

Supplementary Information

In situ Studies Revealing the Effect of Au Surfactant on the Formation of Ultra-Thin Ag Layers Using High-Power Impulse Magnetron Sputter Deposition

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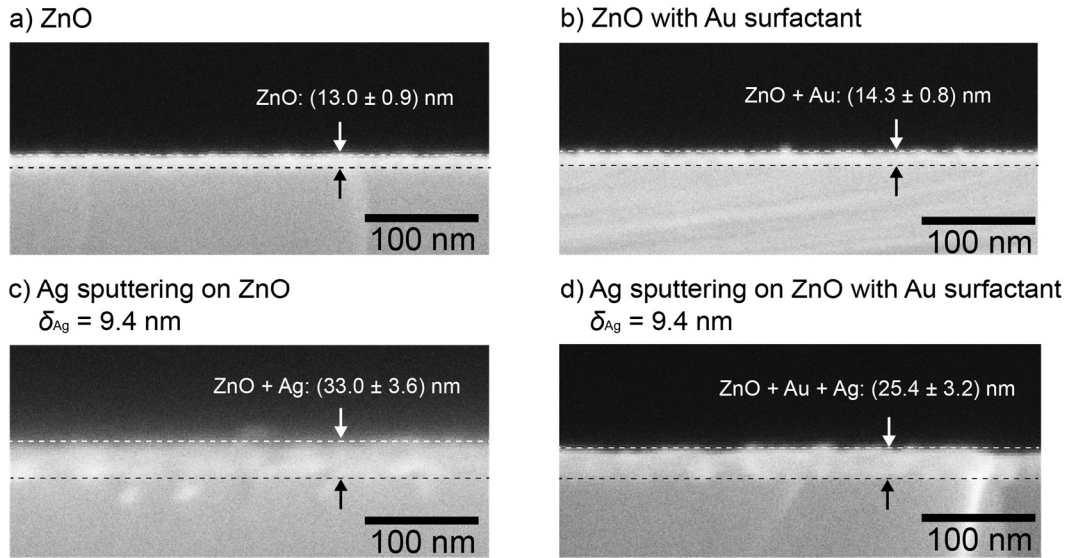


Figure S1. Cross-section FESEM images of (a) bare ZnO support, (b) ZnO support with Au surfactant ($\delta_{Au} = 2$ nm), (c) sputter-deposited UTSL on ZnO support ($\delta_{Ag} = 9.4$ nm), and (d) sputter-deposited UTSL on ZnO support with Au surfactant ($\delta_{Ag} = 9.4$ nm). The thickness values provided in the SEM images denote the entire film including the ZnO layer.

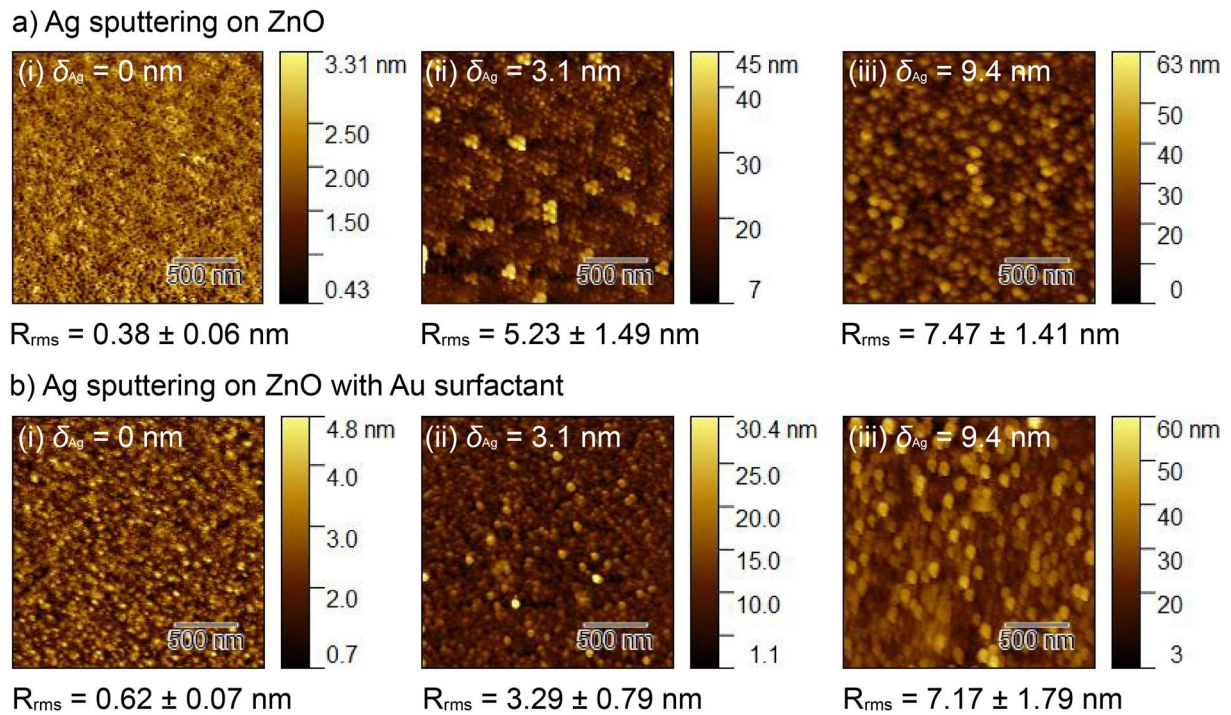


Figure S2. AFM images of HiPMS sputter-deposited UTSLs on (a) the bare ZnO support and (b) the ZnO support with Au surfactant at different $\delta_{Ag} =$ (i) 0 nm, (ii) 3.1 nm, and (iii) 9.4 nm, respectively. The corresponding values of root mean square roughness (R_{rms}) are also provided in the figures.

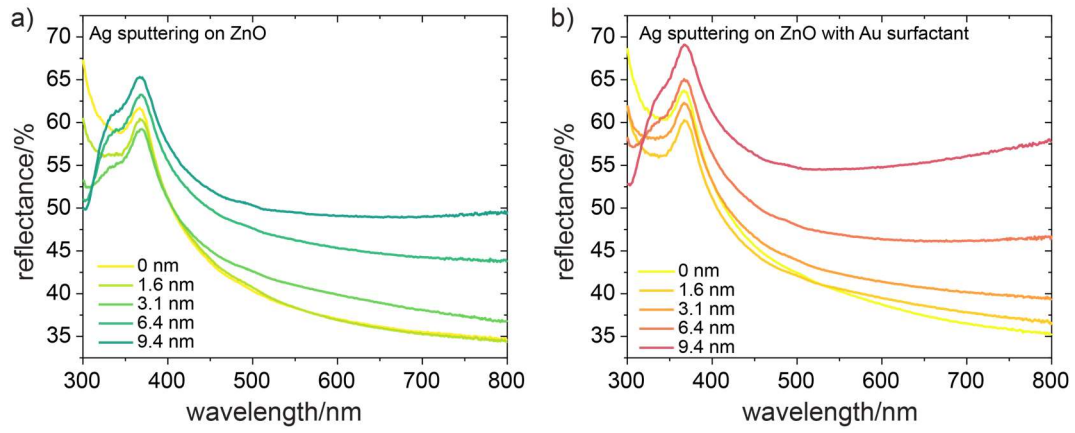


Figure S3. UV-vis reflectance spectra of HiPIMS sputter-deposited UTSLs on (a) the bare ZnO support and (b) ZnO support with Au surfactant with $\delta_{Ag} = 0, 1.6, 3.1, 6.4,$ and 9.4 nm as indicated, respectively.

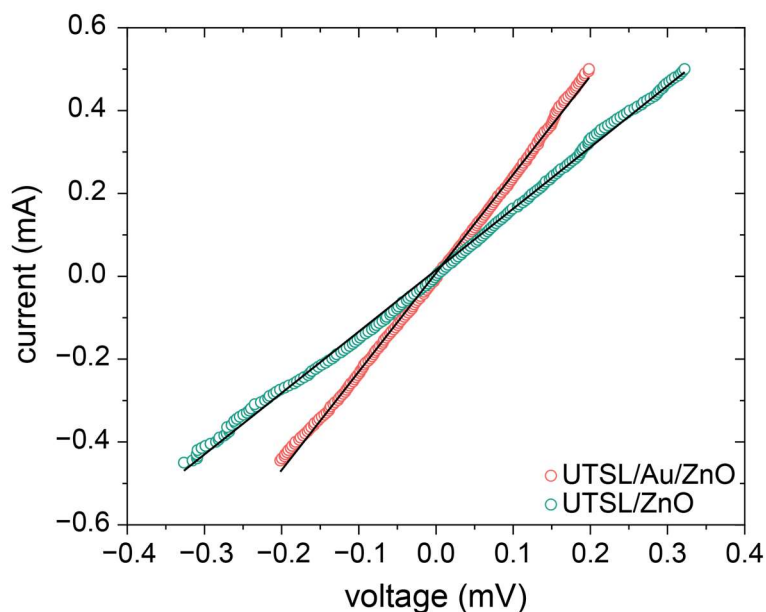


Figure S4. *IV*-curves of the UTSL/ZnO ($\delta_{Ag} = 9.4$ nm) and UTSL/Au/ZnO ($\delta_{Ag} = 9.4$ nm) thin films, together with the fits (black lines). The conductivities (σ) are calculated based on the relationship $\sigma = 1/r_{sheet} \cdot t_{film}$, where r_{sheet} refers to the sheet resistance of the sample, which equals to the reciprocal value of the fitted slop of *IV*-curve, while t_{film} refers to the real thickness of the sample, including the deposited Ag, ZnO support, pre-deposited Au nanoparticles, which is obtained from the cross-section FESEM images. It should be noted that the pre-deposited Au surfactant influences the results of resistance measurements. From the perspective of a practical application, when using the deposited UTSL with Au surfactant as a transparent electrode, the pre-deposited Au surfactant is also included as a part of the electrode.

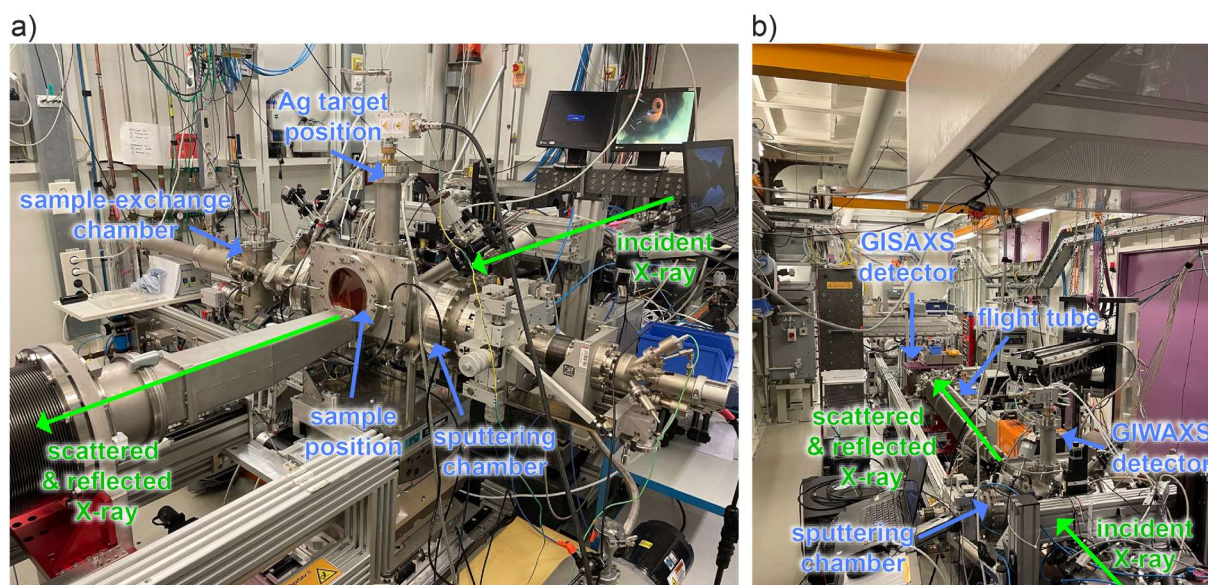


Figure S5. Photographs of (a) the custom-made HiPIMS system and (b) the whole experimental setup for *in situ* GIWAXS and GISAXS measurements integrated with HiPIMS system, which was mounted in the P03 beamline of the PETRA III storage ring at Deutsches Elektronen-Synchrotron (DESY, Hamburg, Germany).

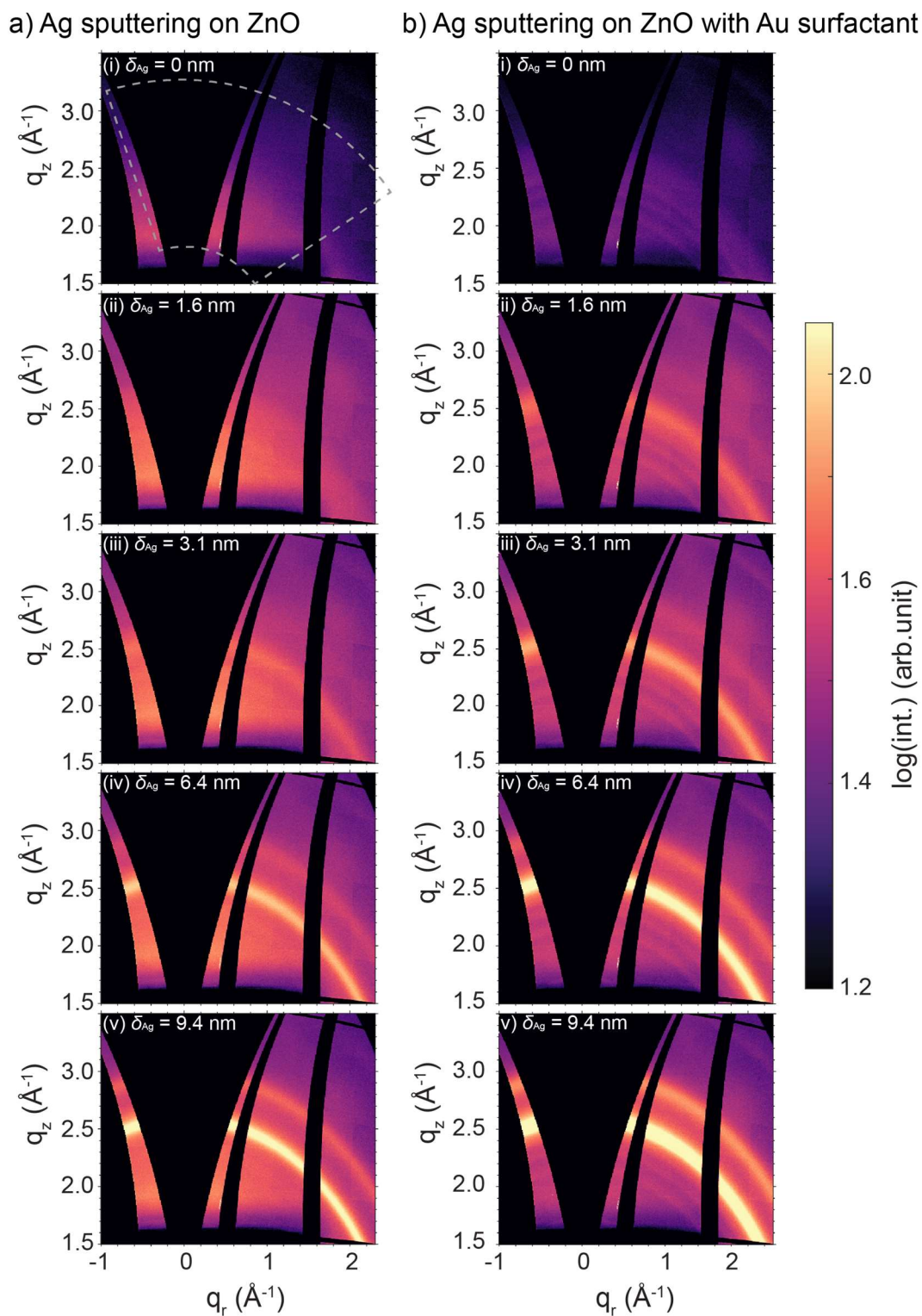


Figure S6. Selected reshaped 2D GIWAXS data recorded during the HiPIMS Ag sputter deposition processes on (a) pure ZnO support and (b) ZnO support with Au surfactant at different Ag effective thicknesses. The grayish dash sector in (a-i) represents the area for azimuthal integration (χ : $25^\circ - 100^\circ$) for further analysis.

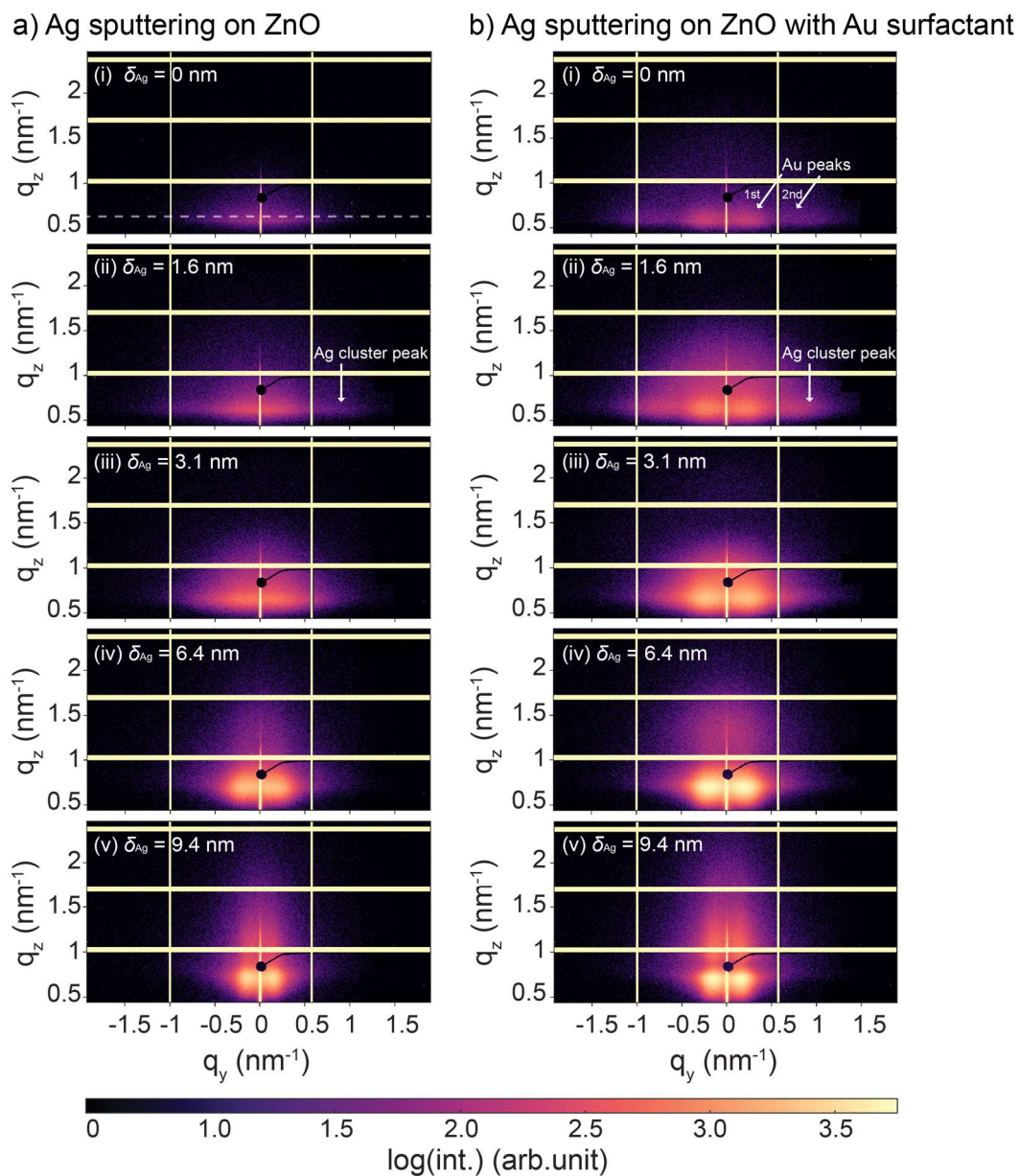


Figure S7. Selected 2D GISAXS data recorded during the HiPIMS Ag sputter deposition processes on (a) pure ZnO support and (b) ZnO support with Au surfactant at different Ag effective thicknesses. The grayish dash line in (a-i) refers to the position for horizontal line cuts for further analysis.

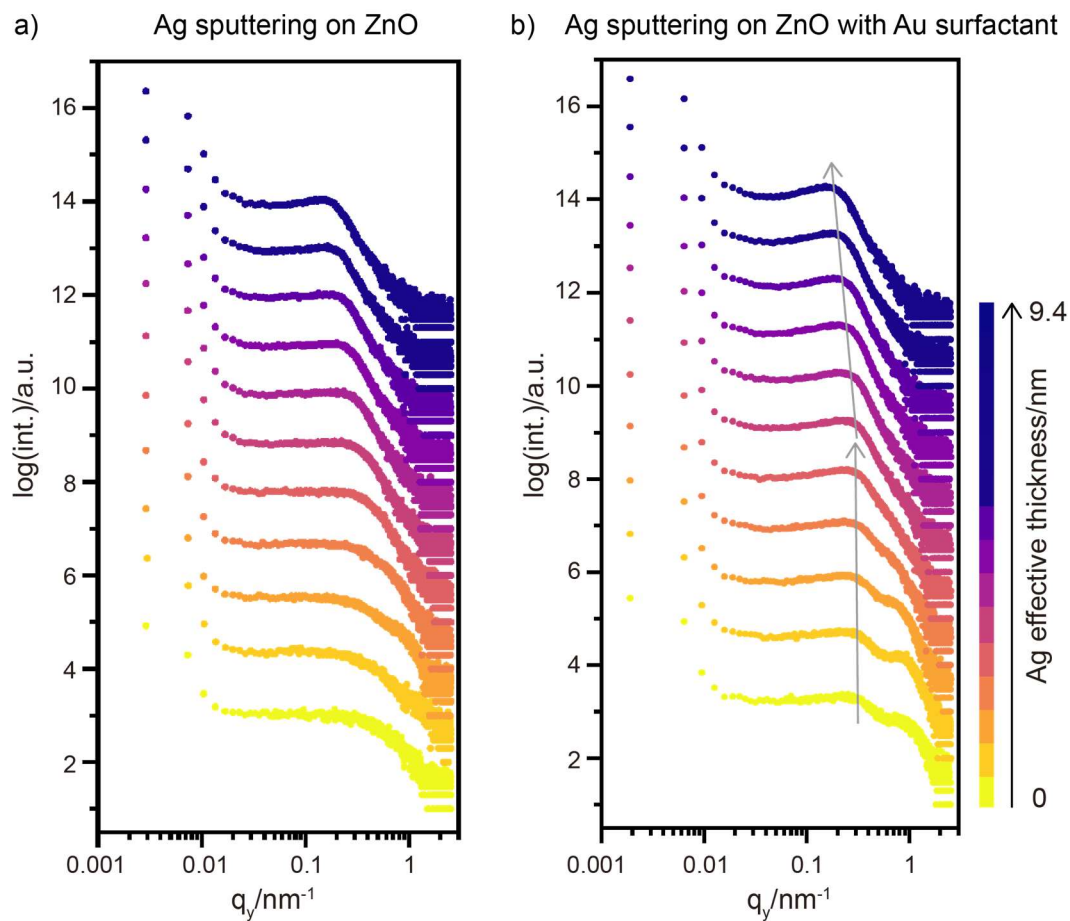


Figure S8. Horizontal line cuts of the 2D GISAXS data collected during the Ag sputter deposition on (a) bare ZnO and (b) ZnO with pre-deposited Au surfactant supports, taken at $0.607 \text{ nm}^{-1} < q_z < 0.640 \text{ nm}^{-1}$, taken every 3 s starting at sputtering time (t_s) = 0 s.

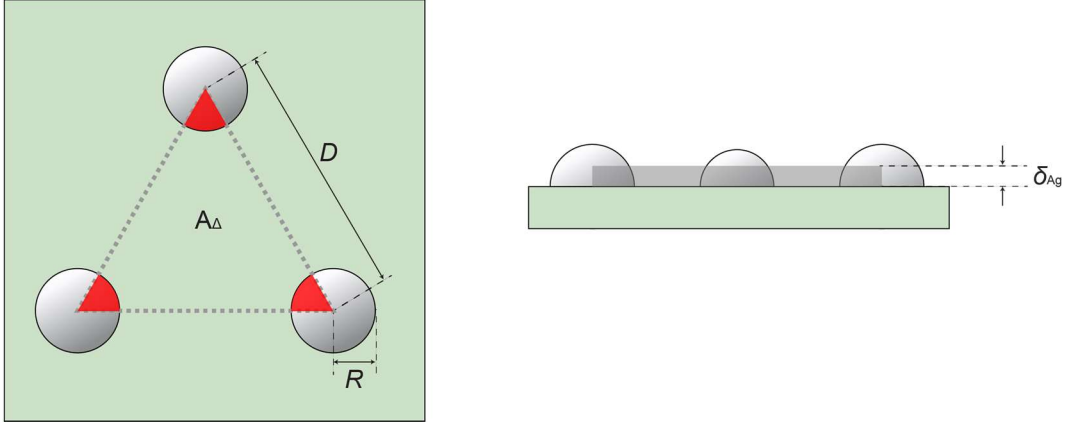


Figure S9. Top view and side view of the geometrical model in the local area applied for the quantitative analysis of the *in situ* GISAXS data collected during the Ag sputtering.

The geometrical model assumes that the sputter-deposited Ag clusters exhibit a hemispherical shape during growth with uniform radius R being distributed in a 2D hexagonal lattice with the correlation distance D . The correlation distance D can be obtained by the relation $D \approx 2\pi q_i^{-1}$, where q_i is the fitted peak position from the horizontal line cuts of GISAXS data that are obtained by using a combination of Lorentzian and Gaussian functions. To calculate the average radius R , we assume that the centers of three adjacent hemispherical Au clusters connect with each other to form an equilateral triangle with the side length of D , as shown by the dashed line triangle in **Figure S9**. The area of this equilateral triangle is marked as A_Δ . It is assumed that all deposited Ag on this triangle area can be separated into three individual uniform Ag clusters. Therefore, it assumes that the volume of Ag clusters located in this triangle area (as shown by the red sections) is equal to that of an equilateral triangle prism with this equilateral triangle as the base and δ_{Ag} as the height. Based on the above assumption, R can be calculated by the following equation:

$$R = \sqrt[3]{\frac{3^{3/2}}{4\pi} D^2 \delta_{Ag}} = \left(3^{3/2} \pi \frac{\delta_{Ag}}{q_i^2}\right)^{1/3} \quad (\text{S-1})$$

The Ag layer surface coverage \mathcal{S} is defined as the ratio of A_C to A_Δ , where A_C is the area, which is covered by the deposited Ag clusters in the equilateral triangle unit cell.

$$\mathfrak{G} = \frac{A_C}{A_\Delta} = \frac{2\pi R^2}{\sqrt{3} D^2} = \frac{R^2 q_i^2}{2\pi\sqrt{3}} \quad (\text{S-2})$$

In addition, the Ag layer porosity Φ is defined as the ratio of the void volume (V_v) to the total volume V_Δ within the unit cell of the equilateral triangle prism with the area A_Δ as the base.

$$\Phi = \frac{V_v}{V_\Delta} = \frac{\frac{\sqrt{3}}{4} D^2 (R - \delta_{Ag})}{\frac{\sqrt{3}}{4} D^2 R} = 1 - \frac{\delta_{Ag}}{R} \quad (\text{S-3})$$