Supporting Information

Guided Assembly of Gold Colloidal Nanoparticles on Silicon Substrates Pre-Patterned by Charged Particle Beams

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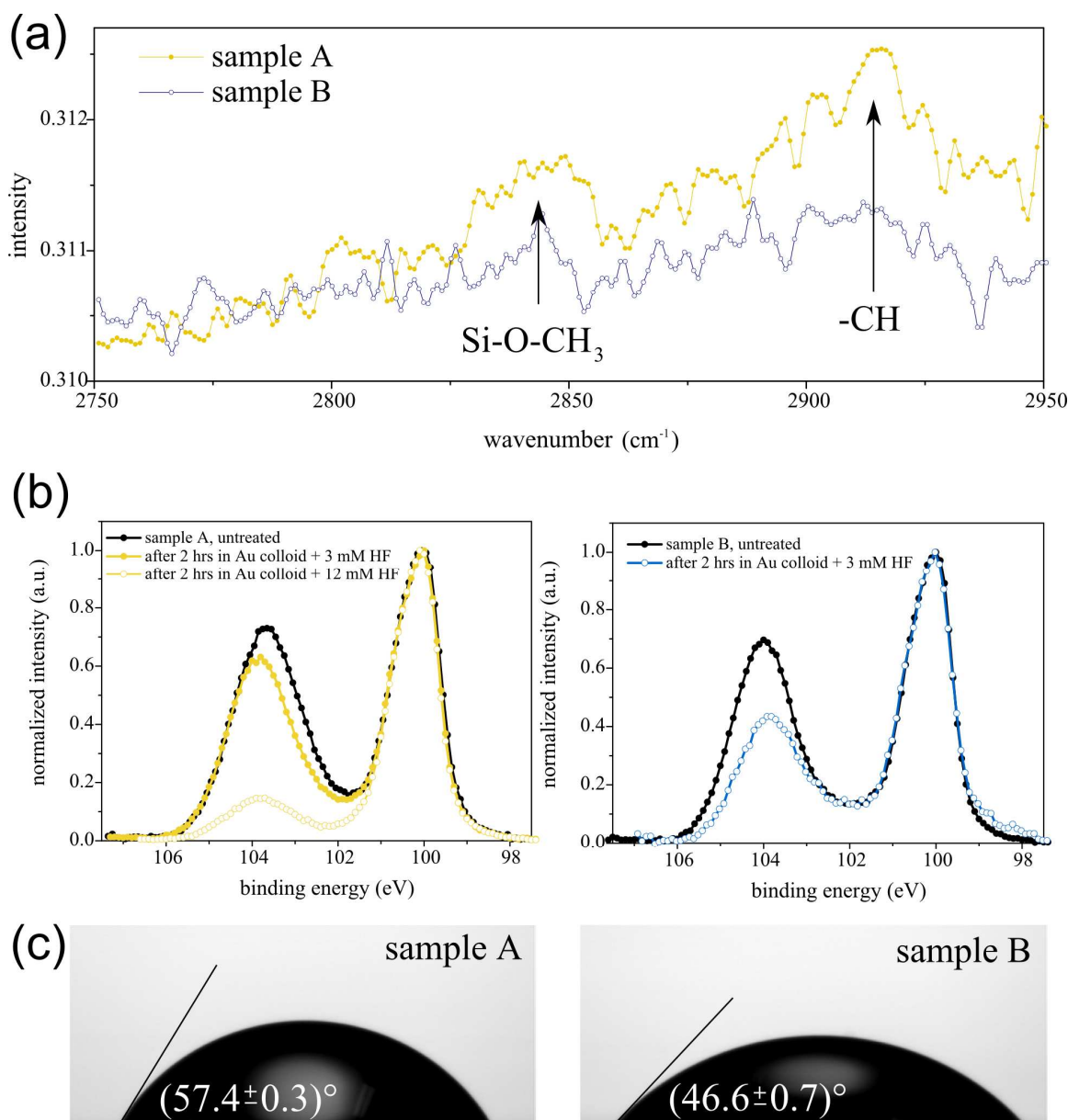[4]Institut für Angewandte Physik, Technische Universität Wien, A-1040 Wien, Austria

Figure S1. Additional sample characterization. a) FTIR spectra of both samples A and B, showing the region of –CH$_x$ stretching vibrations. b) Evolution of XPS Si 2p peaks for both samples after immersion in HF-modified colloidal solutions. The sample A is more resistant against oxide etching in diluted HF in comparison to the sample B, mainly due to –H and –CH$_x$ termination.[1] Even after immersion in the HF solution having pH=2.5 (12 mM-HF-modified solution) the oxide on the sample A is not etched completely off. c) Wetting angle measurements, proving the increased hydrophobicity of sample A.

[1] Li, H.; Lin, Z.; Wu, Z.; Lusk, M. T. First Principles Analysis of the Initial Oxidation of Si(001) and Si(111) Surfaces Terminated with H and CH$_3$. *J. Chem. Phys.* **2012**, 136, 064507.
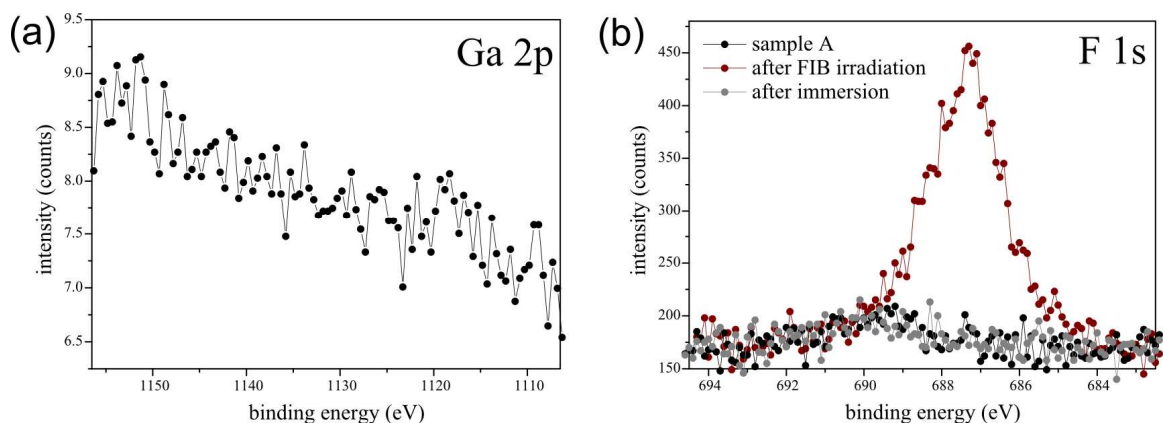
Figure S2. Sample contamination build-up after high fluence 5 keV Ga irradiation (1.3×10^{15} cm^{-2}). a) The XPS region where the peaks attributed to the Ga 2p state should have been visible in case of Ga contamination. Note that Ga was not detectable even after immersion in the 12-mM-HF-modified solution (not shown). b) After irradiation by 5 keV Ga^{+} ions (1.3×10^{15} cm^{-2}), a peak associated to fluorine emerged in the spectrum, coming from decomposition of fluorocarbon molecules from residual atmosphere in the microscope chamber by the ion beam. After immersion in the 3-mM-HF-modified solution this peak disappears, indicating a dissolution of fluorine contamination or, more probably, substitution of fluorine by other species, mainly carbon or hydrogen.
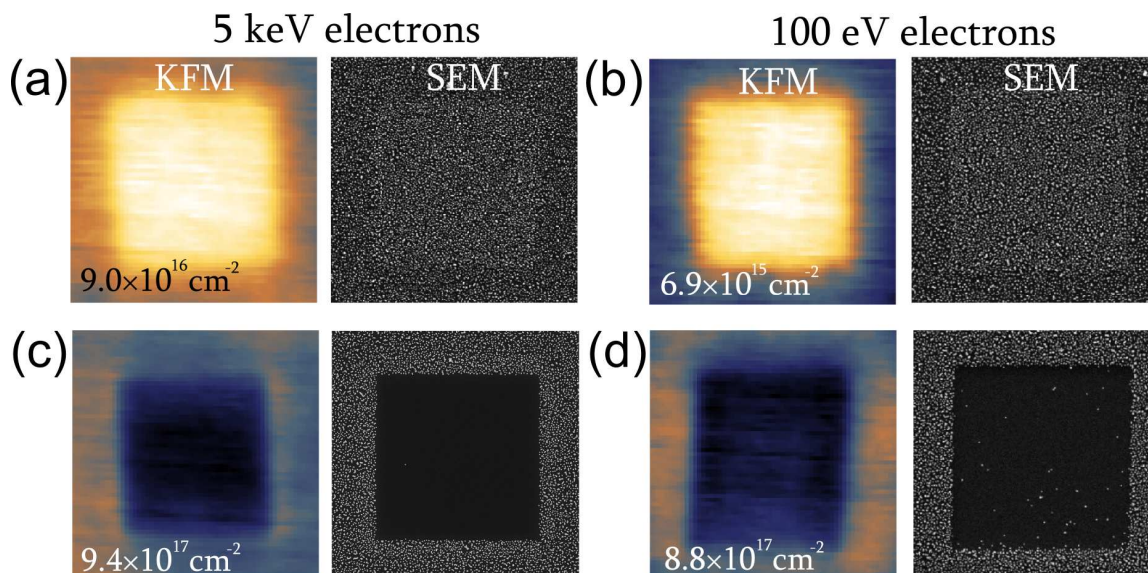
Figure S3. Electron beam modification of the surface potential and the effect on the Au particle depositon. 5 keV (a,c) and 100 eV (b,d) electrons were used with fluences of 9.0×10^{16} cm^{-2} (a), 6.9×10^{15} cm^{-2} (b), 9.4×10^{17} cm^{-2} (c) and 8.8×10^{17} cm^{-2} (d). Only the data obtained on the sample B are presented, because unlike for ions the surface potential changes with electron beam irradiation are similar for both studied substrates. Similar to the areas modified by low ion fluences, the surface potential increases with the low electron fluence, inducing very similar effects on the Au colloid deposition ((a,b) with SEM images of the sample after immersion shown on the right). Note that the fluence of 100 eV electrons necessary for achieving the adhesion increase is one order of magnitude smaller than that of 5 keV electrons because they are more efficient in surface oxide modification. Interestingly, to prevent the deposition a similar electron fluence is necessary in both cases (c,d).
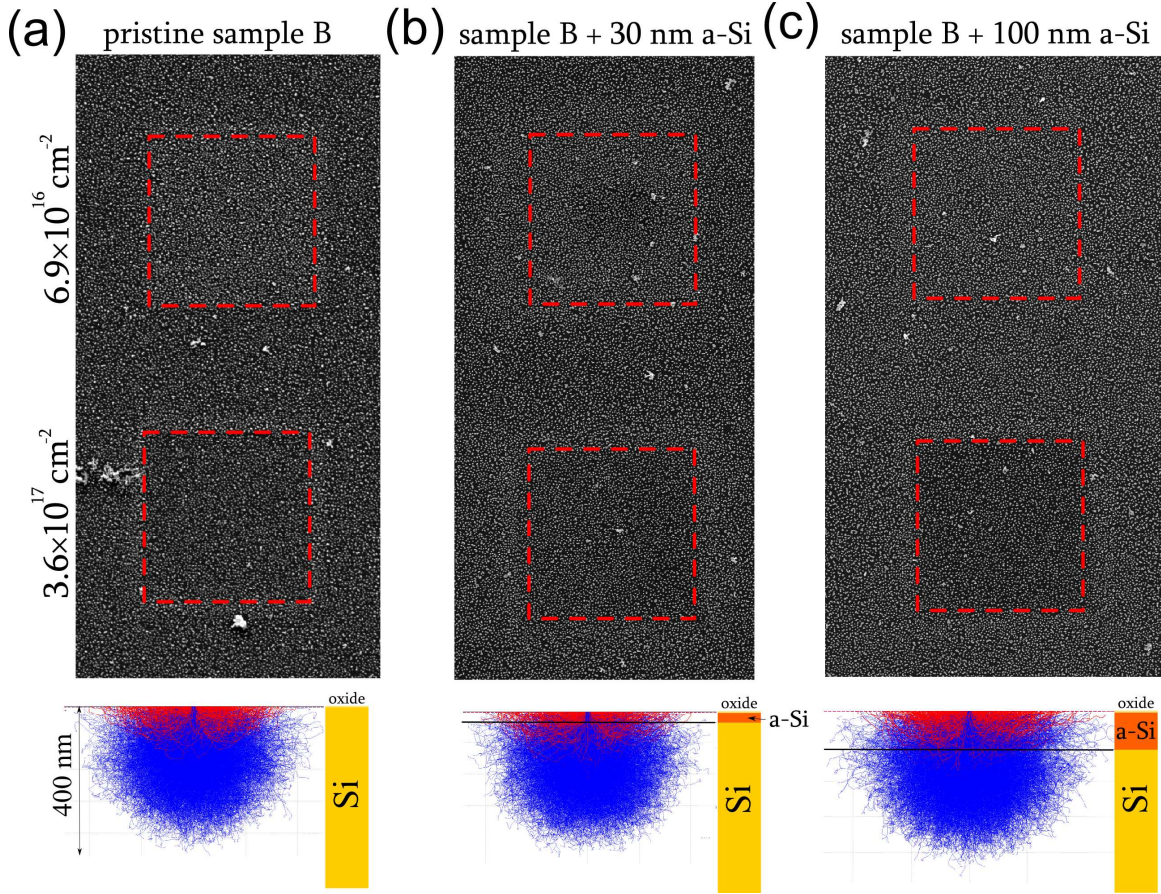
Figure S4. Effect of amorphized silicon layers of different thicknesses on the deposition of gold colloids on the areas patterned by the 5 keV electron beam. SEM images show squares (outlined in red) formed by a fluence of 6.9×10^{16} electrons.cm^{-2} (top row) and 3.6×10^{17} electrons.cm^{-2} (bottom row) onto a) sample B, b) sample B with the deposited 30 nm-thick amorphous silicon layer on top and c) sample B with the 100 nm-thick amorphous silicon layer on top. The immersion time in the solution of 20 nm Au colloids modified with 3 mM HF was 2 hours. The images at the bottom show the electron beam ranges calculated using the Monte Carlo simulation package Casino.[2] Incident electron trajectories are marked in blue, backscattered electrons in red. In the structure models there is (a) only 1.4 nm thick native oxide on top of the silicon substrate, (b) 30 nm-thick amorphous silicon between the silicon oxide (1.4 nm) and the silicon substrate and (c) 100 nm-thick amorphous silicon between the silicon oxide (1.4 nm) and the silicon substrate. The lower interface of the layer is marked by the black line. The thickness of the native oxide was deduced from the XPS spectra, the density of the amorphous silicon was taken as 93% of the crystalline one.[3] The surface charging could be due to the uncompensated secondary electron emission, electron-hole pair generation along the electron paths and unbalanced charge trapped within defects in the amorphous silicon layer. As the charge trapping layer has a different thickness in each experiment, supposing that the charging is responsible for enhanced deposition of gold colloids, the colloidal coverage should differ significantly between the samples, with sample (c) potentially most efficient in charge trapping. Since this behavior is not observed, the

hypothesis of charge trapping induced deposition has to be refused and the surface chemistry of the native oxide must be considered instead.

[2] Drouin, D.; Couture, A. R.; Joly, D.; Tastet, X.; Aimez, V.; Gauvin, R. CASINO v2.42 – A fast and easy-to-use modelling tool for scanning electron microscopy and microanalysis users. *Scanning* **2007**, 29, 92-101.

[3] Wang, J. B.; Datta, A.; Wang, Y. L. Morphological Changes of Si(100) Induced by Focused Ion Beam Irradiation. *Appl. Surf. Sci.* **1998**, 135, 129-136.
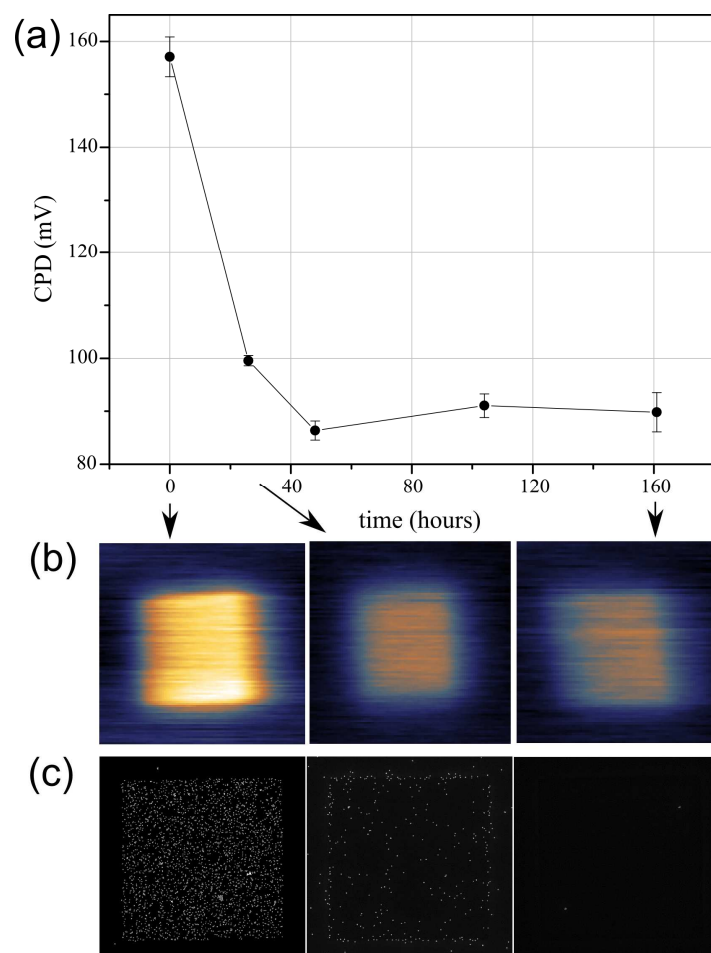
Figure S5. Ageing effect on a 5 keV-ion-beam-patterned area (fluence 1.3×10^{14} cm^{-2}) on the sample A. a) Dependence of the contact potential difference on time (measured at different equivalent areas). The samples were stored in air (humidity 40%). Selected KFM measurements as well as results of colloid deposition carried out in corresponding times are shown in (b) and (c), respectively. It should be pointed out that the CPD between the silicon substrate and the ion beam exposed area does not diminish even after a year, which makes the implanted charge hypothesis unfeasible. The CPD decrease here is caused by a natural loss of the adsorbed -OH groups[4] as well as due to a shielding effect of adsorbed water molecules. [5,6]

[4] Hattori, T. In *Ultraclean surface processing of silicon wafers*; Hattori, T., ed.; Springer-Verlag: Berlin Heildelberg, **1998**.

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[6] Michalak, D. J.; Amy, S. R.; Aureau, D.; Dai, M.; Estève, A.; Chabal, Y. J. Nanopatterning Si(111) Surfaces as a Selective Surface-Chemistry Route. *Nature Mat.* **2010**, 9, 266-271.