SUPPORTING INFORMATION

Correlating Nanostructure, Optical and Electronic Properties of Nanogranular Silver Layers during Polymer-Template-Assisted Sputter Deposition

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Sputter deposition chamber

More details about the sputter chamber (see Figure S1) can be found in the publication of Döhrmann et al.¹

Figure S1: Photograph of the RF sputter chamber equipped with a UV-Vis setup in reflection mode (purple), the rotatable QCM (orange) and a resistance measurement device (yellow).
Two Point Resistance Measurement

**Figure S2:** The resistance measurement device consists of coaxial cables which are insulated. The end of the cables is replaceable insulated with shrinking tube. The cables are fixed at the sample holder. The sample is insulated with kapton from the sample holder.

**Four point resistivity measurements**

A Four point resistivity measurement is a common technique to measure the sheet resistance of thin films\(^2\).
Figure S3: Ex situ four point resistance measurements after sputter deposition of silver on PS, PMMA and PS-b-PMMA thin films. The results are in good agreement with the in situ resistivity measurements. $\delta_{\text{IMT,PMMA}} = (11.4 \pm 0.2) \text{ nm} < \delta_{\text{IMT,PS}} = (12.3 \pm 0.4) \text{ nm} < \delta_{\text{IMT,PS-b-PMMA}} = (13 \pm 0.3) \text{ nm}$.

**UV-Vis**

![Graphs showing absorption spectra and average absorption as a function of thickness for PS-b-PMMA, PMMA, and PS.](image)

Figure S4: a) Absorption spectra of PS-b-PMMA for different silver thickness on glass substrate. From 3 nm to 18 nm the spectra has a red shift due to the particle size and distance changes during the sputter deposition. The spectra smears out with higher amount of silver thickness. Comparison between the insulator-metal transition (blue line) and the average absorption of visible light for different silver thickness on the b) PS-b-PMMA, c) PMMA and d) PS. The mean absorption is the sum of intensity in the spectra from 400 nm to 800 nm.

**Correlation of Plasmon Resonance and Conductivity for different Polymer templates**

Transmission and reflection UV-Vis measurements were performed on the different polymer thin films to correlate the optical properties and the electrical properties. For all three polymer films for different silver thickness the absorption was calculated by the measured transmission and relative reflection with the following formula:
\[ A = 1 - \Delta R_\lambda - T, \]

with \( A \) being the average absorption, \( \Delta R_\lambda \) the relative reflectance change and \( T \) the transmission. The average absorption can be seen in Fig. S4 for all three templates, which is the average absorption in a wavelength range from 400 nm to 800 nm for a specific silver thickness. The spectral evolution for the diblock copolymer template can be seen in Fig. S4a. The average absorption is then compared with the insulator-to-metal transition (IMT) obtained from resistivity measurements. The results show that the IMT is near the maximum of average absorption for all polymer templates. Nearly before the film is percolated the absorption reaches its maximum due to the small distances between the clusters, which enhances the electric fields at the clusters and therefore the localized surface plasmon resonance (LSPR). For the static metal-polymer films the optical and the electrical results show the same tendency in the order of increasing IMT.

**Solvent annealing & metal deposition**

The solvent swells the film and attracts primarily the PMMA blocks. Thus, the solvent increases PMMA chain mobility more than the PS, which in turn induces a rearrangement of the thin film morphology due to energy minimization. The parameter which describes the morphology of copolymers depending on the physicochemical properties of polymer and environment is the Flory-Huggins parameter. The morphology depends on the coupling between the blocks, the surface energies of the substrate-to-polymer interface and the polymer-to-air interface. This can lead to different morphologies of the polymer thin film, whereby only lamellar arranged polymer blocks were considered as templates in this work. The FESEM images in Fig. S6a show an as annealed PS-b-PMMA copolymer. Fig. S6b shows the PS-b-PMMA copolymer with 1 nm silver
sputter deposited. The dark block could be identified as the PMMA block, where the cluster growth seems to be more homogeneous than on the lighter block (PS).

**Figure S5**: AFM image of a) pristine PS-b-PMMA, b) solvent vapor annealed PS-b-PMMA and c) sputter-coated PS-b-PMMA with 2 nm of Ag.

**Figure S6**: FESEM image of a) PS-b-PMMA solvent vapor annealed with acetone and b) PS-b-PMMA sputter-coated with 1 nm of Ag. One domain is more selective to Ag cluster growth than the other, which is seen by more and larger clusters on the PMMA/PS block.
Figure S7: FESEM image of a) PMMA sputter-coated with 2 nm Ag, b) PS sputter-coated with 2 nm Ag.

AFM Homopolymers

Figure S8: A comparison of the evolution of the topography from the homopolymer PS (upper row) and PMMA (lower row) at different effective silver thickness. The silver thickness is measured using a Quartz crystal microbalance (QCM). Without silver coating, the polymer films are flat and smooth. After silver sputter deposition of $\delta_{Ag} = 1$ nm the clusters are visible on PS, whereas they seem to be more embedded in the PMMA film. For $\delta_{Ag} > 4$ nm, the difference of the surface coverage of the clusters is less and less visible on the AFM image.
GISAXS Homopolymers

Figure S9: Average cluster radii derived from a hemispherical model for 1 and 4 nm of silver thickness on PS (blue symbols) and PMMA (red symbols) derived from static GISAXS pattern.

FTIR

Figure S10: FT-IR spectra of pristine PS-b-PMMA (red), PS (light green), PMMA (light blue) and sputter-coated with 1 nm Ag PS-b-PMMA (orange), PS (dark green) and PMMA (dark blue) and 2 nm Ag PS-b-PMMA (brown), PS (darkest green) and PMMA (darkest blue). The intensity of C=O carbonyl stretching vibrations at a wavelength of 1733 cm\(^{-1}\) changes for all templates from 0 nm to 2 nm Ag.
XPS

Figure S11: a) XPS spectra at C1s edge of pristine PMMA ($\delta_{Ag} = 0$ nm) and b) of sputter-coated PMMA with $\delta_{Ag} = 1$ nm. c) XPS spectra at O1s edge of pristine PMMA ($\delta_{Ag} = 0$ nm) and d) of sputter-coated PMMA with $\delta_{Ag} = 1$ nm. C-O bonding (blue), C=O bonding (green), C-C and C-H bonding (pink), Ag-O (grey), the envelope (red) and the background (brown) are shown in the XPS spectra. The intensity of C=O, C–O and O=C, O–C bonds is decreasing after sputtering of 1 nm Ag for the C1s and O1s electrons in PMMA. Furthermore, an AgO bonding is arising with silver deposition for PMMA. e) XPS spectra at C1S edge of pristine PS (blue) and of sputter-coated PS (black) show no significant changes. f) XPS spectra at O1S edge of pristine PS (blue) and of sputter-coated PS (black) with negligible changes.
In situ GISAXS measurements of Ag on PS-b-PMMA

Figure S12: Evolution of selected in situ 2D GISAXS data with increasing silver thickness deposited on PS-b-PMMA ($\delta_{Ag} = 0.5$ nm, 1 nm, 2 nm, 3 nm, 4 nm, 8 nm, 10 nm, 13 nm, 15 nm and 20 nm).

Distances and radii measured from the In situ GISAXS experiment

Figure S13: Evolution of the mean interparticle distance (D) and the cluster radius (R) of PMMA (black / grey symbols), PS (blue symbols) and PS-b-PMMA (green symbols).
In situ UV-Vis measurements of Ag on PS-b-PMMA

**Figure S14:** Full in situ UV-Vis spectra of Ag on PS-b-PMMA during the Ag sputter deposition for every 0.1 nm. The color code represents the time with showing the start in blue and the end in red color with the whole spectrum for $0.1 \text{ nm} \leq \delta_{Ag} \leq 14 \text{ nm}$. 
References:
