Support Information File

Influence of metal-support interaction on the surface structure of gold nanoclusters deposited on native SiO_x/Si substrates

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KEYWORDS Gold nanoparticles, Metal support interaction, EXAFS, GISAXS, AFM, native SiO_2.

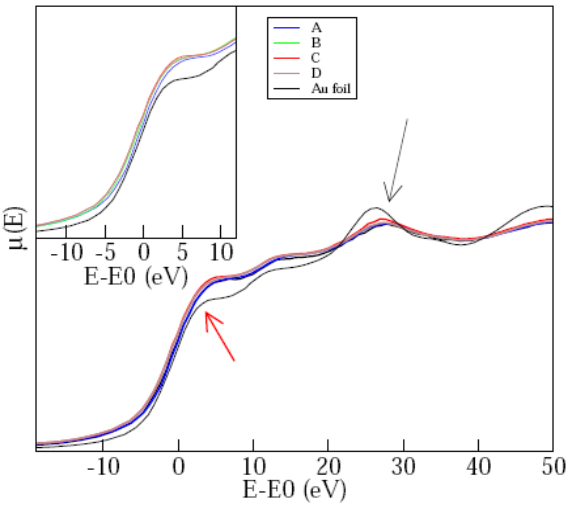

Figure S1. XANES of Au nanoparticles on SiO_x/Si A, B, C ,D samples. The Au foil XANES is reported for comparison. The arrows highlight the first (red) and the third XANES peak respectively. See the text for the details.

The features of XANES spectra are similar in all the samples (see Figure S1). The position and the

width of the peaks after the edge are correlated to the Au cluster size. All the samples possess the main peak centered on 25 eV (indicated by the black arrow in Figure S1) less intense and wider than that of the Au foil. Further, the 25 eV peak position is shifted with respect to the reference sample towards higher energies. These observations and the fact that the width is the almost the same for all spectra, suggest a small dimension of the deposited metal clusters whose value is similar for all the samples.

The p-d transitions and their possible changes which might modify the first XANES peak (indicated by the red arrow in Figure S1) are blurred by the presence of the small particles. Due to the blurring, the variations induced by the possible metal-support interaction are not clearly visible.

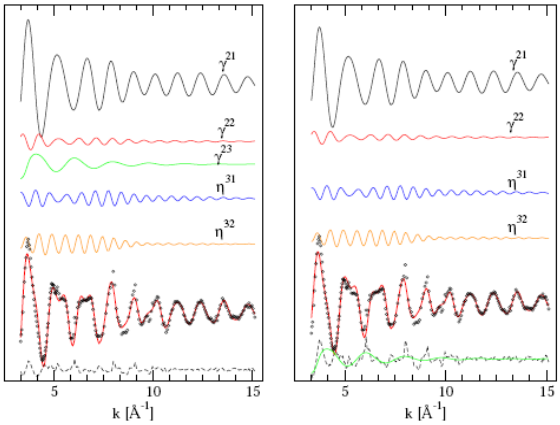

Figure S2. The observed (black symbols)and the calculated (red line) EXAFS signals for the sample D. The residual is indicated by the dash line. The components used in the fitting are also reported in the upper part with different colors. According to the GNXAS procedure, the γ^{2i} (i=1,3) are the two-body configurations whereas, the η^{3i} (i=1,2) are the three-body ones. See the text for the details. A Au-O distance equal to the γ^{23} has been taken into account in the fitting reported in the left panel. In the right panel, the Au-Os distance is absent. To mark its importance it has been superimposed to the residual.

To obtain a satisfactory result, it has been necessary to include an Au-O distance in the fitting (Figure S2 left panel). If the Au-O distance is not taken into account, a low frequency is clearly visible in the residual (Figure S2 right panel). The presence of the Au-O component suggests that the gold atoms are bonded to the oxygen of the support resulting in the interaction between metal particles and the surface support. The Au-O distance is absent in the sample obtained when the metal clusters are deposited on the thermal oxide substrate (sample A). The discussion concerning this result is reported in the full paper.

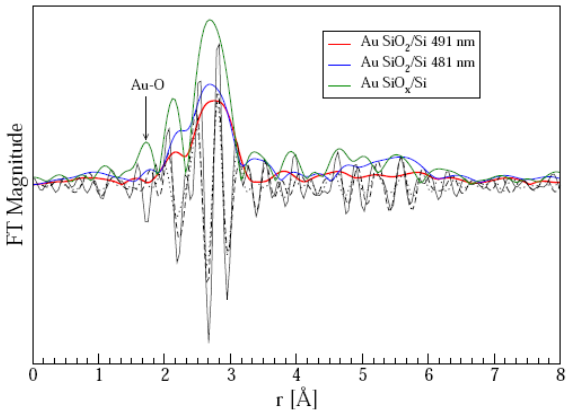

Figure S3. Fourier Transforms uncorrected for phase shift of the Au metal clusters deposited on two different thermal treated substrates together with a sample supported on native oxide. For the sake of clarity, the imaginary part (Au-SiOx/Si black line, Au-SiO_2/Si 491 nm thick dot and Au-SiO_2/Si 481 nm thick bold dash-dot respectively) are not inserted in the legend box.

Figure S3 shows the Fourier Transforms for three samples deposited on thermal treated and native silica substrates. It is evident that the clusters of the two samples deposited on the thermal treated oxide have very similar imaginary part with respect to those obtained on the native substrate. So, they have similar structural parameters in term of distances, sizes and thermal disorder. However, the Au-O distance is present in the samples deposited on the native oxide substrate at r=1.8 Å (uncorrected for the phase shift) as indicated by the arrow (Figure S3).

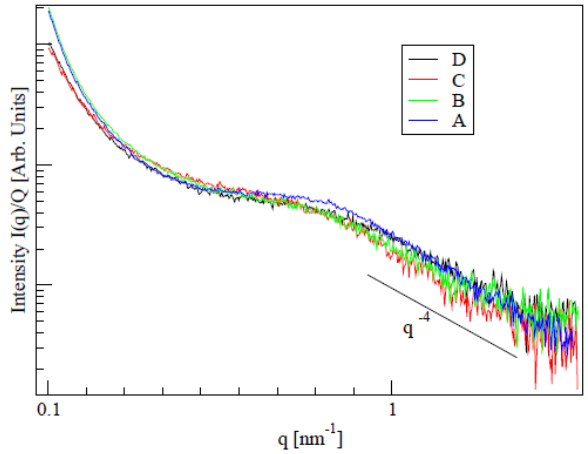

Figure S4. GISAXS data of samples A, B, C and D respectively. The presence of a marked interference peak in the sample A (Au-SiO_2/Si) can be noted. The straight line represents the Porod law q^{-4}.

In Figure S4, the overlapped GISAXS patterns for all the analyzed samples are reported. The sample obtained by depositing gold clusters on thermal treated substrate shows a marked interference peak centered at 0.85 nm^{-1}. The interference peak arises from the interaction of the two

scattered waves when the spherical particles are nearly in contact. The difference in the interference term among the different samples can be explained in terms of the small difference in the cluster size.

Keeping in mind that the metal amount is the same in all the samples, as well as the dimension of Silicon substrate (2 cm x1 cm), the effect of larger size of the metal clusters in the sample B, C and D respectively is equivalent to a concentration decrease, so in this case the structure factor is weaker in the pattern. On the contrary this is evident in the sample A that has the smallest metal particle size.

The X-ray reflectivity (XRR) curve for sample C is reported in Figure S5.

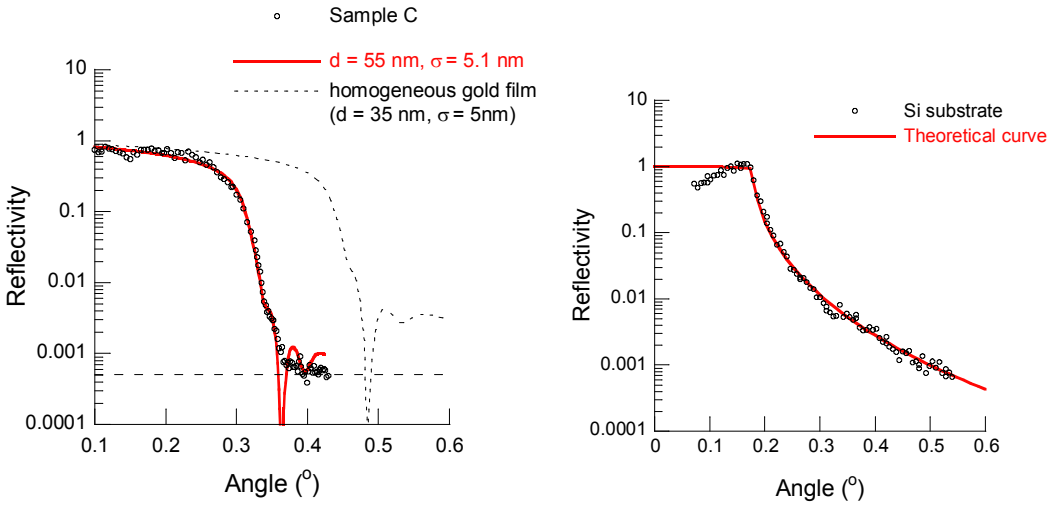

Figure S5. (Left) Raw XRR curve for sample C. The background level of the measurement due to the diffuse intensity originating from the highly rough and inhomogeneous nature of the film is indicated by the broken line. (Right) Comparison between the measured XRR curve for bare Si substrate and the theoretical XRR profile for a 2 nm SiO_2 layer with 0.23 nm roughness on thick Si substrate (red curve).

Due to the rough and inhomogeneous nature of the deposited nanocluster films, the reflected intensity drops rapidly above the critical angle. The observed critical angle of 0.28-0.3° is sensibly lower than that for bulk gold (0.443° for a wavelength of 0.124 nm). Such a large shift, often reported in literature for porous nanocrystalline films, can be understood as the result from an inhomogeneous layer full of voids that extends deeply towards the substrate as evidenced from AFM. An average mass density of the film of about 9.5 g/cm^3 is obtained from the simulations.

Some weak oscillations are present for angles below 0.4°. A film thickness around 55 nm and an average roughness of 5.1 nm are estimated from XRR intensity simulations. The surface roughness value of 5.1 nm obtained from XRR simulation is in excellent agreement with the value obtained

from AFM. The inhomogeneous nature of the deposited nanoparticle films is expected to smooth drastically the oscillations of the XRR curves, preventing a more detailed analysis. Higher angle oscillations were difficult to record due to the high background level introduced by the diffuse scattering originated from the inhomogeneous film.

Considering the deposition time of 180s, a deposition rate of about 0.3 nm/s is estimated.

In addition, a comparison between the experimental and theoretical XRR curves for a Si substrate with 0.23 nm roughness measured with the same experimental setup is also reported.

XRR curves have been simulated using the software PARRAT32 with a single layer on top of the substrate.