Electronic Supplementary Information (ESI) for

New insights into colloidal gold flakes: structural investigation, micro-ellipsometry and thinning procedure towards ultrathin monocrystalline layers

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Micro-Ellipsometry

Figure S1 shows a detailed sketch of the micro-ellipsometry measurement setup.

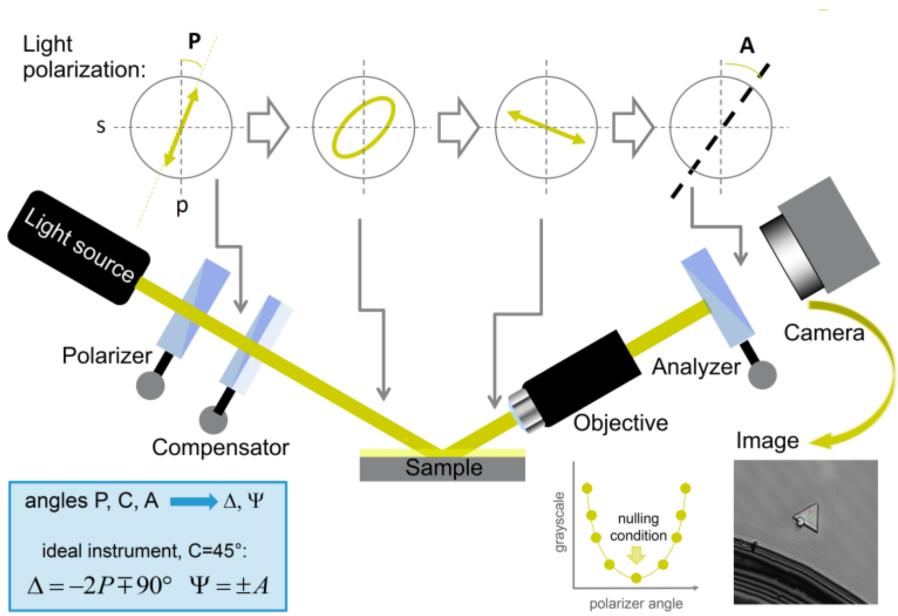

Figure S1: Schematic of the working principle of the Accurion imaging ellipsometer "nanofilm ep4" used for the spectroscopic measurements of the ellipsometric parameters Ψ and Δ in the middle of the investigated Au flake.

Simulations of ion beam damage and electron probing depth

To investigate the depth distribution of damage generated by the focused ion beam during the thinning process, the open source software SRIM-2013 (Stopping and Range of Ions in Matter) was used. In the simulation 100.000 Ga^+ ions with energy of 30 keV were shot into gold. The blue curve in figure S2 shows the damage distribution (vacancies generated by ions and recoils). To answer the question if the EBSD measurements probe the damaged region or if it is capable of probing the underlying undamaged volume, the free software Casino_v2.4.8.1 was used. The green curve in figure 1 shows the depth distribution from which primary backscattered electrons reach the surface and can theoretically hit the phosphorous screen of the EBSD detector. Since Monte Carlo simulations do not take the crystal lattice into account (which generates the Kikuchi patterns), this simulation is only a rough estimation, but in general it can be stated that the electrons probe only a very shallow depth of 10-20 nm, which is also the depth with the most ion beam generated damage. Therefore we can conclude that the single-crystallinity which we measured in the thinned antennas is a real feature and not an artifact from a deeper probing than damaging.

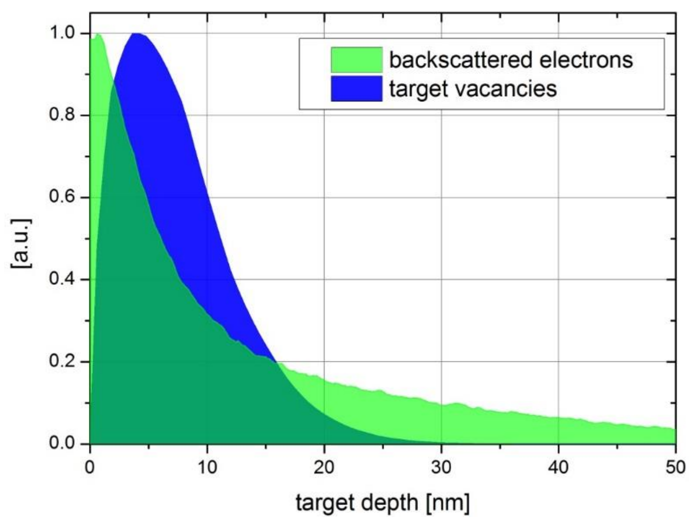

Figure S2: Normalized ion beam damage (vacancies) and backscattered electron depth distribution in gold, derived from SRIM and Casino software.

Generation of ultrasmall and 3-dimensional features

Since the etching rate in monocrystalline gold is very homogeneous, even very small differences in etching depth can be realized. To demonstrate the possibility of ultrasmall thickness differences, we etched a 2 x 3 µm² small Mona Lisa into a gold plate. Therefore we used a special feature of the Tescan Lyra FIB software, where a greyscale image is translated into etching parameters. The maximal etching depth for this structure was 20nm (equals white in the greyscale bitmap file) and was reduced to 0nm (black in greyscale file) in 256 steps (8bit). Figure S3 shows the result of this experiment and can be called the „smallest Mona Lisa in the world". In a sputtered layer of gold such a precise generation of a nanostructure with fine details would not be possible as shown in the main manuscript.

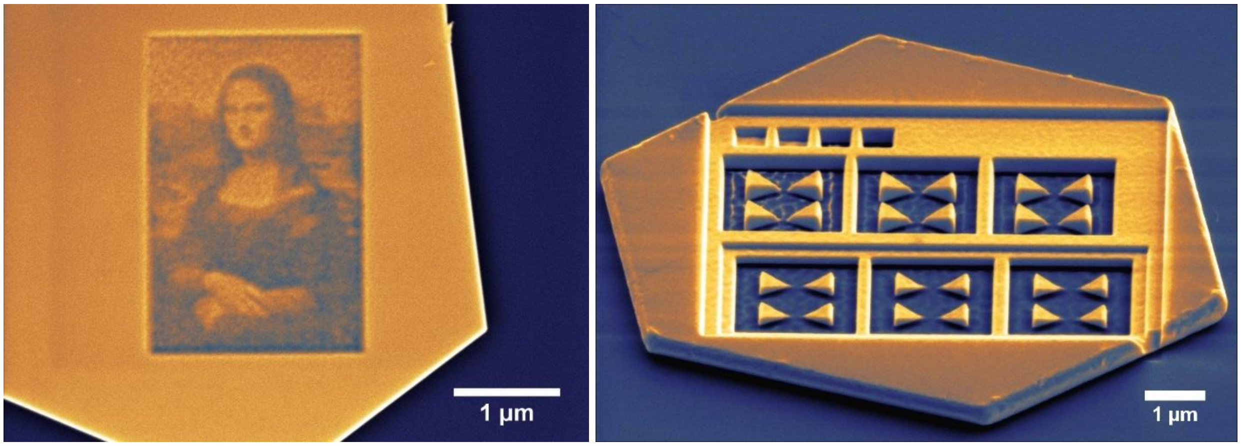

Figure S3: Left: Colored SEM micrograph of the fabrication of a Mona Lisa image in a monocrystalline gold plate. The extreme homogeneous etching enables the generation of structures with very fine details and thickness variations. Right: Fabrication of 3-dimensional bowtie antennas in a thick flake. FIB-etched Inclined and smooth edges are only possible in monocrystalline material.

Thinning Process

For the thinning experiment we chose a very large triangular flake with an edge length of 70 µm. Figure S4 shows the chosen flake with the performed experiments. In the beginning the necessary dose to etch through the flake was determined by rectangles with increasing ion dose (upper left), then the first thinning and structuring process was done in the lower right, but due to an attached gold particle and parasitic growth coming from that particle, this area was thicker than the rest of the flake. The final pattern which was also analyzed by EBSD and shown in the main article was written on the right side of the flake.

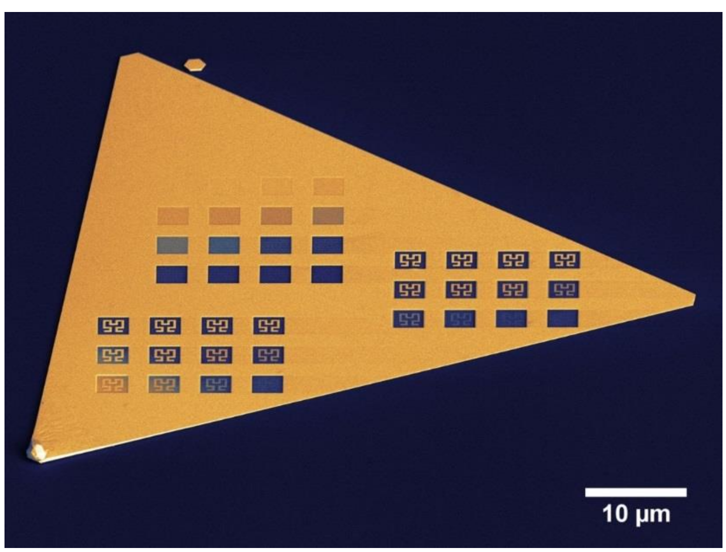

Figure S4: Colored SEM micrograph of a large gold flake on which the thinning and structuring experiments shown in this article were performed.

Effects of purification

In the main text we shortly mention a purification after the synthesis. Here, we show the impact of centrifugation and careful dropcasting of the flakes. Figure S5 shows a good and a bad example for deposition of flakes and for contamination with other particles than flakes.

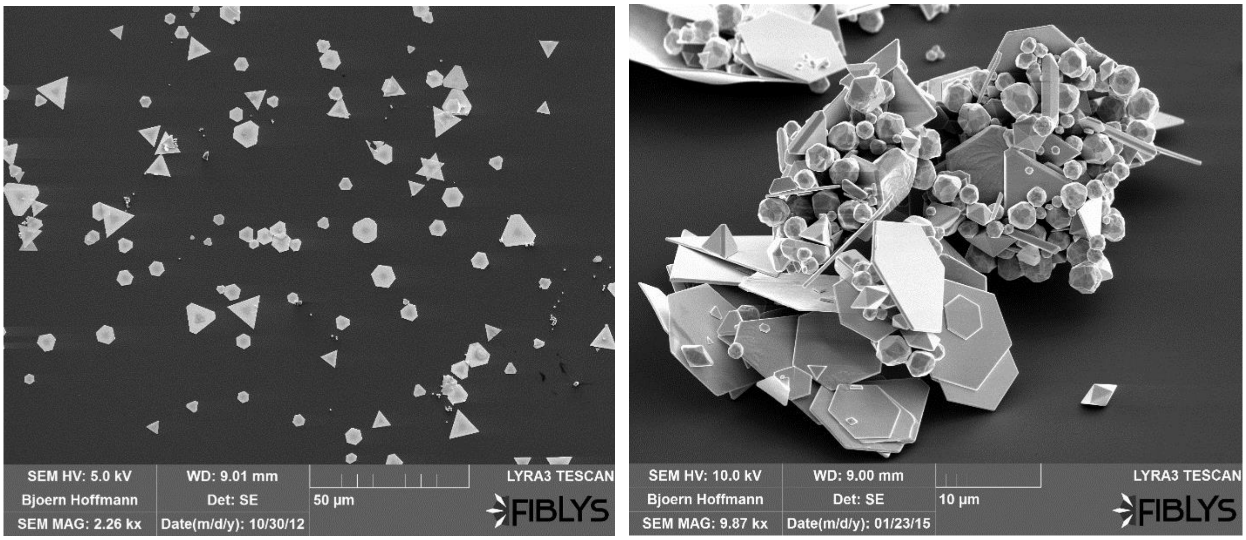

Figure S5: The left image is a good example for a high flake-to-particle ratio and flat lying flakes. The right image demonstrates a bad purification which leads to agglomeration and a bad flake-to-particle ratio.

Additional TEM investigations

We have performed additional high-resolution TEM (HRTEM) investigations to further prove the existence of twins already before the FIB cutting for a detailed defect analysis. The HRTEM results (see Figure S6) confirm that the flake is twinned. As expected, the Fast-Fourier Transformation (FFT) of the HRTEM image gives comparable results obtained from electron diffraction analysis shown in Figure 1d in the main manuscript.

Furthermore, we have carried out a high-resolution scanning TEM (HRSTEM) analysis of the Au flake cross-sections that were initially prepared by the shadow FIB technique for a conventional TEM analysis shown in Figure 2 in the main manuscript. Figure S7 shows two HRSTEM images of an Au flake which contains a twin and a flake without twins.

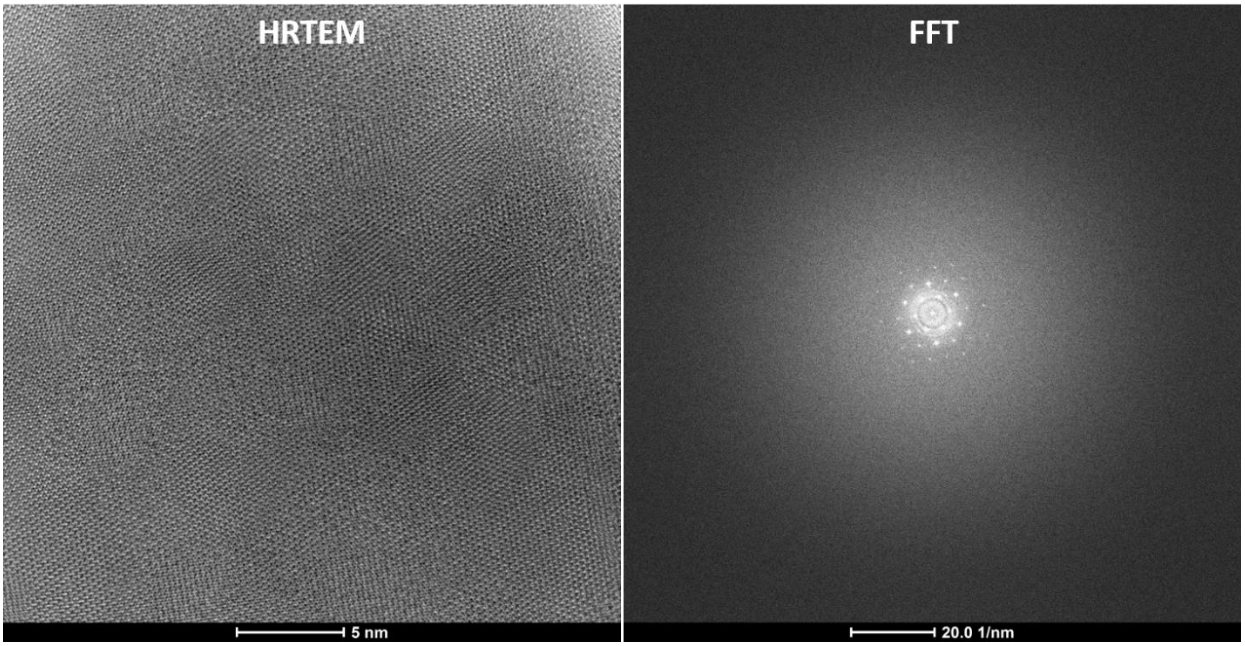

Figure S6: left: HRTEM image in [111] viewing direction of a gold flake suspended on a copper / carbon TEM grid. Right: FFT of the HRTEM image on the left. In agreement with the electron diffraction pattern shown in Figure 1d in the main manuscript, the FFT exhibits the same formally-forbidden reflections next to the regular reflections.

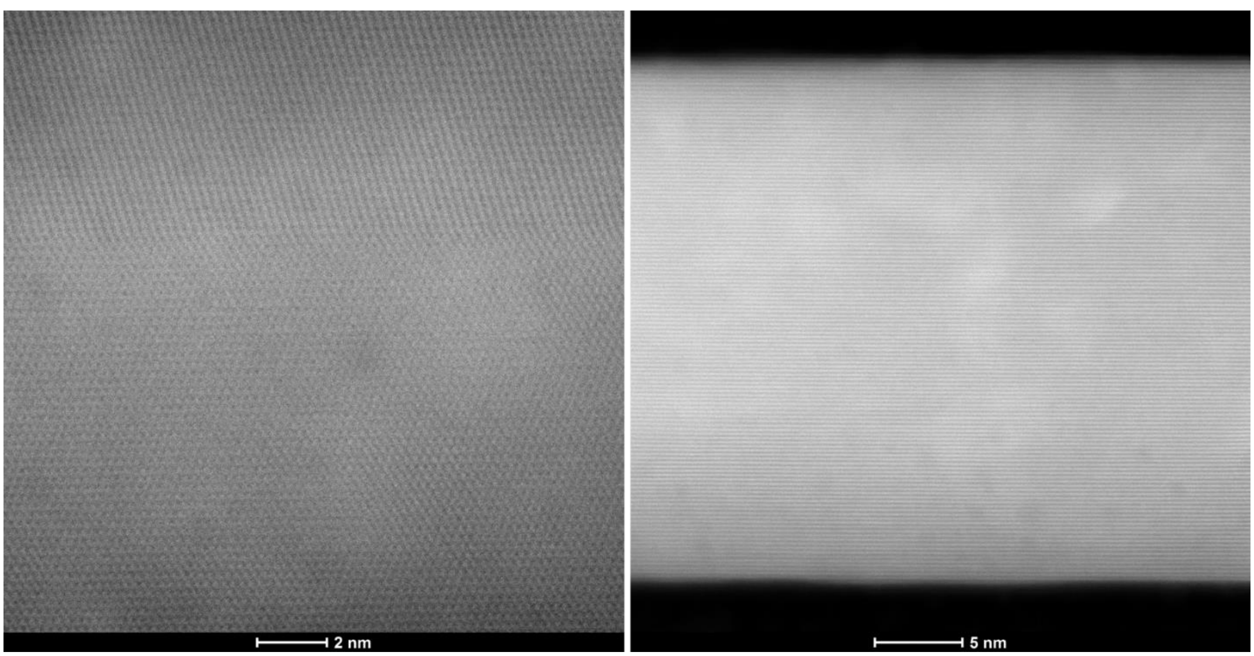

Figure S7: Left: HRSTEM image of a Au flake in cross section which contains one twin. Right: HRSTEM image of a Au flake that contains no twins.