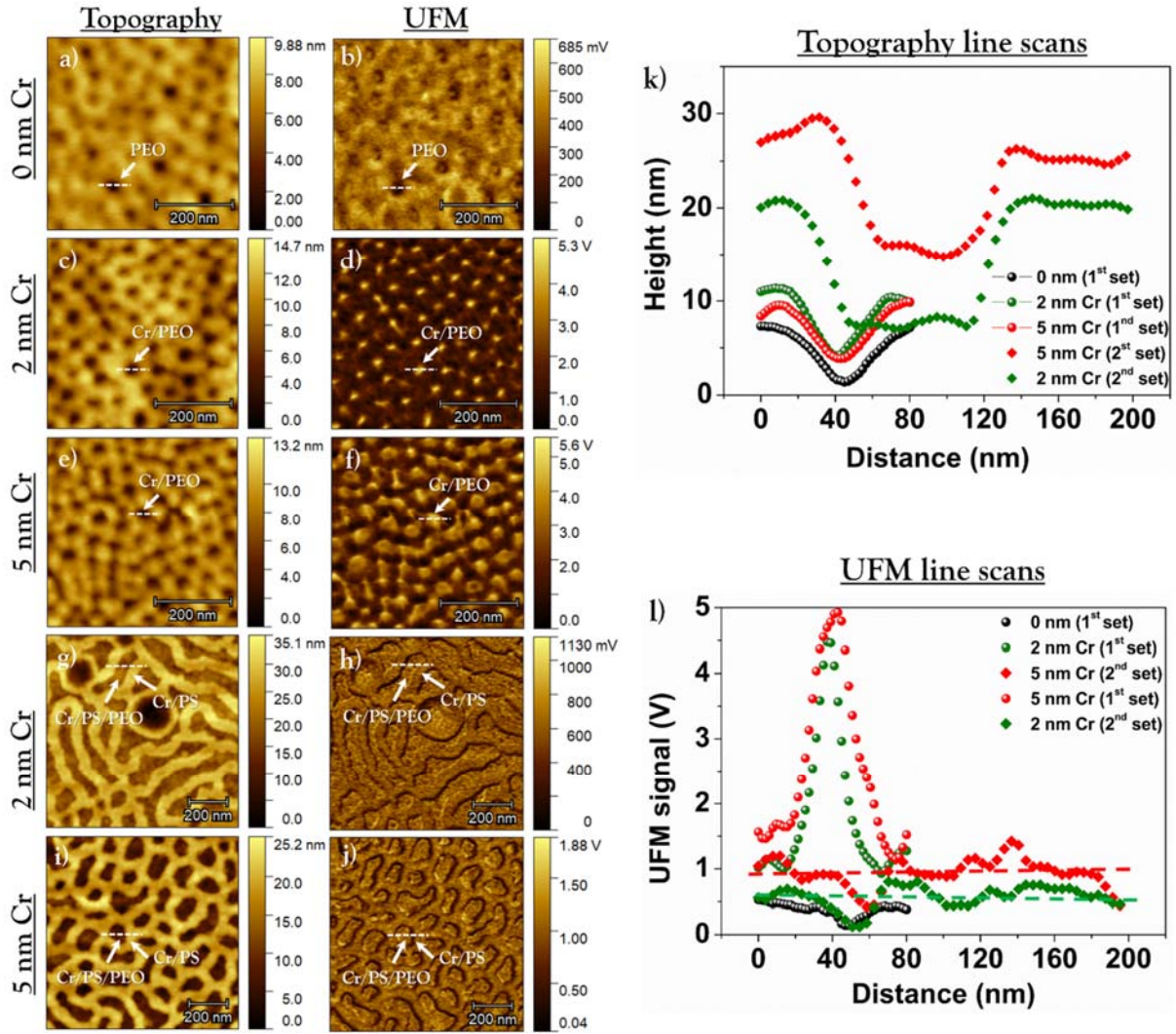
Topography and UFM scans performed on both set of BCP samples. In Figure 4, we show UFM maps of the bare BCP without Cr layer and of the metal covered BCP films with 1, 2 and 5 nm Cr. Looking at the non-coated sample (Figure 4b) with the vertical oriented cylinders, we observe bright areas (stiffer materials) corresponding to the PS matrix and dark regions (softer materials) for the PEO cylinders. Even if some discrepancies in the UFM response are recorded, areas highlighted by white arrows are wide compared to the tip dimensions and thus cannot be solely attributed to topography artifacts. These results agree with a larger Young's modulus ( $E$ ) value obtained for PS ( $E_{\text{PS}} \sim 4 \text{ GPa}$ )<sup>56-57</sup> than for PEO ( $E_{\text{PEO}} \sim 0.2 \text{ GPa}$ ).<sup>58-59</sup> Therefore, the PS appears stiffer in the absence of a covering Cr layer.

The presence of a Cr film on top of the BCP is expected to increase the stiffness of the surface as the Young's modulus of Cr thin films<sup>60</sup> and oxidized Cr<sup>61</sup> is found much larger compared to PS and PEO ( $E_{Cr} \sim 180$  GPa). However, after Cr deposition on the BCP with the vertical oriented cylinders, the nanomechanical behaviour of the two polymer blocks changed (Figures 4d, f). Instead of probing a lower UFM response in the PEO phase, we observe an inversion of the contrast, e.g. the Cr covered PS appears softer than the Cr covered PEO. The inversion of the UFM signal with increasing Cr thickness is shown in the 80 nm long line scans of Figure 4l. The relative change of the UFM signal between PS matrix and PEO cylinders increases more than 1 order of magnitude after Cr evaporation.

The origin of this result can be understood considering the different interfacial adhesion between Cr/PS and Cr/PEO interfaces, which strongly influences their mechanical response.<sup>62</sup> The different adhesion arises from the different deposition of the Cr atoms on the surface of the two blocks, as already confirmed from the TEM measurements (see 1<sup>st</sup> set in Figures 1j, k, l and Figures S4a, b in ESI), which results in the formation of distinguished metal-polymer bonded interfaces. In particular, from the TEM images we see that by increasing the evaporated Cr layer thickness on the BCP surface, the diffusion of the Cr atoms within the hydrophilic PEO block is increasing. This increased penetration of the Cr atoms within the PEO block (additional C-O and O-O bonds) most likely modified the local stiffness of the PEO/Cr contacts and created an inversion of the UFM contrast. Note that according to a previous work a decrease in the elastic modulus of a PS/metal surface is expected compared to a pure PS surface, which finally results in a more compliant and low-density interphase.<sup>63</sup> Previous reports also have showed similarly different mobility and adhesion of metal nanoparticles on PS and PMMA surfaces.<sup>64-67</sup> In addition, the fact that the free energy of a metal inside a polymer is lower than that of a metal at

the polymer surface and close related with the polymer-metal interfacial tension,<sup>65, 68-69</sup> further supports the previous explanation.

In the solvent annealed BCP templates with 2 and 5 nm Cr layer, the UFM maps show similar stiffness in all the areas of the BCP surface (see Figures 4h, j). This result can be explained taking into account the homogeneous metal deposition on the BCP surface, as is shown in the TEM images (see Figures 1m, n, 2<sup>nd</sup> set and Figures S4e, f). The 200 nm long line scan profiles in Figure 4l show similar measured UFM response in all the areas of the metal covered films. Small fluctuations of the UFM signals can be attributed to the topography variations in transitions between Cr/PS/PEO and Cr/PS areas.



**Figure 4.** (a), (c), (e) Topography and (b), (d), (f) UFM maps of the 1<sup>st</sup> set of samples with 0, 2 and 5 nm Cr layer, respectively. (g), (i) Topography and (h), (j) UFM maps of the 2<sup>nd</sup> set of samples with 2 and 5 nm Cr layer, respectively. (k) Topography and (l) UFM line scan profiles obtained from the white dashed lines depicted in the topography and UFM images, respectively.

Last, it's interesting to note that although the UFM measurements allow subsurface investigations of the sample,<sup>54-55</sup> the depth probed is highly dependent on the material under the probe and on size of the contact.<sup>70</sup> As we discussed, the contact diameter is less than the features

observed (<10 nm). Therefore, the dominant UFM response will then be provided by the first 10 nm directly under the tip apex. We point out that in general metal atoms have two orders of magnitude much higher surface energy compare to the polymers.<sup>65</sup> Therefore, with the presence of Cr, the UFM response is dominated mostly by the Cr layer.

### 3. Conclusions

In conclusion, the fabrication of bare and Cr covered micro-phase separated block copolymer templates has been investigated. TEM-EDX and EELS measurements were performed to confirm the separation of the two block copolymer phases (PEO, PS) and presence of Cr on the surface of the BCP films after evaporation process. SThM measurements in high vacuum environment revealed the increased impact of the heat spreading into the metal, which results in a decrease of the thermal resistance measured by the SThM from  $6.1 \times 10^7 \text{ KW}^{-1}$  in the surface of the bare BCP film to  $2.5 \times 10^7 \text{ KW}^{-1}$  in the surface of a BCP film covered by only 5 nm thick Cr film. Different nanomechanical behaviour was observed in the BCP films with vertical and parallel oriented PEO cylinders after Cr deposition. In the former, the individual blocks show an increasing stiffness contrast by increasing the evaporated metal thickness, most likely, due to the inhomogeneous incorporation of the metal in their domains. However, in the solvent annealed PS-b-PEO films with Cr coatings, we found an homogeneous surface stiffness. These results provide valuable information of the relationship between structure, morphology and properties of BCP thin films and give further knowledge of how the metal incorporates on the surface of the BCPs, which is important for present applications in lithography. Moreover, the study of the thermal and mechanical properties at the nanoscale is important for emergent applications of BCPs where, for example, heat management and mechanical stability are at the core of their function.

## ASSOCIATED CONTENT

**Supporting Information.** SThM probe calibration, AFM, TEM and EDX measurements, thermal maps of Cr covered BCP templates, heat transport model, spreading resistance model, UFM set up, thermal conductivity measurements with the  $3\omega$  set up.

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### Author Contributions

A.E.<sup>†</sup> and J. S.<sup>‡</sup> contributed equally to this work. M. K. and A. E. prepared the samples. J. S., A. E., C. E., A. R., C. S. T., F. A. and O. K developed the protocols required for SThM and UFM measurements. A. E., J. S. and C. E. carried out the SThM and UFM measurements and the data analysis. A. E. performed the AFM, SEM and TEM measurements. J. S. performed the modelling. M. R. L. and E. C. A performed the thermal conductivity measurements with the



three omega method. M. S. performed the oxygen plasma etching. The manuscript was written by A. E., J. S. and F. A. All authors contributed with comments to its final version. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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