

Bottom-Up Mechanical Nanometrology of Granular Ag Nanoparticles Thin Films

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SCBD Source Geometry

The Supersonic Cluster Beam Deposition (SCBD) set-up exploits pulses of high pressure inert gas (He@45bar) injected in the ablation chamber and a synchronized delayed discharge to generate a plasma spot at the Ag cathode. Sputtered atoms condense inside the ablation chamber forming NPs which rapidly solidify and reach the thermodynamic equilibrium with the carrier gas due to its high pressure (around atmospheric pressure). The pressure gradient extracts the He and NP mixture through a nozzle and a set of focusing lenses into the first big chamber of the setup (operation pressure 10^{-4} mbar) where the carrier gas is evacuated by a turbomolecular pump. To narrow the size distribution of the NPs, in this chamber a skimmer selects the central part of the beam which is subsequently deposited on the substrate. Once deposited in the vacuum chamber, the samples are extracted to air and transferred either to the measurement apparatus or left exposed to the environment. The deposited coating thickness is estimated in real-time using a home-made quartz microbalance, calibrated through AFM, and can be varied only by changing the deposition time.

The SCBD source parameters are fixed and depend on the source design.

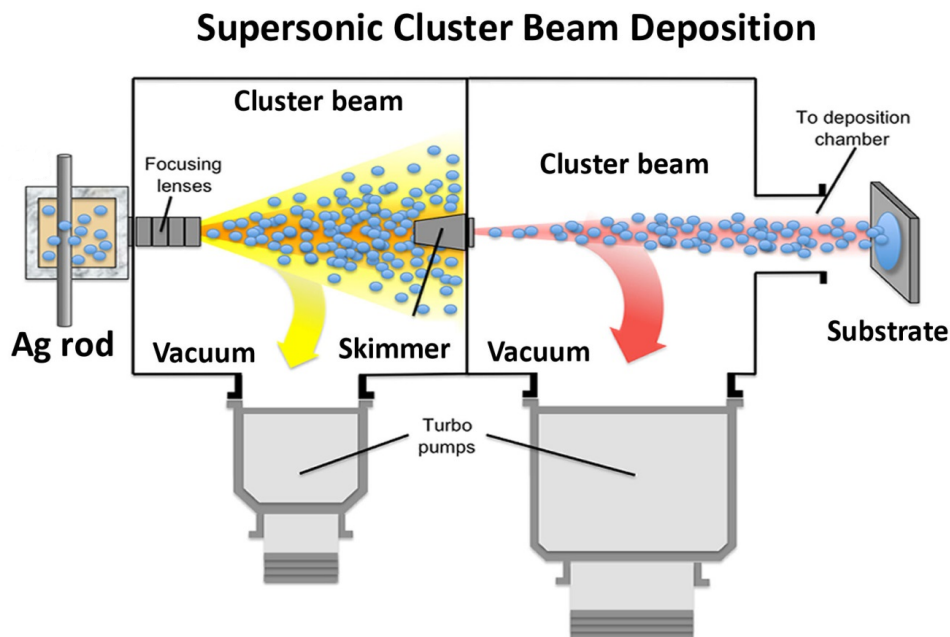


Figure S1: Scheme of the SCBD apparatus

MD Simulation Details

The velocity-Verlet algorithm is used to solve the equations of motion. The Nosé-Hoover thermostat with relaxation time equal to 100 fs was used to control the simulation temperature. All the interactions were cut off at 0.8 nm. As for the description of the Ag-Ag interactions, we use a 12-6 Lennard-Jones potential. This choice is computationally efficient, as compared for instance to Embedded Atom Method (EAM) potentials, and trustworthy, the exploited Lennard-Jones ϵ and σ parameters for Ag having been optimized to yield several properties (e.g. density, surface tension and others) in good agreement with experiments.¹ As for the substrate, a 35x20x5 nm³ Ag slab was built with the (111) surface exposed to the deposition of the NPs. The four bottom layers were kept fixed to simulate a macroscopic bulk material and a frame region (1.7 nm thick) adjacent to the fixed atoms layers was thermalized at room temperature. The role of the frame region is to mimic a bulk absorbing the excess of heat generated upon the cluster impact.² A possible choice to reduce the computational cost is to increase the timestep, provided that the calculated properties are unaffected and that the energy is conserved in microcanonical (NVE) runs. To this aim, we performed several simulations at increasing timesteps of the impact of 100 NPs on a Ag substrate, followed by a NVE 1 ns long run. The final configuration and mass density were unaffected by the timestep size up to more than 10 fs, and energy was conserved during the NVE run. We thus set the timestep of all our simulations to 10 fs. theoretical results were tested on various MD realizations and found to be realization- independent.

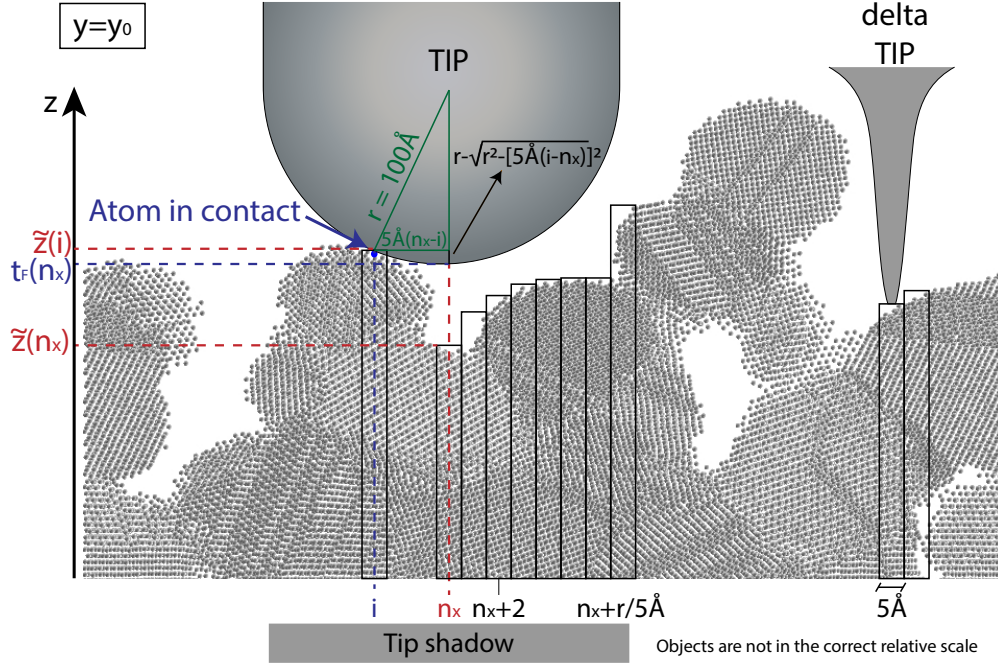


Figure S2: Scheme of the theoretical AFM topography reconstruction. For the ideal case of a delta-like tip (right) the recorded AFM height is simply given by the top-most atom coordinate $\tilde{z}(n_x, n_y)$ falling in the basic cell size of $5 \times 5 \text{ \AA}^2$. For the real case of a tip with radius r exceeding the basic cell size (left) the computation must take into account also the cells falling within the tip "shadow", so as to find the one containing the atom in actual contact with the tip. For sake of visualization the items are not in scale.

Filling Factor and AFM Topography from the Virtual Nanoparticle Film

Filling Factor. Formally the Filling Factor (FF) of the Ag NPs film is defined as the ratio between the volume occupied by the Ag NPs V_{NP} and the total volume of the film V (for a slab of non porous silver, $FF = 1$). The relation between the FF and the film porosity hence reads: $\phi = 1 - FF$.

The MD simulations are performed by shooting the NPs on a rectangular domain of size $L_x \times L_y = 35 \times 20 \text{ nm}^2$. The film thickness is calculated by reticulating the rectangular domain (serving as the sample base) into square cells of $0.5 \times 0.5 \text{ nm}^2$. Each cell is indexed by a pair of integers (n_x, n_y) , where $n_x \in \{1, 2, 3, \dots, 70\}$ and $n_y \in \{1, 2, 3, \dots, 40\}$. The z-coordinate of the top-most atom falling inside the cell (n_x, n_y) is $\tilde{z}(n_x, n_y)$. The average film thickness over the domain $L_x \times L_y$ is indicated with $\langle \tilde{z} \rangle$. From the average thickness, the total number of deposited atoms N and the volume of the Ag primitive cell V_{1Ag} , the film filling factor is retrieved as:

$$FF = \frac{V_{NP}}{V} = \frac{N V_{1Ag}}{\langle \tilde{z} \rangle (L_x L_y)} = 0.73 \pm 0.05 \quad (1)$$

Consequently the porosity is $\phi = 0.27 \pm 0.05$.

Virtual AFM. An AFM image is a matrix of pixels, again indexed by (n_x, n_y) . The value of each pixel is indicated by $t_F(n_x, n_y)$. Namely $t_F(n_x, n_y)$ indicates the AFM piezo height with respect to the supporting substrate when the center of the AFM tip is positioned on the cell (n_x, n_y) . Unlike the previously defined function $\tilde{z}$, which is tip independent, t_F depends on the tip finite size.

When the tip radius collapses to zero - or more precisely to the cell size of $0.5 \times 0.5 \text{ nm}^2$ - t_F converges to $\tilde{z}$. In the latter case, represented on the right side of Figure S2 (delta TIP), the tip can only contact and assume the coordinates of the top-most atom, that is $t_F = \tilde{z}$. We pinpoint that, for sake of visualization, in Fig. S2 items are not to scale one with each other.

For a tip radius $r=100 \text{ \AA}$, exceeding by twenty times the cell lateral size - a situation depicted on the left side of Figure S2, the computation of $t_F(n_x, n_y)$ is not trivial. Indeed a spherical AFM tip of radius r and centered in the cell (n_x, n_y) might also contact the top-most atoms of other cells falling within the tip "shadow". This scenario is visualised in Fig. S2 inspecting the cell indicated with (i, y_0) . The tip "shadow" is the tip circular z-projection centered in the cell (n_x, n_y) . Scanning (by cycling the indexes (i, j)) all the cells falling within the tip "shadow", we may thus calculate:

$$t_F(n_x, n_y) = \max_{(i,j) \in shadow} \left[\tilde{z}(i, j) - r + \sqrt{r^2 - [5\text{\AA}(n_x - i)]^2 - [5\text{\AA}(n_y - j)]^2} \right] \quad (2)$$

where i and j scan the region delimited by the inequality $(n_x - i)^2 + (n_y - j)^2 < (r/5\text{\AA})^2$, the factor $5\text{\AA}$ in the previous formulas being the cell dimension. The "shadow"-scan procedure is re-iterated for each pixel (n_x, n_y) . Since the MD simulation was operated under x-y periodic boundary conditions (i.e. an atom exiting from the cell on one side enters again on the opposite surface), also the theoretical AFM image was simulated in this way. The $t_F(n_x, n_y)$ values are converted to $t_F(x, y)$ by rescaling the domain according to $x = (n_x - 1/2) \times 5\text{\AA}$ and $y = (n_y - 1/2) \times 5\text{\AA}$. Finally we compute the function $h(x, y) = t_F(x, y) - \langle t_F \rangle$ with $\langle t_F \rangle = 9, 14, 23, 27$ and 31 nm (the five different heights resulting from the different shots 1 through 5). The function $h(x, y)$ allows visualising the topography obtained on the five samples of different thicknesses adopting the same z color scale (Figure ??b). The dashed histogram in Figure ??c summarises the occurrences of the h values obtained from all the 5 intermediate steps images.

AFM Images Comparison: Surface Texture Analyses

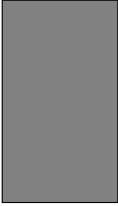
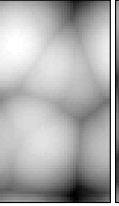
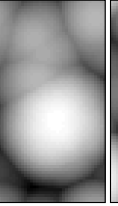
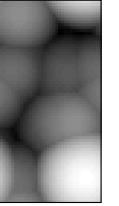
							
	Uniform	Random	Step1	Step2	Step3	Step4	Step5
St. Dev	0.000	2.325	1.400	1.344	1.360	1.380	1.392
Uniformity	1.000	0.063	0.079	0.078	0.110	0.091	0.099
Entropy	0.000	3.996	3.783	3.799	3.431	3.648	3.607

Figure S3: Virtual AFM images and their statistical indicators. The indicators have been selected to quantify the similarity among AFM reconstructed images obtained in subsequent NPs shots. The first two images, Uniform and Random, are paradigmatic cases here reported, together with their statistical indicators value, to exemplify the meaning of the chosen statistical parameters. Images three through 7 are obtained from the intermediate simulation steps (shot 1 through 5) and are the same images addressed in Figure ??b.

To quantify the notion of similar surfaces, that emerges looking at the five simulated AFM images of Figure S3, a possible approach is texture analysis.³ Texture analysis is based on statistical properties of the image intensity histogram. The statistical properties are defined in terms of a discrete variable h_i - in this case the height variation of the pixel with respect to the mean of the image - and the normalized histogram of the intensity levels in a region (the pixel counts with the same gray level) $p(h_i)$. We chose three indicators:

1. The standard deviation (square root of the distribution second moment):

$$\sigma = \sqrt{\sum_{i=1}^N (h_i - m)^2 p(h_i)} \quad (3)$$

where $m = \sum_{i=1}^N h_i p(h_i)$ is the mean and N is the number of intensity levels in the normalized histogram.

2. The uniformity U_i :

$$U = \frac{\sum_{i=1}^N p(h_i)^2}{\sum_{i=1}^N p(h_i)} \quad (4)$$

The uniformity is 1 when the gray levels of all pixels are equal (maximum uniformity) and tends to $1/N$ when all gray levels have the same probability (minimum uniformity), see Figure S3.

3. The entropy E :

$$E = - \sum_{i=1}^N p(h_i) \log_2[p(h_i)] \quad (5)$$

The entropy is a standard measure of randomness, with values in the range $0 \leq E \leq \log_2(N)$.

The sense of these indicators is better understood after inspecting their values with reference to two paradigmatic limit cases, that is a uniform vs a random image (See fig S3, Uniform and Random). In the same figure the statistical indicators calculated for images labelled as Step1 to Step5 are reported. The indicators obtained from the five images are quite similar, the dispersion around their mean values (mean value and standard deviation of the indicators calculated on the set of the five images) being minute. The average standard deviation is 1.37 ± 0.02 nm, the average uniformity 0.091 ± 0.014 and the average entropy 3.65 ± 0.15 . The deviation between the indicators we reported in fig S3 and the average is always smaller than twice the dispersion about the mean for the 5 virtual AFM images (Step 1 to 5), indicating that they are parts of the same data set. This is not true if we consider also the random and the uniform distributions (they fall outside the 2σ interval), since they are not compatible with the mean values obtained from the virtual AFM images. Hence it is reasonable to assume that the topography of the consecutive intermediate NPs films is unchanged and to compare the height distribution of the real AFM image with the one obtained by merging the 5 simulated images.

On the experimental side, experimental AFM topographies, obtained on deposited films of comparable heights as the one here theoretically addressed, have been shown to be equivalent⁴

Rescaling of the $C_{11,exp}$ Value to Low Temperature

For the sake of comparison with the $C_{11,MD}=89 \pm 6$ GPa, obtained from MD simulations on the virtual NP thin film at T=0 K, the experimental room temperature value $C_{11,Exp}(300\text{ K})=70 \pm 5$ GPa, obtained on the very same NP film by means of time-resolved optoacoustics experiments, has to be rescaled to low temperatures. The rescaling is performed as follows:

$$C_{11,Exp}(0K) = C_{11,Exp}(300K) \times \frac{C_{11,Exp}^{SC}(0K)}{C_{11,Exp}^{SC}(300K)} = 75 \pm 5GPa \quad (6)$$

where $C_{11,Exp}^{SC}(300\text{ K})=122$ GPa is the room temperature experimental value obtained on single crystal Ag⁵ and $C_{11,Exp}^{SC}(0\text{ K})= 131$ GPa is the extrapolation to T=0 K of low temperature data.⁶

Using the same EAM potential exploited to obtain $C_{11,MD}$ we also calculated the value of $C_{11,MD}^{SC}(0K) = 143 \pm 12GPa$ for a single crystal Ag at 0K. With this value we calculated the ratio between C_{11} obtained for the NPs film and for a single crystal for both the real experiment and the MD simulation. Their values are:

$$\frac{C_{11,Exp}}{C_{11,Exp}^{SC}}(300K) = \frac{70 \pm 5}{122} = 0.57 \pm 0.04 \quad (7)$$

$$\frac{C_{11,MD}}{C_{11,MD}^{SC}}(0K) = \frac{89 \pm 6}{143 \pm 12} = 0.62 \pm 0.07. \quad (8)$$

References

- (1) Heinz, H.; Vaia, R. A.; Farmer, B. L.; Naik, R. R. Accurate Simulation of Surfaces and Interfaces of Face-Centered Cubic Metals Using 12-6 and 9-6 Lennard-Jones Potentials. *J. Phys. Chem. C* **2008**, *112*, 17281–17290.
- (2) Cardia, R.; Melis, C.; Colombo, L. Neutral-Cluster Implantation in Polymers by Computer Experiments. *J. Appl. Phys.* **2013**, *113*, 224307.
- (3) Gonzalez, R. C.; Woods, R. E.; Eddins, S. L. *Digital Image Processing Using MATLAB*; Prentice-Hall, Inc.: Upper Saddle River, NJ, USA, 2003.
- (4) Peli, S.; Cavaliere, E.; Benetti, G.; Gandolfi, M.; Chiodi, M.; Cancellieri, C.; Giannetti, C.; Ferrini, G.; Gavioli, L.; Banfi, F. Mechanical Properties of Ag Nanoparticle Thin Films Synthesized by Supersonic Cluster Beam Deposition. *J. Phys. Chem. C* **2016**, *120*, 4673–4681.
- (5) Martienssen, W.; Warlimont, H. *Springer Handbook of Condensed Matter and Materials Data*; Springer Science & Business Media, 2006.
- (6) Neighbours, J.; Alers, G. Elastic Constants of Silver and Gold. *Phys. Rev.* **1958**, *111*, 707.