

Sequential growth of Ag nanoparticles on ripple-patterned Si: Insights from GISAXS/GIWAXS and MD simulations

Tarundeep Kaur Lamba^{a,b,*}, Tejasva Vashistha^{c,1}, Sharanjeet Singh^d, K.P. Sooraj^{a,b},
Sebin Augustine^{a,b}, Raghavan Ranganathan^c, Sarathlal Koyiloth Vayalil^e, Dileep Kumar^d,
Mukesh Ranjan^{a,b,**}

^a Institute for Plasma Research, Gandhinagar, 382428, Gujarat, India

^b Homi Bhabha National Institute, BARC Training School Complex, 2nd floor, Anushaktinagar, Mumbai, 400094, Maharashtra, India

^c Department of Materials Engineering, Indian Institute of Technology Gandhinagar, Gandhinagar, 382355, Gujarat, India

^d UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore, 452001, India

^e Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607, Hamburg, Germany

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ABSTRACT

The spatial arrangement and morphology of metallic NPs critically influence performance in plasmonic and spintronic applications. Substrate topography, especially ion-irradiation induced ripple patterns, strongly affects NP nucleation, growth dynamics, and final geometry. For Ag-NPs on nanoripple silicon, assembly depends on deposition direction because the morphology is intrinsically asymmetric; GISAXS confirms one slope is steeper. Single-direction deposition promotes uniaxial, ellipsoidal Ag-NPs aligned in the ripple direction, whereas sequential deposition yields truncated NPs with more uniform spacing. GIWAXS indicates an FCC structure with preferred (111) and (200) orientations; d-spacings remain consistent at 0° and 90°, indicating structural stability. Molecular dynamics simulations support these findings, showing single-sided flux favors tilted, elongated growth, while sequential flux forms near-spherical NPs near ridge regions and distributes them across slopes. Together, experiment and simulation establish how coupling surface asymmetry with deposition geometry governs NP shape, ordering, and crystallinity, offering a substrate-guided route to engineering isotropic assemblies.

1. Introduction

Metal nanoparticles (NPs) deposited on nanostructured surfaces exhibit unique optical, chemical, and physical properties, making them valuable for various applications [1]. Among these, their structural parameters play a crucial role in enhancing substrate performance particularly for the Surface Enhanced Raman Scattering (SERS) applications [2–4]. The ion beam irradiation method, a well-known bottom-up approach, is commonly employed to create nanostructured ripple patterns on silicon substrates, which can then serve as templates for the growth of NP arrays tailored for SERS applications [5,6]. Previous studies [7,8] have demonstrated that when depositing NPs along the ion beam direction on rippled substrates, the resulting structures tend to be elongated due to uniaxial growth along the ripple. However, Lamba

et al. [9] introduced an innovative approach involving the sequential deposition of silver (Ag)-NPs from both directions relative to the ripple axis. This method effectively restricting elongation and promoting the formation of nearly spherical NPs. This helped to make isotropic SERS substrate. While Lamba et al.'s study primarily focused on the outcomes of sequential growth, such as near-field Finite Difference Time Domain (FDTD) simulations and the SERS performance of different deposition strategies, it did not explore in detail the underlying growth mechanism responsible for the formation of nearly spherical NP arrays during sequential deposition.

Small-Angle X-ray Scattering (SAXS) is a powerful non-invasive technique for structural characterization of NP systems under native or near realistic conditions. When performed at grazing incidence, SAXS enables illumination of a large surface area, allowing for the collection

* Corresponding author. Institute for Plasma Research, Gandhinagar, 382428, Gujarat, India.

** Corresponding author. Institute for Plasma Research, Gandhinagar, 382428, Gujarat, India.

E-mail addresses: hlamba81@gmail.com (T.K. Lamba), ranjanm@ipr.res.in (M. Ranjan).

¹ Contributed equally.

of statistically significant data on NP growth at the nanoscale, typically up to around 100 nm in size. Additionally, SAXS also provides insights into the excess electron density differences between NPs and their surrounding medium [10,11]. On the other hand, WAXS (Wide-Angle X-ray Scattering) offers complementary information by probing the crystalline structure, atomic arrangements, and phase transitions of NPs. GIWAXS (Grazing-Incidence Wide-Angle X-ray Scattering), in particular, allows for the study of structural ordering and strain effects in nanomaterials, making it a valuable tool for understanding the fundamental mechanisms governing NP growth and stability [12,13].

Biermanns et al. [14] used the GISAXS (Grazing-Incidence Small-Angle X-ray Scattering) technique to study the interface region of amorphous domains, noting that damage (radiation-induced disorder) is present and propagated along the ripple direction, while, this expansion is suppressed across the ripple. Similarly, Sarathlal et al. [15] reported anisotropic growth behavior of Co thin films on rippled silicon substrates, where island coalescence preferentially occurred perpendicular to the ripple wave vector, resulting in tensile stress along that direction. Keller et al. [16] investigated using GISAXS and found that at a grazing incidence angle (77°), there is a transition from initial shadow deposition forming one-dimensional nanowires on the ripple side facing the flux, to anisotropic columnar growth resulting in rapid loss of film-substrate conformity. Camelio et al. [17] further explained that at a grazing angle, metal NP deposition favors the formation of aligned and elongated NP geometries, which result in strong plasmonic coupling along the ripple direction. Nelli et al. [18] reported that silver clusters grow into icosahedral structures via a shell-by-shell process, driven by collective atomic rearrangements. The growth was studied in situ on thermally oxidized Si (100) wafers covered with an amorphous carbon layer, using GISAXS and GIWAXS. Molecular dynamics simulations supported by ab initio calculations confirmed that this growth mode arises from concerted atomic displacements within the growing shell. Similarly, Satoshi et al. [19], through MD simulations, proposed that the self-organization of NPs along the ripple pattern arises from the local flux distribution and preferential atom sticking on the tilted ripple surface, even when ripple modulation is minimal. Mukul et al. [20] performed MD simulations revealing that Ag clusters grow on the exposed plane of a ripple surface at a 70° incidence angle, while cluster migration across the ridge occurs only for angles less than 70° within the temperature range of 600–800 K. However, none of these studies explored sequential deposition, where NPs are deposited from both sides of the ripple for different durations (t_1 and t_2) to control growth behavior. This deposition strategy is central to the current work, where we investigate the effect of sequential growth on the atomic rearrangement of Ag-NPs using GISAXS, GIWAXS, and MD simulations.

Very few studies have explored in-depth atomic rearrangement of Ag-NPs on silicon ripples. In the present study, low energy ion beam irradiation is used to fabricate the ripple pattern on silicon substrate followed by sequential deposition of Ag-NPs. GISAXS and GIWAXS are employed in addition to traditional imaging methods such as atomic force microscopy (AFM) and scanning electron microscopy (SEM), providing deeper insights into the growth mechanisms and structural evolution of NPs on rippled silicon surfaces. We examine that sequential deposition method promotes the formation of truncated spherical NPs.

Our findings reveal that the crystalline size ratio $\left(\frac{D_{\parallel}}{D_{\perp}}\right)$ decreases, when the sequential deposition method is employed. To further support the experimental results, MD simulations are performed, which align well with our experimental observations. Such a controlled NP morphology and crystallinity are critical for SERS applications, where the uniformity and density of plasmonic "hotspots" directly influence the enhancement factor and signal reproducibility. Thus, our study provides valuable insights into tailoring NP growth on patterned surfaces for high-performance, reproducible substrates.

2. Experimental section

A Kaufman broad ion beam source operating under ultra-high vacuum conditions is utilized for fabricating ripple patterns. The system operates with a base pressure of 1×10^{-7} mbar and maintains a constant working pressure of 2×10^{-4} mbar. The silicon (Si) (100) substrate, measuring $1 \times 1 \text{ cm}^2$, undergoes ultrasonic cleaning in acetone, distilled water, and isopropyl alcohol for 5 min each to ensure surface cleanliness before processing. Nanoripples are formed on the Si substrate at an incidence angle of 67° relative to the surface normal, as shown in Fig. 1 (i). After this step, Ag-NPs are deposited at a working pressure of 1×10^{-7} mbar using an electron beam evaporator at an oblique angle of 70° from the surface normal, with a flux of $1.06 \times 10^{13} \text{ atoms} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$. For characterization, four samples are prepared under different deposition conditions of Ag-NPs. In the Ag_{60_in} sample, Ag-NPs are deposited for 60 min in the direction of the ion beam, whereas in the Ag_{60_opp} sample, the deposition is performed for 60 min opposite to the beam direction (Fig. 1(i)). Additionally, a sequential deposition method is employed for the Ag_{30 + 30_in} and Ag_{30 + 30_opp} samples. In the Ag_{30 + 30_in} sample, Ag-NPs are first deposited for 30 min in the direction of the beam, after which the sample is rotated, and deposition continued for another 30 min in the opposite direction. Conversely, in the Ag_{30 + 30_opp} sample, the first 30 min of deposition are performed opposite to the beam direction, followed by sample rotation for the remaining 30 min of deposition in the beam direction (Fig. 1(ii)). AFM is employed to examine the surface topography of the ripple-patterned Si substrate using a commercial NT-MDT NTEGRA system operated in tapping mode, with WSXM software utilized for image processing. Fig. 1 (iii) presents the AFM image of the fabricated rippled silicon (R-Si) substrate, with an arrow indicating in the direction of the incident ion beam. The inset in the right top corner displays the Fast Fourier Transform (FFT) analysis, confirming the periodic nature of the ripple structure. The line profile taken along the blue marker reveals that the ripple's average height and wavelength are approximately 2 nm and 30 nm, respectively (as shown in inset at bottom left corner).

The morphology of the Ag-NPs is characterized using a high-resolution SEM (Carl ZEISS, Merlin VP, Germany). The SEM measurements are carried out at an accelerating voltage (EHT) of 5 kV, with a magnification of 200 KX and a working distance of 6.9 mm. Furthermore, morphological and structural analysis of the Ag-NPs are carried out using synchrotron-based GISAXS and GIWAXS techniques [21,22]. The measurements are conducted at beamline P03 of PETRA III at DESY [23], using X-rays with a photon energy of 11.83 keV (wavelength $\lambda = 1.025 \text{ \AA}$). The experiments are performed at an incidence angle of 0.4° , with the X-ray beam focused to a spot size of $32 \times 27 \mu\text{m}^2$. For GISAXS and GIWAXS measurements, the sample-to-detector distances are set to 4205 mm and 288.1 mm, respectively. GISAXS data are collected using a PILATUS 2M detector (Dectris Ltd., Switzerland) with a pixel size of $172 \times 172 \mu\text{m}^2$, whereas GIWAXS measurements are recorded with a LAMBDA 9M detector (X-Spectrum GmbH, Germany), which provides a finer pixel resolution of $55 \times 55 \mu\text{m}^2$. The DPDAK software [24] is utilized to analyze both GISAXS and GIWAXS images, ensuring accurate interpretation of the scattering data. Finally, the MD simulations are carried out using the LAMMPS software.

3. Results and discussion

3.1. Ripple morphology and characterization of Ag-NPs using SEM

The SEM images of all the samples are presented in Fig. 2(i)–(iv). For the samples Ag_{60_in} and Ag_{60_opp}, where Ag-NPs are deposited from a single direction, the NPs exhibit an ellipsoidal shape with aspect ratios (a/b) (where 'a' and 'b' represent the major and minor axis of NP, respectively) measured to be of 1.45 and 1.50, respectively. This indicates that the deposition from a single side, leading to elongated geometries, resulting in anisotropy in the sample. In contrast, for the

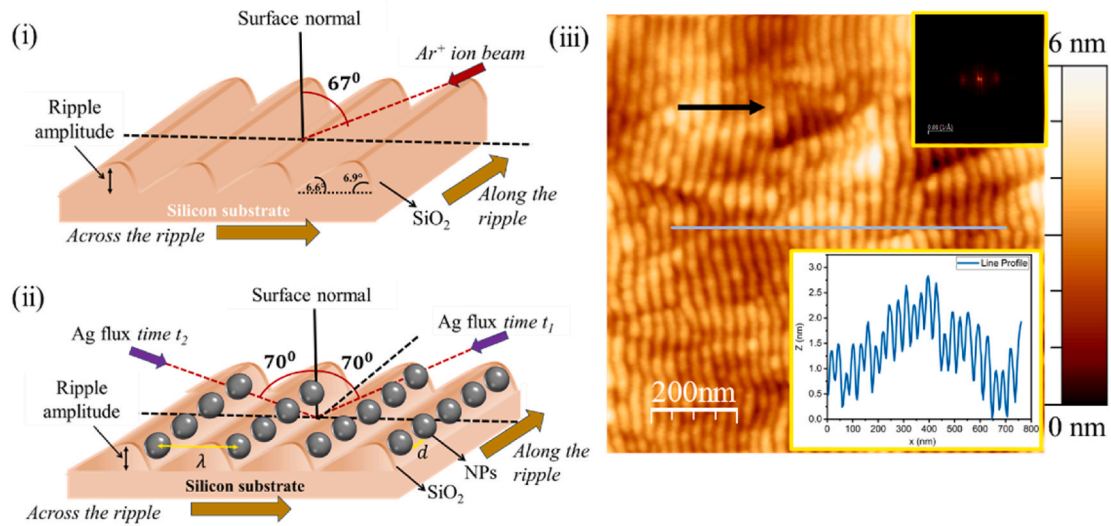


Fig. 1. (i) The schematic illustrates the formation of ripples on a silicon substrate induced by ion beam irradiation at an angle of 67° relative to the surface normal (ii) The schematic representation of sequential deposition of Ag-NPs on silicon ripple for the time t_1 and t_2 . (iii) AFM image of silicon ripple with periodicity of ~ 30 nm as depicted in line profile with inset of FFT at the right above corner (where black arrow where the black arrow indicates the direction of incident ion beam).

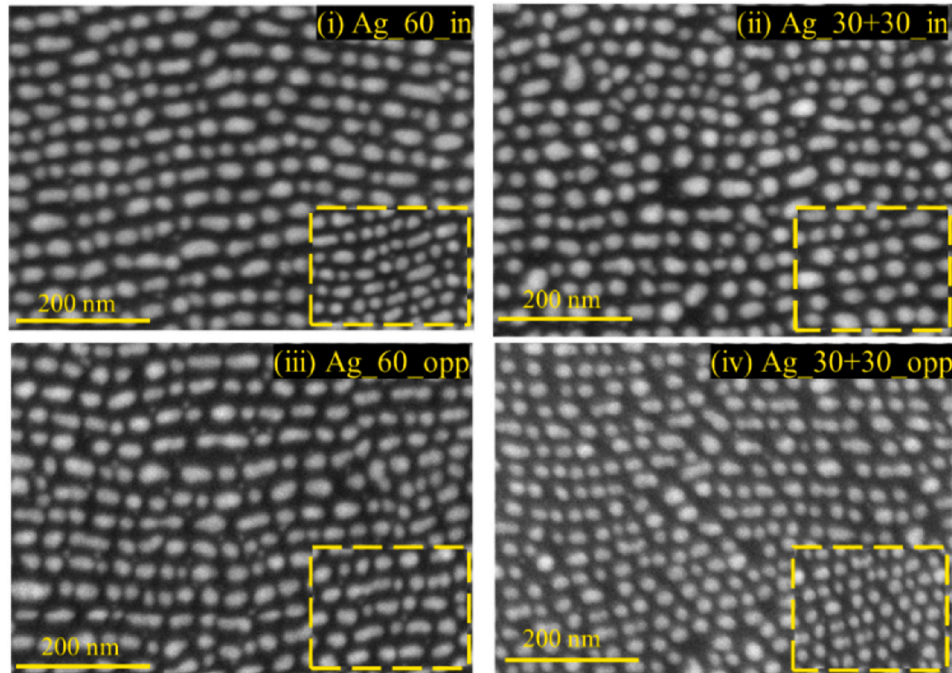


Fig. 2. SEM images are displayed for (i) Ag_{60_in}, (ii) Ag_{30 + 30_in}, (iii) Ag_{60_opp}, and (iv) Ag_{30 + 30_opp}, with a magnified section included as an inset in the bottom right corner of each image.

samples Ag_{30 + 30_in} and Ag_{30 + 30_opp}, where the sequential deposition method is employed to deposit Ag-NPs (as illustrated in Fig. 1 (ii)), the aspect ratio decreases significantly to 1.20 and 1.17, respectively. This suggests that the bidirectional deposition promotes more isotropic growth, resulting in truncated spherical NPs [9]. Furthermore, the size distribution of the NPs, measured along and across the ripples referred to as the major and minor axes, respectively, is provided in Fig. S1–S2 (Supplementary Data) and summarized in Table 1.

3.2. GISAXS investigation of rippled silicon surfaces and their morphological evolution upon Ag deposition

The surface morphology of the pristine rippled substrate is analyzed

Table 1

Results from the analysis of SEM images i.e., the major radius, minor radius, and aspect ratio of NPs.

Sample Name:	Major Radius (nm)	Minor Radius (nm)	Aspect Ratio
Ag _{60_in}	15.2 ± 0.3	10.4 ± 0.1	1.45 ± 0.1
Ag _{30 + 30_in}	11.0 ± 0.4	9.9 ± 0.1	1.20 ± 0.2
Ag _{60_opp}	16.0 ± 0.6	10.7 ± 0.3	1.50 ± 0.4
Ag _{30 + 30_opp}	10.0 ± 0.1	8.5 ± 0.5	1.17 ± 0.3

using GISAXS, with the X-ray beam aligned both parallel ($\varphi = 0^\circ$) and perpendicular ($\varphi = 90^\circ$) to the direction of the ripples. Fig. 3 illustrates the schematic of the GISAXS and GIWAXS experimental setup,

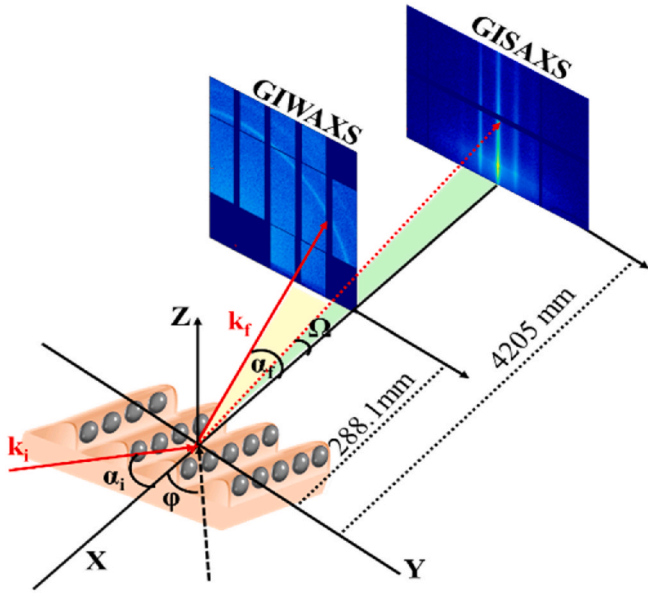


Fig. 3. Schematic diagram of the X-ray scattering setup used for GISAXS and GIWAXS measurements.

highlighting the incident (k_i) and the scattered (k_f) wave vectors that define the scattering geometry. The difference between the incident and scattered wave vectors is defined as the scattering vector (q) and can be mathematically expressed as $q = k_f - k_i$. The scattering vector (q) can be resolved into its in plane (q_y) and the out-of-plane scattering vector (q_z) components based on the angular coordinates of the scattering pattern [25,26]. These components are calculated using the following relationships [27]:

$$q_y = \frac{2\pi}{\lambda} [\sin(\Omega)\cos(\alpha_f)] \quad (1)$$

$$q_z = \frac{2\pi}{\lambda} [\sin(\alpha_i) + \sin(\alpha_f)] \quad (2)$$

Here, α_i is the angle of incidence, α_f is the out-of-plane scattering angle, and Ω is the in-plane scattering angle.

The resulting GISAXS patterns of the silicon ripples are shown in Fig. 4 (i) and (ii) for $\varphi = 0^\circ$ and $\varphi = 90^\circ$, respectively at $\varphi = 0^\circ$, two distinct vertical streaks appear symmetrically on either side of the specular peak ($q_y = 0 \text{ nm}^{-1}$), extending along the q_z axis. These features arise from periodic lateral variations in electron density, indicating a well-ordered surface morphology induced by ion beam patterning. In contrast, no such side streaks are observed at $\varphi = 90^\circ$, confirming the

anisotropic nature of the ripple structure. To quantify the in-plane surface periodicity, horizontal line integration is performed on both directions, as shown in Fig. 4 (iii). For $\varphi = 0^\circ$, clear satellite peaks appear at $q_y = 0.19 \pm 0.01 \text{ nm}^{-1}$ on either side of the central specular rod. The positions of these satellite peaks in the q_y profiles correspond to the characteristic lateral correlation distance (d_y) of the periodic structures. This relationship is described by equation-3, which links the lateral periodicity to the scattering vector q_y . Based on this relation, the average ripple wavelength (λ_y) is calculated to be $33.0 \pm 2 \text{ nm}$, which is in good agreement with the values obtained from AFM measurements. Additionally, the presence of second-order peaks at $q_y = 0.39 \pm 0.01 \text{ nm}^{-1}$ suggests a high degree of long-range order and periodicity in the ripple structure. The difference in intensities of left and right satellite peaks is associated with the asymmetric slopes of the ripples, likely resulting from variations in local ion sputtering rates [28]. For the pristine rippled substrate, the average slopes of the ripples are calculated to be 6.4° and 6.9° , using the method described by Babonneau et al. [28].

$$d_y = \frac{2\pi}{q_y} \quad (3)$$

Establishing the morphological characteristics of the pristine rippled substrate is crucial, as it serves as the template for the subsequent deposition of Ag-NPs. Understanding the initial surface structure allows us to evaluate the extent of conformal growth, nanoparticle ordering, and any morphological modifications induced by the deposition process. Fig. 5 presents the GISAXS images for the deposited samples: (i) Ag₆₀in, (ii) Ag₃₀ + 30_in, (iii) Ag₆₀opp, and (iv) Ag₃₀ + 30_opp. The strong resemblance between these patterns and that of the pristine silicon ripple indicates that the Ag-NPs grow conformally along the underlying ripple morphology.

For a quantitative analysis, the in-plane line profile is extracted from the Yoneda region (indicated by the red box in Fig. 5) for all GISAXS images. This extraction yields intensity (I) versus in-plane momentum transfer vector (q_y) profiles, which are presented in Fig. 6 (i)–(iv). All profiles display satellite peaks symmetrically positioned around the specular peak. A notable feature of the satellite peaks is the asymmetric intensity distribution observed on either side of the specular peak. This asymmetry is related to the slope of the surface ripples. In the case of Ag₆₀in, where Ag-NPs are deposited in the direction of ion beam, the asymmetry of the peaks is reversed compared to the pristine silicon ripple. However, for all other samples (Ag₃₀ + 30_in, Ag₆₀opp, and Ag₃₀ + 30_opp), the asymmetric peak pattern remains like that of the pristine silicon ripple. This suggests that the deposition angle and direction influence the scattering characteristics, leading to distinct intensity distributions in the GISAXS patterns. For the Ag₆₀in sample, the average satellite peak position shifts to $q_y = 0.17 \pm 0.01 \text{ nm}^{-1}$, corresponding to an average λ_y of $37.0 \pm 2 \text{ nm}$. This shift is attributed to

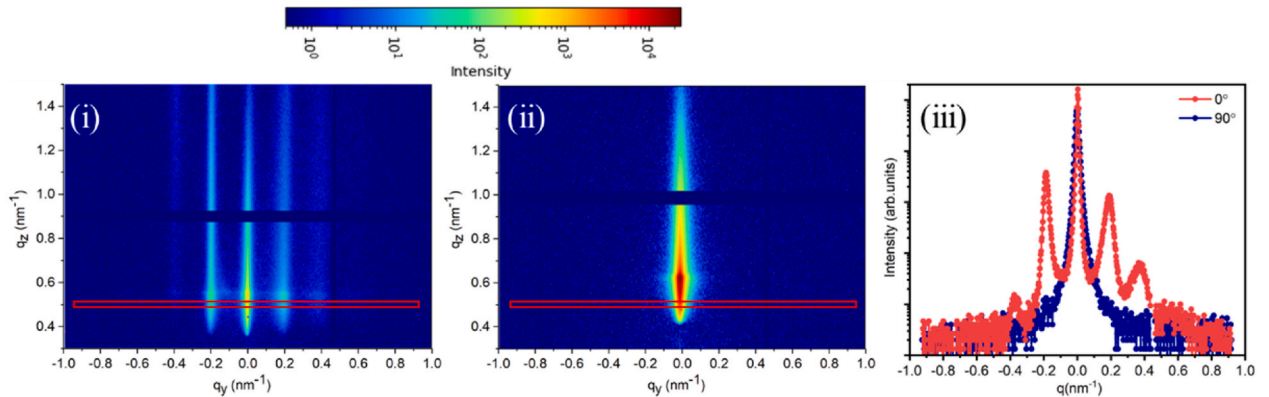


Fig. 4. GISAXS measurements of the rippled Si substrate are performed with the X-ray beam oriented (i) parallel and (ii) perpendicular to the ripple direction. (iii) The associated in-plane 1D line profiles were derived along $q_z = 0.5 \text{ nm}^{-1}$ (highlighted by the red solid box) for beam angles of (i) 0° and (ii) 90° , respectively.

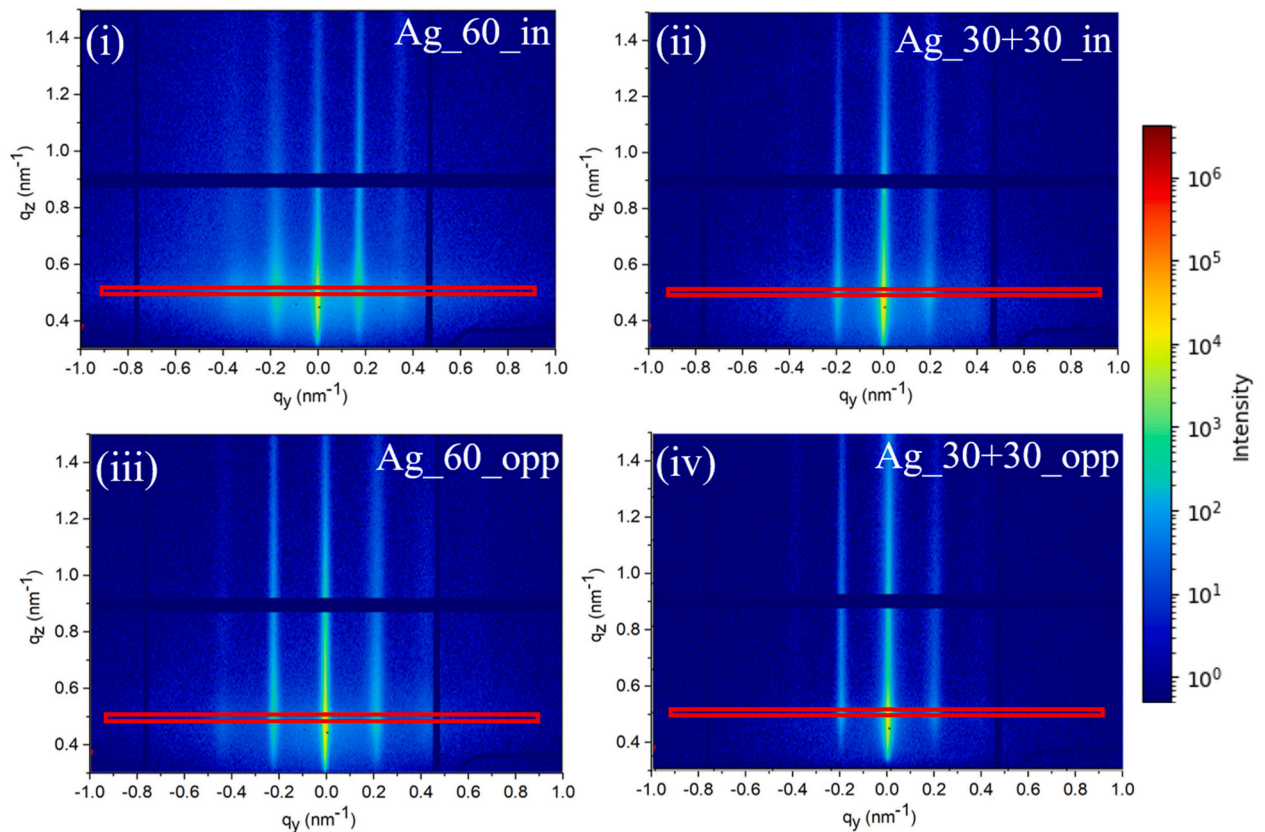


Fig. 5. The GISAXS pattern of the (i) Ag₆₀-in, (ii) Ag₃₀ + 30-in, (iii) Ag₆₀-opp, and (iv) Ag₃₀ + 30-opp with the X-ray beam aligned parallel to ripple length.

the unidirectional deposition of Ag-NPs, which occurs only on one side of the ripple structure. As a result, the slope of the initially steeper side is reduced from 6.9° to 5.9° , while the opposite side retains its original slope of 6.4° . Since the 6.4° side now becomes the steeper of the two, the asymmetry in the scattering intensity reverses accordingly. On the other hand, for the Ag₆₀-opp sample, where Ag-NP deposition was performed in the direction opposite to the ion beam (i.e., onto the less steep side of the ripples), the satellite peaks appear at $q_y = 0.16 \pm 0.01 \text{ nm}^{-1}$, corresponding to an average lateral λ_y of $39.2 \pm 2 \text{ nm}$. In this case, the slope of the targeted side is reduced from its original value of 6.4° – 5.6° . In both cases, the increase in wavelength following single-direction deposition can be primarily attributed to two factors: 1. Shadowing Effect: During deposition, the peaks of the ripples may cast shadows over the troughs, leading to preferential accumulation of material on the peaks while limiting deposition in the troughs. Over time, this effect accentuates the existing ripple structure, effectively increasing the apparent wavelength [29]. 2. Preferential Deposition: NPs tend to accumulate more on the peaks than in the troughs. This preferential growth extends the peaks, making them wider, which in turn increases the apparent wavelength [5].

However, when the sequential deposition method is applied, a different trend is observed. For the Ag₃₀ + 30-in sample, q_y is measured at $0.19 \pm 0.01 \text{ nm}^{-1}$, yielding an average ripple wavelength of $33 \pm 2 \text{ nm}$. Similarly, for the Ag₃₀ + 30-opp sample, q_y is found at $0.20 \pm 0.01 \text{ nm}^{-1}$, corresponding to a ripple wavelength of $31.4 \pm 2 \text{ nm}$. In these cases, the apparent wavelength and the intensity profile remained nearly identical to those of the pristine silicon ripples. This can be explained by the following reasons: 1. Balanced growth: sequential deposition from opposite directions promotes uniform NPs distribution, preventing significant changes in the periodicity of the underlying ripple structure [9]. 2. Minimized shadowing effect: by depositing from both directions, the shadowing effect responsible for preferential growth on ripple peaks is significantly reduced, thereby preserving the original

morphology [30]. 3. Aspect ratio control: the sequential deposition technique enables better control over the aspect ratio of Ag-NPs. By alternating deposition directions, the elongation of particles in a single direction is minimized, as NPs get time to rearrange themselves to achieve a more stable spherical geometry. This results in truncated spherical geometries, thereby maintaining the integrity of the ripple structure [31].

3.3. Crystallinity analysis of Ag-NPs using GIWAXS

The crystalline structure of the deposited Ag-NPs is characterized by GIWAXS at $\phi = 0^\circ$ and 90° , using an X-ray beam incident at $\sim 0.4^\circ$, slightly above the critical angle of Ag ($\alpha_c \approx 0.25^\circ$). The GIWAXS 2D diffraction images of all samples (Ag₆₀-in, Ag₃₀ + 30-in, Ag₆₀-opp, and Ag₃₀ + 30-opp) are shown in Fig. 7 (i)-(viii). Two concentric arc patterns observed in the GIWAXS images at $q = 27.6 \text{ nm}^{-1}$ and 31.8 nm^{-1} as depicted in Fig. 8 (i)-(viii), correspond to the Face Centered Cubic (FCC) (111), and (200) diffraction planes of the Ag (JCPDS-98-002-1923) [32].

To get the quantitative structural information of the Ag NPs both along and perpendicular to the ripples in the sample plane, 1D GIWAXS data are extracted from images recorded at $\phi = 0^\circ$ and 90° . The corresponding in-plane profiles, shown in Fig. 8 (i)-(viii), are fitted to determine the peak positions (q), full width at half maximum (FWHM), and normalized peak area (A), which are then used to evaluate the interplanar spacing (d) and crystallite size (D) using Bragg's law [33] and Scherrer equation [34], respectively. The fitted parameters are summarized in Table 2.

The calculated d -spacings of both planes remain consistent across both orientations, which suggests the absence of any in-plane anisotropic stress in the Ag NPs [35]. However, to find out the presence of any macrostrain (ϵ) induced in the Ag-NPs due to the ripple morphology, we have calculated the lattice parameter in the reciprocal lattice using the

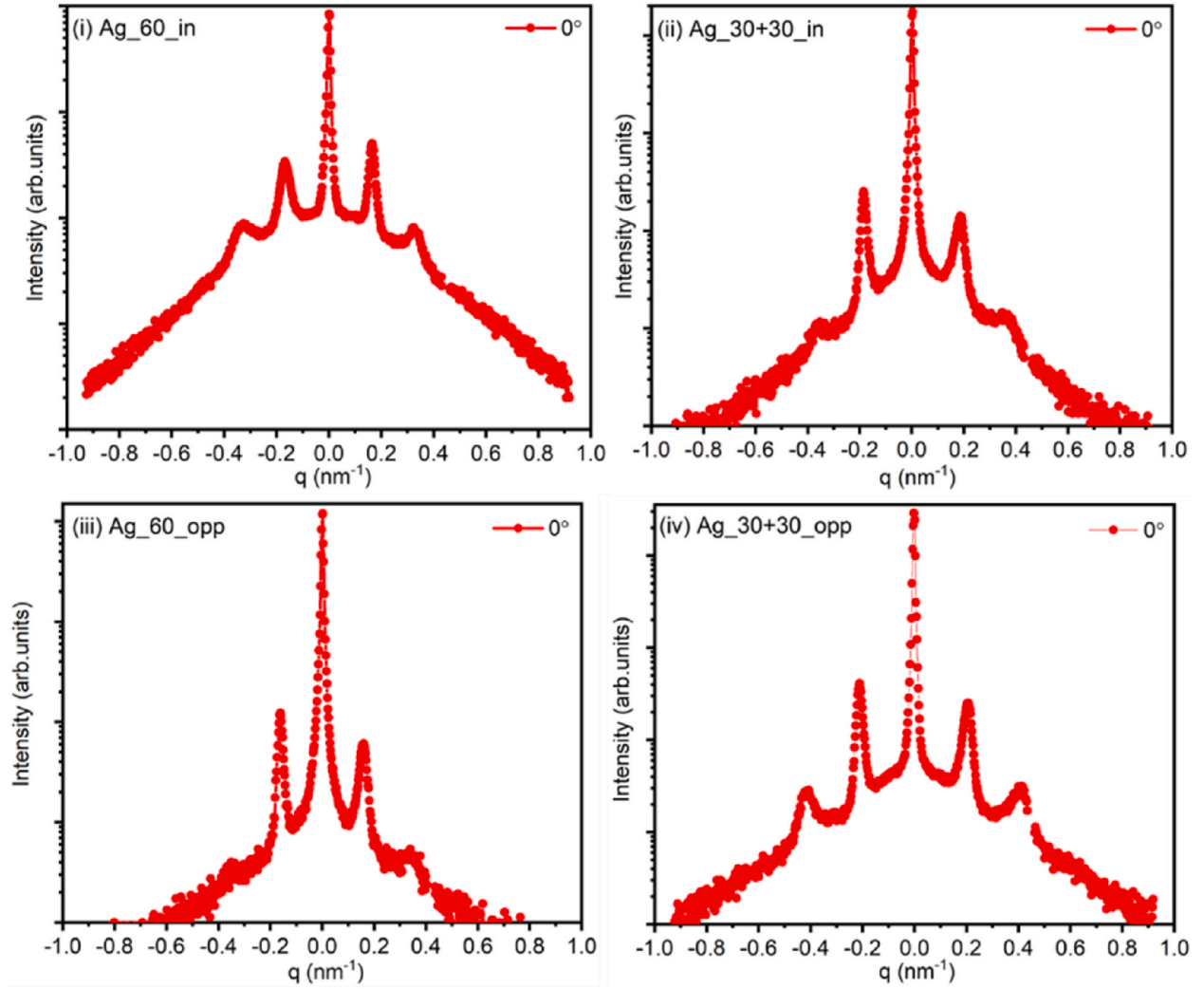


Fig. 6. The corresponding horizontal 1D line profiles (horizontal cuts marked by red box in Fig. 4) for samples (i) Ag_{60_in}, (ii) Ag_{30 + 30_in}, (iii) Ag_{60_opp}, and (iv) Ag_{30 + 30_opp}.

formula $a = \frac{2\pi\sqrt{(h^2+k^2+l^2)}}{q}$ [36], where (h, k, l) are the Miller indices. From which the macro strain can be estimated by Ref. [36]:

$$\epsilon = \frac{a - a_0}{a_0} \times 100\% \quad (4)$$

where 'a' is the experimentally calculated lattice parameter and 'a₀' is the unstrained lattice parameter of FCC silver as reported in the literature is 4.086 Å [37]. For both the (111) and (200) planes, which correspond to $q = 27.6 \text{ nm}^{-1}$ and $q = 31.8 \text{ nm}^{-1}$, respectively, the calculated lattice parameter 'a' is found to be 3.94 Å. Using these values, the induced 'ε' is calculated to be -3.58 %, indicating that the ripple structure generates compressive strain in the Ag-NPs due to their interaction with the underlying ripple morphology.

In the present case, the preferential (111) and (200) textures observed in the Ag film can be attributed to surface energy minimization, where $E_s(111) < E_s(200)$. This trend arises because the (111) plane is the most closely packed, minimizing the number of broken bonds and thus lowering the total surface energy. Consequently, during the NPs growth, atoms tend to arrange preferentially along the (111) orientation to minimize the system's free energy [38]. We have observed no significant variation in the normalized area (see Table 2) along and across the ripples. Also, the nearly uniform intensity of the diffraction ring arc implies the absence of any preferred crystallographic

orientation in the Ag-NPs. This suggests that the NPs are non-textured, with no significant preferential orientation in their crystallographic planes. As a result, the material exhibits isotropic behavior, with no directional dependence in its diffraction pattern. This uniform distribution implies that the Ag-NPs did not undergo significant alignment during deposition [39].

The average crystalline size (D) of the Ag-NPs for in samples is calculated using the Scherrer equation [34] $D = \frac{K\lambda}{\beta \cos \theta}$ where, 'K' is a constant usually taken as 0.9, 'β' is the FWHM value of the peak, and 'q' is the position of the corresponding diffraction peak. The average crystallite size calculated along the ripple is denoted by D_⊥ whereas across the ripple it is D_∥. For the samples Ag_{60_in} and Ag_{60_opp} the ratios $\frac{D_{\perp}}{D_{\parallel}}$ are 1.18 and 1.20 respectively, which decrease drastically for the samples Ag_{30 + 30_in} and Ag_{30 + 30_opp} to 1.07 and 1.05 respectively. Thus, the method of sequential deposition yields an aspect ratio of NPs much closer to 1 in agreement with findings reported in Ref. [9]. The grain size 'D' is larger along the ripple direction as compared to across it. This suggests that the ripples on the silicon surface influence the growth of Ag-NPs. For the samples in which sequential deposition method is employed (Ag_{30 + 30_in} and Ag_{30 + 30_opp}) there is less variation between D_⊥ and D_∥ resulting in truncated spherical NPs. This is in contrast to the deposition from the single direction leads to an ellipsoidal NP. The ripples constrain the growth of Ag-NPs across the ripple direction, possibly due to the surface energy variations caused by the

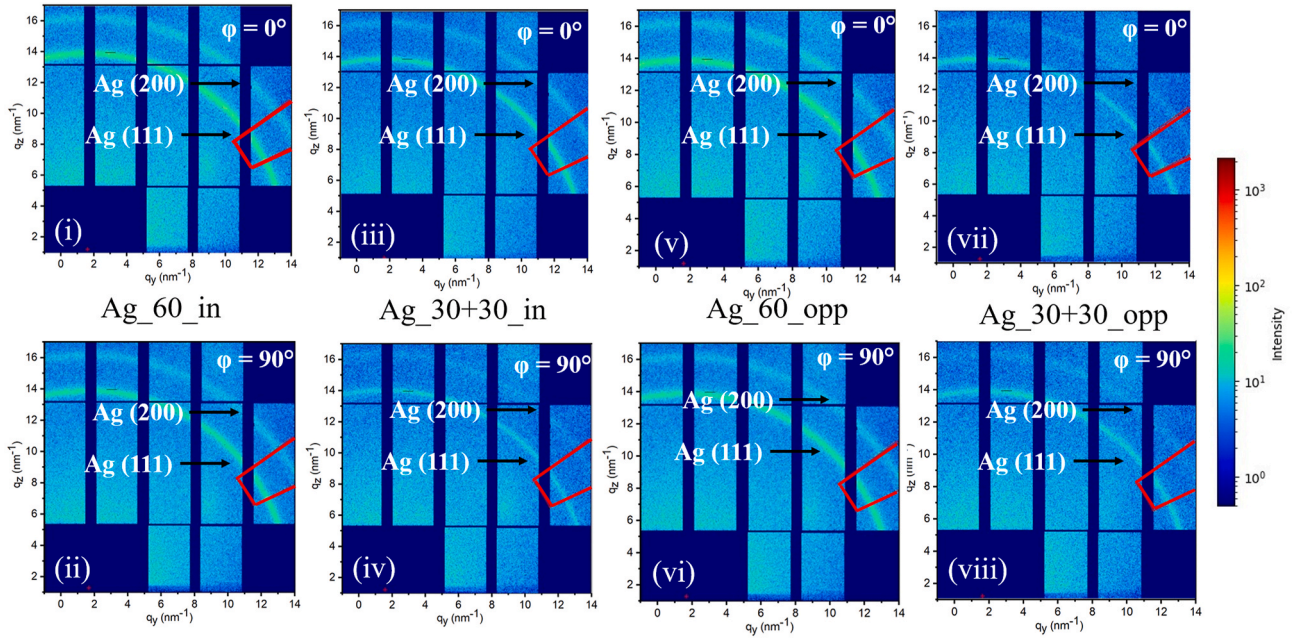


Fig. 7. 2D GIWAXS images (i)–(ii) Ag_{60_in}, (iii)–(iv) Ag_{30 + 30_in}, (v)–(vi) Ag_{60_opp}, and (vii)–(viii) Ag_{30 + 30_opp} taken along $\phi = 0^\circ$ and $\phi = 90^\circ$, respectively. The highlighted red box indicates the area used for extracting in-plane data.

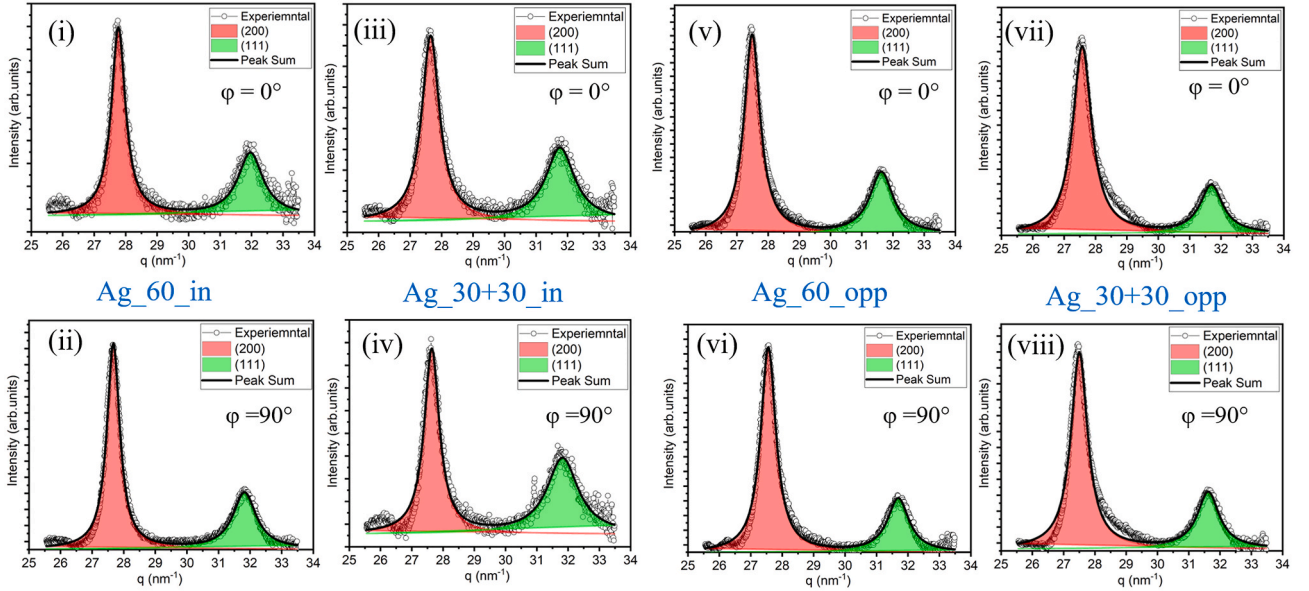


Fig. 8. The in-plane GIWAXS patterns for samples (i)–(ii) Ag_{60_in}, (iii)–(iv) Ag_{30 + 30_in}, (v)–(vi) Ag_{60_opp}, and (vii)–(viii) Ag_{30 + 30_opp} are obtained from GIWAXS data recorded at $\phi = 0^\circ$ and $\phi = 90^\circ$ orientations of the samples.

zipping effect [40], where islands tend to merge preferentially along the ripple direction, particularly within the valleys formed by the nano-ripples, due to surface energy minimization. To avoid this preferential growth and promote uniform morphology sequential deposition method can be very useful.

3.4. Molecular dynamics (MD) simulation of Ag nanoparticles deposited on rippled silica substrate

3.4.1. MD simulation setup

To understand the growth mechanisms of Ag-NPs observed experimentally, we performed MD simulations of Ag deposition on a model rippled amorphous silica substrate. A deposition energy of 0.4 eV is

employed, with four deposition scenarios akin to experiments and the same nomenclature is used: (i) deposition from the right for a duration τ (Ag_{60_in}), (ii) deposition from the right side followed by left for a duration of $\tau/2$ (Ag_{30 + 30_in}) (iii) deposition from left side (long face of the ripple) for a duration of τ (Ag_{60_opp}), and (iv) deposition from the left side followed by right for time $\tau/2$ each (Ag_{30 + 30_opp}). It is important to note that the order of deposition plays a significant role due to the modulation of Ag-Ag sticking probability due to the available surface area on the face exposed to the deposition atoms [41].

The procedure for the creation of the amorphous rippled silica substrate is as follows: starting from a β -cristobalite silica crystal structure consisting of 72,000 atoms corresponding to a crystalline density of 2.17 g/cm³ [42], a step wise amorphization sequence is employed (see

Table 2

The GIWAXS fitting results for different in-plane orientations are summarized, with error determined through least square fitting. The estimated errors are ± 0.03 for the normalized area (A), ± 0.01 nm for the lattice parameter (d), and ± 0.15 nm for the crystallite size (D).

Samples		Ag (111)			Ratio $\frac{D_{\perp}}{D_{\parallel}}$	Ag (200)			Ratio $\frac{D_{\perp}}{D_{\parallel}}$
		d	A	D (nm)		d	A	D (nm)	
Ag _{60_in}	Along the ripple	0.23	0.74	12.3	1.18	0.20	0.26	7.5	1.17
	Across the ripple	0.23	0.76	10.4		0.20	0.24	6.4	
Ag _{30 + 30_in}	Along the ripple	0.23	0.68	8.6	1.08	0.20	0.31	6.3	1.08
	Across the ripple	0.23	0.66	8.0		0.20	0.33	5.8	
Ag _{60_opp}	Along the ripple	0.23	0.72	13.4	1.20	0.20	0.27	6.4	1.25
	Across the ripple	0.23	0.73	11.1		0.20	0.26	5.1	
Ag _{30 + 30_opp}	Along the ripple	0.23	0.55	7.8	1.05	0.20	0.45	5.1	1.06
	Across the ripple	0.23	0.63	7.4		0.20	0.40	4.8	

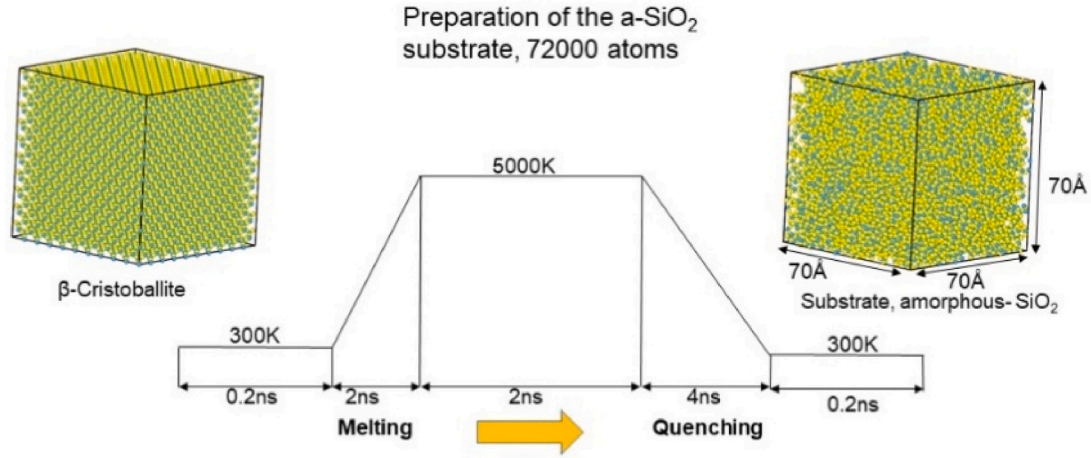


Fig. 9. Formation of 72,000-atom amorphous SiO₂ by melting β -cristobalite at 5000K and quenching to 300K.

Fig. 9) with the flux is same as that of the experiment. The equations of motion are integrated using the Verlet algorithm with a time step of 1.0 fs. Interactions between silicon and oxygen atoms are modeled using the Tersoff potential [43]. To exceed the experimental melting temperature of 1713 °C, the crystalline SiO₂ sample is initially heated to $T = 5000$ K. Then the system underwent a 2 ns equilibration phase under NVT (constant Number of atoms, Volume, Temperature) ensemble [44].

At this stage, the silica is fully melted and then gradually cooled to a final temperature of 300 K at a controlled rate of 11.75 K/ps, leading to the formation of an amorphous SiO₂ (a-SiO₂) structure. Subsequently, 5000 silver (Ag) atoms are deposited onto the rippled silica surface at an angle of incidence same as that of experiment. All MD simulations presented in this study are carried out using the LAMMPS simulation package [45].

A ripple on the silica surface is by cutting the quenched SiO₂ solid using two prism-shaped volumes, with dimensions of $X = 105$ Å, $Y = 140$ Å, and $Z = 70$ Å. The structure is cut on both sides using a prism-like shape, with each side trimmed at different angles 70° and 77° from the surface normal as shown in Fig. 10. Following surface cleavage, the system undergoes energy minimization through damped MD relaxation protocols. Post-relaxation analysis reveals minimal morphological evolution, with only partial flattening observed at the crest region's apex. Crucially, the sectioned planes exhibited remarkable stability, confirming the structural integrity of the engineered surfaces during the relaxation phase. A thermal bath of atoms positioned above the fixed layers maintained the substrate temperature at 300 K. Equilibration is performed for 100 ps, which is sufficient to achieve thermal equilibrium and enable surface diffusion of silver atoms. All simulations began at a constant height but from a random position in the X-Z plane. Since the simulation results exhibited a trend consistent with previously published experimental observations [20,46], we considered a model with a silver

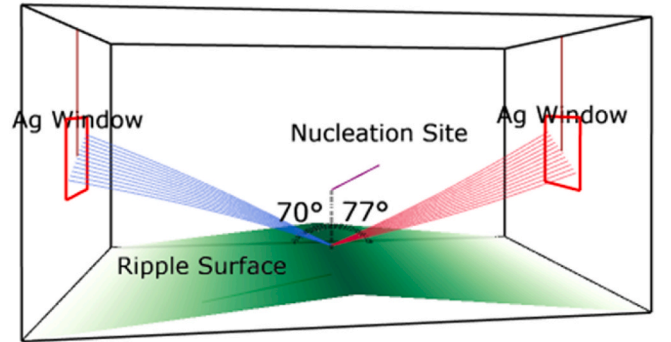


Fig. 10. Schematic of ion beam incidence from opposing directions converging at a nucleation site on the substrate surface.

deposition energy of $E_a = 0.4$ eV [19]. For each deposition, three independent simulations (starting from different random seeds for the deposition atoms) is performed to accumulate statistics. The final NP size is approximately 4526 atoms).

3.4.2. MD simulation results

Fig. 11 systematically illustrates the morphological evolution of Ag-NPs deposition on a silica substrate at different time points t_{initial} , t_{half} , and t_{end} using multiple visualization perspectives for the sample Ag_{60_opp}. Each row corresponds to a distinct view: the first row presents a 3D perspective, the second row shows the top view, the third row displays the front view, and the fourth row provides the side view along the Y direction. At t_{initial} , the substrate (yellow) is pristine, with no visible Ag (blue) accumulation. By t_{half} , silver atoms begin to aggregate

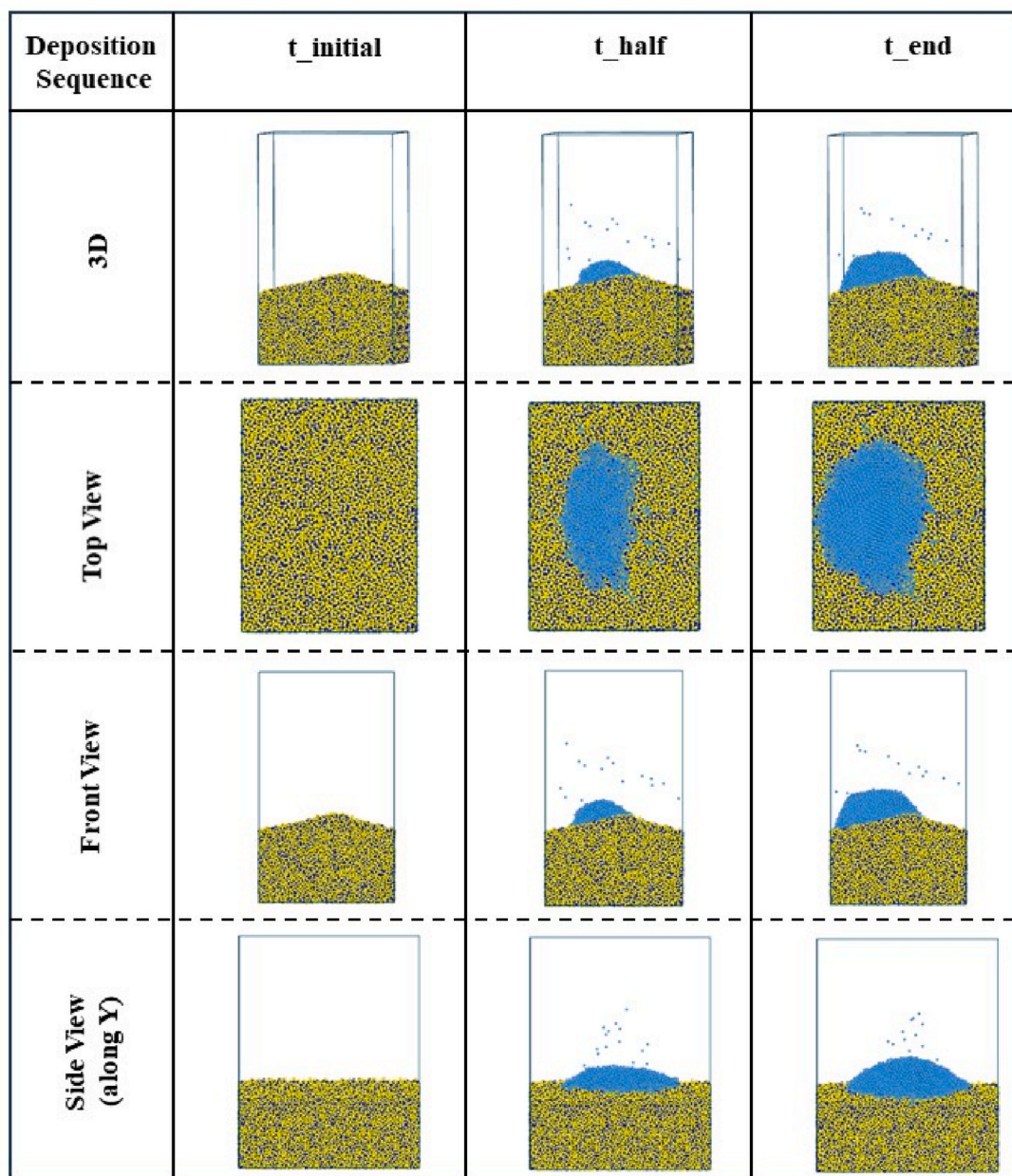


Fig. 11. 3D, top, front, and side views (along Y) for the case of Ag_{60_opp} showing the time evolution of cluster deposition and growth on an amorphous SiO₂ substrate at the initial, intermediate (half way), and final stage of the deposition.

on the substrate surface, forming a nascent NP that is clearly visible in both the 3D and orthogonal projections. At t_{end} , the NP is fully formed, appearing as a prominent blue cluster atop the yellow substrate. The top view highlights the lateral spread and footprint of the NP, while the front and side views reveal its vertical growth and interaction with the substrate. Fig. S3–S5 (Supplementary Data) shows the morphological evolution of remaining three samples. This multi-angle visualization effectively captures the dynamic process of NP nucleation and growth, demonstrating how Ag atoms progressively assemble into a compact structure on the silica surface over time.

Fig. 12 presents a comprehensive morphological analysis of Ag-NP deposition on a rippled silica substrate across four distinct deposition cases, visualized through both top and side views. The Ackland-Jones structural analysis [47], a widely used computational method in atomistic simulations, is employed to identify local atomic arrangements. Specifically, in cases (i) and (iii) with single-side deposition (Ag_{60_in} and Ag_{60_opp}), the NPs form a flattened, dome-like ellipsoidal

structure, whereas in cases (ii) and (iv), sequential deposition (Ag_{30_in} + Ag_{30_opp}) results in more uniformly spread and truncated spherical Ag clusters. Sequential deposition allows the NPs atoms, especially at the periphery to equilibrate more evenly over time, promoting the formation of energetically favorable spherical morphologies. Table 3 presents the structural and growth characteristics of the NPs arising from the different deposition protocols.

To compare the aspect ratios (y/x) of the simulated Ag-NPs with experiments, the component of the radius of gyration along y and x directions are calculated, as reported in Table 3. The Radius of Gyration (ROG) is a crucial parameter in MD simulations to assess the spatial distribution and compactness of NPs deposited on substrates. It estimates the root-mean-square distance of atoms from the NP's center of mass, providing information on structural changes, surface interactions, and environmental influences [48]. MD derived values can validate experimental measurements (e.g., TEM, SAXS). For Ag-NPs, calculated via the Guinier approximation in SAXS matches simulated trends when

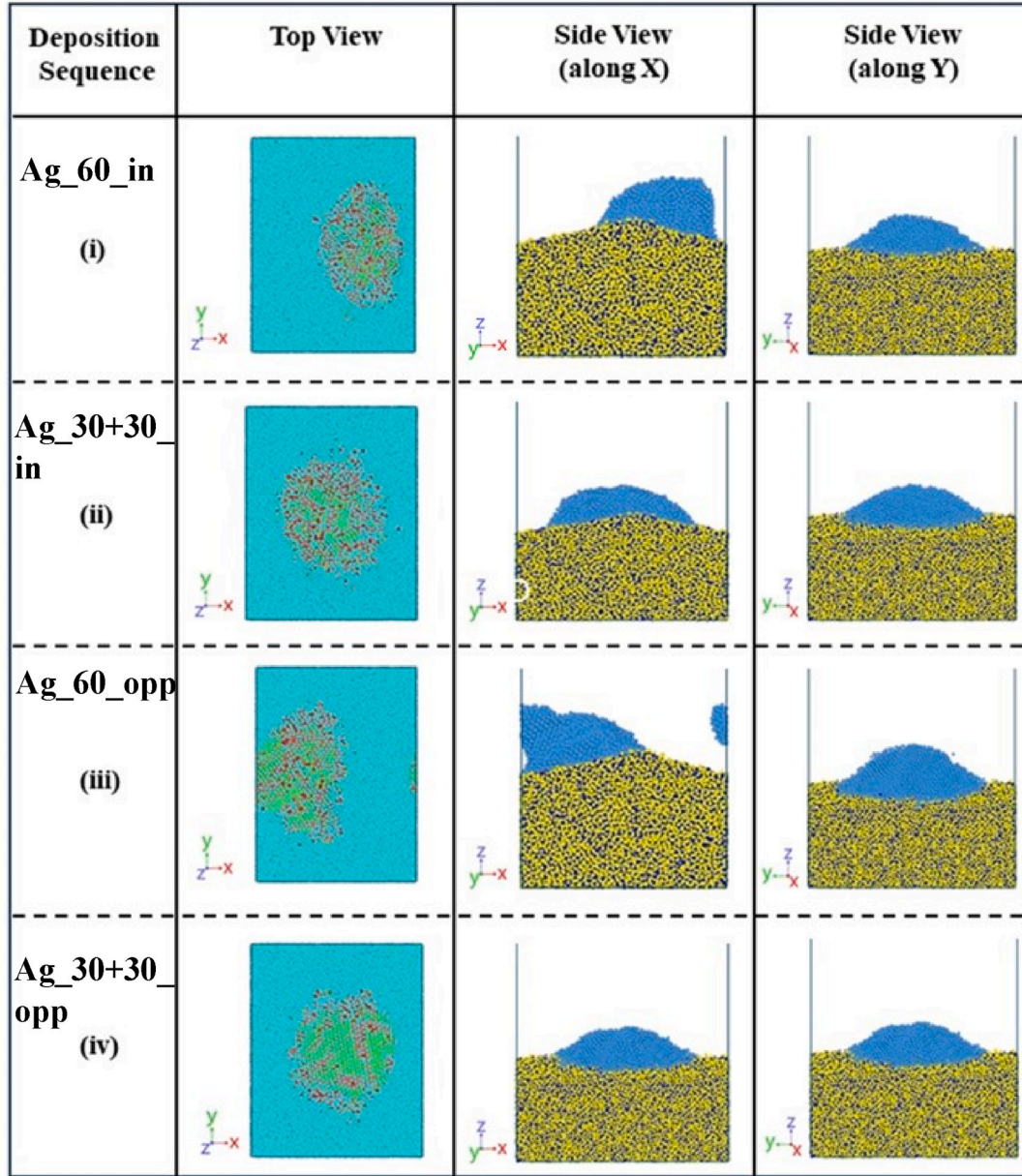


Fig. 12. Top and side views (along X and Y) showing the sequential deposition and growth of a cluster on an amorphous SiO₂ substrate across four deposition stages (i) Ag_{60_in}, (ii) Ag_{30 + 30_in}, (iii) Ag_{60_opp}, and (iv) Ag_{30 + 30_opp}. The Top View snapshots include atoms in their crystal structure.

Table 3

Structural composition and growth characteristics of deposited clusters at 0.4 eV across four deposition stages (i) Ag_{60_in}, (ii) Ag_{30 + 30_in}, (iii) Ag_{60_opp}, and (iv) Ag_{30 + 30_opp} as identified by Ackland-Jones analysis.

Deposition protocol	(i) Ag _{60_in}	(ii) Ag _{30 + 30_in}	(iii) Ag _{60_opp}	(iv) Ag _{30 + 30_opp}
y/x	1.46 ± 0.08	1.12 ± 0.04	1.27 ± 0.06	1.18 ± 0.03
Growth Rate (x)(Å/ps)	1.96 ± 0.16	1.89 ± 0.06	1.79 ± 0.07	1.76 ± 0.07
Growth Rate (y) (Å/ps)	2.68 ± 0.17	2.38 ± 0.11	2.46 ± 0.08	2.34 ± 0.16

aggregation artifacts are minimized. The ROG for NPs in MD simulation can be calculated by the equation - 5 [49]:

$$R_g = \sqrt{\frac{1}{M} \sum_{i=1}^N m_i (r_i - r_{com})^2} \quad (5)$$

Where M is total mass of number of atoms in the NP, m_i is the mass of i th atom of the NP, r_i is the atomic coordinates and r_{com} is the center of mass. For robust statistical analysis, R_g is computed across '3' independent simulations (with different initial velocities or randomized configurations) to account for trajectory-dependent variations. This approach aligns with SAXS where aggregation effects are minimized through ensemble averaging. For the sequential deposition cases, Ag_{30 + 30_in} and Ag_{30 + 30_opp}, the aspect ratios reduced to 1.12 and 1.18, respectively, compared to the single-side deposition cases (Ag_{60_in} and Ag_{60_opp}). The trend of these results is consistent with the aspect ratios obtained from SEM and GIWAXS analyses.

A notable variation is observed in the lateral (x-direction) growth rates, which range from 1.76 Å/ps to 1.96 Å/ps across the four deposition strategies [50,51]. The highest lateral growth rate is found in Ag_{60_in} (1.96 Å/ps), while the lowest occurs in Ag_{30 + 30_opp} (1.76 Å/ps). This trend indicates that deposition direction significantly influences lateral growth kinetics, likely due to enhanced surface diffusion

and re-emission effects during oblique angle deposition [50]. In single-side deposition, more nucleation sites form initially, and as deposition continues, this results in anisotropic, uniaxial growth due to strong Ag–silica interactions. Conversely, in sequential deposition, the arriving Ag atoms encounter pre-existing NPs formed during the first deposition phase. This promotes Ag–Ag bonding over new nucleation on the substrate, favoring isotropic, nearly spherical NP growth and thereby limiting asymmetric growth.

In contrast, the vertical (y-direction) growth rates remain relatively constant, ranging from 2.34 Å/ps to 2.68 Å/ps for all cases. This suggests that vertical growth is primarily governed by substrate NPs interactions and is relatively insensitive to changes in deposition direction [52].

The sequential method show modified structural distributions compared to single-direction depositions, suggesting that the changing flux directions influence nucleation and growth pathways. This is consistent with research showing that NP growth can occur through either thermodynamically controlled or kinetically controlled mechanisms, where kinetic control results in preferential and directional growth leading to anisotropic structure [53]. The sequential deposition approach appears to balance these competing mechanisms, enhancing growth rates while preserving overall particle morphology. This is consistent with reference [9] which reports that sequential deposition helps to tune the aspect ratio of NPs and aim to minimize the optical anisotropy.

The Radial Distribution Function (RDF) plot derived from molecular MD simulations, displays how atomic pairs are spatially distributed within a material. The main plot illustrates the RDF, $g(r)$, as a function of the interatomic distance r in Å is shown in Fig. S6 (Supplementary data). Two curves are presented: one for Si–O pairs (in blue) and another for Ag–Ag pairs (in green). The RDF essentially describes the likelihood of finding a pair of atoms at a distance r , relative to a completely random distribution. The Si–O curve shows a sharp peak near 1.6 Å, indicating a strong, well-defined local structure characteristic of covalent bonding in silicate materials, such as SiO₂ where each silicon atom is typically coordinated with four oxygen atoms [54]. In contrast, the Ag–Ag RDF exhibits a very sharp and intense peak at around 2.9–3.0 Å and more peaks at larger distances, signifying crystalline domains of dense packing [55].

The inset graph displays the coordination number as a function of radial atomic separation r . For Si–O, the coordination number is around four, reinforcing the idea of tetrahedral coordination in the silicate network. The Ag–Ag coordination number rises more gradually and continuously, reaching higher values, which is consistent with metallic bonding where atoms tend to have many nearest neighbors [56]. Furthermore, sample Ag₃₀ + 30_opp show the highest percentage of FCC structure.

4. Conclusion

This study investigates the atomic-scale reorganization of Ag-NPs deposited on ion-beam-induced nanorippled silicon substrates. Ripples were fabricated via ion beam irradiation, followed by Ag-NP deposition under three configurations: along, opposite, and sequential (from both sides) to the ion beam direction. GISAXS analysis revealed an inherent asymmetry in the ripple morphology, with slopes of approximately 6.4° and 6.9°, leading to slightly steeper facets on one side. After Ag deposition, the sequential configuration exhibited a GISAXS 1D profile similar to pristine ripples, indicating symmetrical NP growth. GIWAXS measurements identified diffraction peaks at $q = 27.6 \text{ nm}^{-1}$ and 31.8 nm^{-1} , corresponding to the (111) and (200) planes of FCC Ag. For sequential deposition, the crystalline ratio $D_{\perp}/D_{\parallel}$ is found to be in the range of 1.06–1.08, suggesting the formation of truncated spherical NPs.

Molecular dynamics simulations supported these findings, showing that unidirectional deposition leads to elongated Ag clusters, while sequential deposition yields flatter, uniformly distributed nanostructures concentrated near the ripple tips. RDF analysis confirmed

consistent Si–O and Ag–Ag bonding across all configurations.

Overall, the study demonstrates that the deposition direction critically influences NP morphology and growth symmetry, providing valuable insights for optimizing plasmonic performance through controlled NP geometry. These findings also hold promise for applications in plasmon-enhanced photovoltaics, nanophotonic devices, SERS and photocatalysis, underscoring the potential of ripple-assisted nanopatterning as a scalable, reproducible, and versatile route for fabricating large-area substrates.

CRedit authorship contribution statement

Tarundeep Kaur Lamba: Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Tejasva Vashistha:** Writing – review & editing, Writing – original draft, Software, Investigation, Formal analysis, Data curation. **Sharanjeet Singh:** Writing – review & editing, Visualization, Software, Formal analysis, Data curation. **K.P. Sooraj:** Writing – review & editing, Data curation. **Sebin Augustine:** Writing – review & editing, Formal analysis. **Raghavan Ranganathan:** Writing – review & editing, Validation, Software, Resources, Conceptualization. **Sarathlal Koyiloth Vayalil:** Supervision, Resources. **Dileep Kumar:** Resources. **Mukesh Ranjan:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Methodology, Conceptualization.

Novelty statement

This work presents an integrated experimental and computational study of silver nanoparticles grown on ion-irradiation-induced, nano-ripple silicon patterns. It highlights how surface asymmetry and deposition geometry tune morphology, ordering, and crystallinity. Combining GISAXS, GIWAXS, and SEM with molecular dynamics simulations, we elucidate growth mechanisms along and across the ripples. GISAXS reveals an asymmetric profile with one slope steeper than the other, while GIWAXS provides a detailed analysis of silver crystallographic orientations, compressive strain, and interplanar spacings (d -spacings). We further show that single-direction deposition yields uniaxial, ellipsoidal particles aligned with the ripples, whereas sequential deposition produces near-spherical nanoparticles with more uniform spacing. These insights advance substrate-guided strategies for engineering isotropic nanoparticle assemblies for plasmonic and spintronic applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.physb.2025.418066>.

Supplementary material

Supplementary Information provides additional analyses of SEM images, simulation supporting figures and data.

Data availability

Data will be made available on request.

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