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<http://dx.doi.org/10.1016/j.nimb.2016.10.005>

PUBLISHER

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VERSION

AM (Accepted Manuscript)

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"Thermal Dynamics of Silver Clusters Grown on Rippled Silica Surfaces". figshare.
<https://hdl.handle.net/2134/24017>.

Thermal dynamics of silver clusters grown on rippled silica surfaces

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Abstract

Silver nanoparticles have been deposited on silicon rippled patterned templates at an angle of incidence of 70° to the surface normal. The templates are produced by oblique incidence argon ion bombardment and as the fluence increases, the periods and heights of the structures increase. Structures with periods of 20 nm, 35 nm and 45 nm have been produced. Moderate temperature vacuum annealing shows the phenomenon of cluster coalescence following the contour of the more exposed faces of the ripple for the case of 35 nm and 45 nm but not at 20 nm where the silver aggregates into larger randomly distributed clusters. In order to understand this effect, the morphological changes of silver nanoparticles deposited on an asymmetric rippled silica surface are investigated through the use of Molecular Dynamics simulations for different deposition angles of incidence between 0° and 70° and annealing temperatures between 500K and 900K. Near to normal incidence, clusters are observed to migrate over the entire surface but for deposition at 70° , a similar patterning is observed as in the experiment. The random distribution of clusters for the periodicity $\approx$ of 20 nm is linked to the geometry of the silica surface which has a lower ripple height than the longer wavelength structures. Calculations carried out on a surface with such a lower ripple height also demonstrate a similar effect.

Introduction

The wide tunability of Localised Surface Plasmon Resonance (LSPR)^{1,2} shown by silver nanoparticles (np) in the visible and near infrared spectrum has made them very useful in diverse applications including thermal applications³, photovoltaics^{4,5} and bio nanoscience⁶. LSPR based research has seen a boom at the present time which is primarily due to the ease of fabrication of metallic nanoparticles in a variety of environments^{7,8}. Especially, the case of ordered chains of silver nanoparticles on patterned templates^{9,10} is interesting for their use in nanoplasmonic waveguides^{11,12}.

There have been a number of different studies of cluster growth on metal surfaces which combine experimental and modelling investigations. References¹³ and¹⁴ consider the ripening process in detail after the deposition of individual atoms whereas reference¹⁵ investigates the impact of clusters themselves onto a surface. Only few studies have focussed to understand the atomic interaction of silver with silica¹⁶⁻¹⁸. In a previous paper¹⁹ we parametrised an interatomic potential function for the Ag-SiO₂ interaction, based on matching sticking probabilities to Rutherford backscattering data. Although a few research groups have studied the temperature dependent interaction of silver thin films and silver cluster with silica^{20,21}, there has been no investigation to understand the thermal dynamics of silver clusters

deposited on nanopatterned templates.

Recently, a study based on the Kinetic Monte Carlo (KMC) method was undertaken to understand the mechanisms of the growth of silver nanoparticles on the patterned surfaces¹⁷. The reported study has limitations in some of the assumptions of the model such as no reflection of the Ag atom from the surface and no cluster migration on the surface. In addition, the energy and the angle of incidence (AOI) of the incoming atom were not parameters of the model¹⁷. In the present work, we have performed ex-situ SEM characterisation of the silver nanoparticles which shows patterned growth on rippled patterned templates of varying periodicity before and after annealing. We have used MD to understand the coalescence behaviour of the silver clusters deposited at different angles of incidence on the simulated rippled silica surface at 300 K and annealed at temperatures from 500 K to 900 K. The simulated dynamical behaviour aids in the understanding of the experimentally observed patterns of silver np deposited at an angle of incidence of 70°, which occurs for the ripple wavelength 35 nm and above.

Experimental Section

The modification of a silicon surface to a rippled structure is a well-studied topic^{22,23}. We report in brief, the fabrication process of silver nanoparticles on the rippled silica surface. An epipolished silicon wafer (100) was bombarded by a 500 eV broad beam of Ar⁺ ions at an AOI of 67° with respect to the surface normal. The fluence was varied from $10^{16} - 10^{19}$ ions/cm² to generate rippled templates with periodicities of 20 nm, 35 nm and 45 nm. This generated rippled silicon structures with heights $\approx$ 1-2 nm for a wavelength of 20 nm, 2-3 nm for 35 nm and slightly higher at 45 nm. The structure has an asymmetric nature where two planar surfaces lie at different angles with respect to the flat surface (see Fig. 1, inset in image 2). The substrates were then exposed to atmosphere which leads to the formation of a native oxide layer of approximate thickness 2 nm on the freshly bombarded surface. Subsequent deposition of silver was performed with a deposition rate of

1 nm/sec for 30 minutes at an AOI of 70° using an electron beam evaporation system. The time duration of the deposition of silver was kept the same for the three periodic templates with pressure maintained at 10^{-8} mbar. The deposited samples were then annealed at 573 K for 1 hour and 4 hours, respectively. The underlying ripple pattern was not observed to change even at temperatures of upto 1000 K.

Results

The top row of figure 1 shows the deposited silver on the rippled silica surface. Silver grows through a Volmer Weber mode that leads to the formation of separate clusters until the thickness of the film reaches several nanometres²⁴. This feature of the growth is confirmed by the micrographs which show well separated np on the patterned template. It is seen by comparing images 1,2 and 3 that self-aligned silver np are obtained for a ripple periodicity greater than 20 nm whereas one observes less alignment at 20 nm and this disappears completely after annealing. Another feature visible from the images is that the np deposited on $\lambda = 35$ nm and above are well separated from np present on the neighbouring ripples as compared to $\lambda = 20$ nm. This indicates that the onset of ordering starts at room temperature itself for these structures. The deposited silver np were then exposed to atmosphere and then annealed in vacuo at 573 K for a period of 1 hour as this leads to an approximately circular cross-section of np on account surface energy minimisation^{14,25}. This is confirmed by the micrographs A, B and C which show the np morphology of the annealed samples for $\lambda = 20$ nm, 35 nm and 45 nm, respectively.

A common observation from all the images is the increase in the size of the silver np and evolution of the shape to a spherical one which is due to coalescence. Images B and C show that a configuration of ordered np chains is obtained for $\lambda = 35$ nm and $\lambda = 45$ nm whereas it is clearly visible that for $\lambda = 20$ nm silver np are randomly distributed similar to the flat substrate. The inset in image C shows the np morphology for the case where sample 3 was an-

Figure 1: Scanning electron micrographs (SEM) showing the deposited silver nanoparticles on rippled silica surfaces. Images 1, 2 and 3 show the silver nanoparticle morphology on the rippled template with periodicity $\lambda = 20$ nm, 35 nm and 45 nm, respectively. The inset in image 2 shows a cross sectional transmission electron micrograph of a 35 nm rippled structure. The asymmetry of the structure is clearly visible with the angle of inclination marked for each plane of the surface. Images A, B and C show the system configuration for the three periodicities after being annealed at 573K for a time duration of one hour. The inset in image C shows the morphology after annealing for 4 hours.

Figure 2: Histograms showing the number of particles and the measured average diameter for the annealed silver np for the three different ripple periodicities.

nealed for a time duration of 4 hours. It is seen from the image that the ordered configuration is still not lost and a clear features are observed with an ordering that follows the ripple pattern on the template. For the 20 nm wavelength case not only are the annealed np more randomly spread, they also have a larger average diameter than in the other cases (see Fig. 2). This indicates a more uniform deposition and isotropic coalescence which is attributed to the lower height of the structure for the smaller wavelength case. Figure 2 shows the histograms plotted from the micrographs for the samples annealed at 573 K for 1 hour. Although the variation in average size is around one nm for the three cases, the

spread in the np size distribution is much more for $\lambda = 20$ nm as seen through the standard deviation (SD) and the variance (var) given in the figure. The maximum diameter of np for $\lambda = 20$ nm is measured to be 34.6 nm whereas it is 27.8 nm and 26.9 nm for $\lambda = 35$ nm and 45 nm, respectively. To understand these effects, we performed MD simulation of the Ag-SiO₂ system and discuss the results in the following section.

Molecular Dynamics Simulations

We simulated the interaction between silver adatoms and a rippled silica template using mo-

lecular dynamics (MD). MD simulations are limited to time scales up to microseconds at best and experimental time scales are generally not accessible by MD alone. Recently a multi-time scale technique has been developed that uses MD to model individual particle impacts over picosecond time scales followed by an off-lattice KMC approach to model diffusion between particle impacts²⁶. This works well when the diffusion barriers are large so that atom movement only occurs as series of rare events. If the energy barriers for diffusion are low then the time acceleration is much more modest. We performed some simulations using this off-lattice KMC technique but found that the computed barriers were low and that Ag atoms diffused quickly to form clusters on the surface. The barriers for a single Ag to diffuse from one local minimum to another, calculated using the nudged elastic band technique²⁷, varied between 0.1 and 0.2 eV depending on the attachment site. Small clusters containing up to 4 Ag atoms were also found to be mobile on the surface over picosecond time scales at room temperature. Once the larger Ag clusters were formed it was difficult for them to break apart although in some cases during a deposition event, an entire cluster could detach from the surface due to the weak bonding with the substrate. Even the deposition of a few atoms using the off-lattice KMC involved weeks of computing time. As a result we performed MD simulations at unrealistically high deposition rates for comparison. It was found that the results were qualitatively the same as using off-lattice KMC.

In a MD simulation, all material properties such as bond angles, bond lengths, coordination numbers, bulk modulus etc. are defined within the interatomic potential²⁸. A two body fixed charge potential developed by Kieu et al. containing a Coloumb term and a dipole term was used to simulate the SiO₂ substrate²⁹. We used a Morse potential to simulate the silver silica interaction. The potential was chosen to be consistent with reflection coefficients calculations and with results from Rutherford backscattering experiments¹⁹. The equation for Morse po-

tential is given as;

$$V(r) = \frac{D_e}{S-1} \left\{ \exp \left[-(2S)^{\frac{1}{2}} \beta (r - r_e) \right] \right\} - S \exp \left\{ \left[-(2/S)^{\frac{1}{2}} \beta (r - r_e) \right] \right\}$$

where r_e is the equilibrium bond length, D_e is the potential energy well depth at r_e , β and S are free parameters which take the value 2 in the standard Morse potential. The first term on the right hand side simulates the short range repulsion whereas the latter term accounts for the long range attraction²⁸. Tables I shows the value of these parameters for average binding energy value of 0.2 eV for an Ag atom on the surface.

Table 1: Parameters of Morse potential for average $E_b = 0.2 \text{ eV}$

Bond	$D_e(\text{eV})$	$r_e(\text{\AA})$	$\beta(\text{\AA}^{-1})$	S
Ag-Si	0.05	2.6	3.0	2.0
Ag-O	0.05	2.6	3.0	2.0

The Ag binding energy is defined as $E_b = E_{Ag-SiO_2} - E_{SiO_2}$. Here E_{Ag-SiO_2} is the potential energy of the system with a silver atom present on the silica surface and E_{SiO_2} is the potential energy of the silica substrate. The Ackland potential was used to simulate the Ag-Ag interaction³⁰. All the potentials used in this work are splined to the ZBL potential through a sixth order polynomial to describe the nucleus-nucleus repulsion at very small distances³¹. However this part of the energetic interaction does not come into play for the low energies involved in the simulations presented here.

We report in brief, the setup used to generate the rippled silica substrate (R1). The dimensions of the simulation box was calculated to hold 999 atoms ($N_{Si} = 333$ and $N_O = 666$) with a density 2.65 g/cm³ with periodic boundary conditions in all directions. This gave the Cartesian dimensions of the bounding box as $X = 2.92 \text{ nm}$, $Y = 1.46 \text{ nm}$ and $Z = 2.92 \text{ nm}$. The system was then quenched as reported elsewhere²⁹. Periodic copies of the system

Figure 3: (Colour online) A: Plot shows the rdf for the Si-O atomic pair. The image on the right shows a profile for a cross deposition event at an AOI 70° . The topmost atom of the surface is at a height of 1.56 nm above the bottom. The translucent yellow bar marks the region of the substrate ($\approx 2 - 3$ atomic layers) which was coupled to the thermostat during the time period of the simulation.

were made so that the two edge lengths of the quenched substrate in the Y and the Z direction became $Y = 2.92$ nm and $Z = 5.84$ nm. This substrate was then cut at angles consistent with those shown in the TEM image (Fig. 2B) to produce a surface with average surface normal in the Y direction. This leads to a triangulated structure where the top most atom of the silica substrate has a height of 1.56 nm. The empty space from $Y = 1.56$ nm to 2.92 nm within the simulation box serves as vacuum above the surface of the substrate. The bottom layer of the system was fixed and the substrate was then relaxed using damped MD³² which did not cause an appreciable change in the angles of inclination of the two planes. The system was finally thermalised to 300 K using the Berendsen thermostat³³ before the start of the production run. The system set up is shown in Fig. 3. During the production run, the system was kept coupled to the thermostat so as to remove excess energy due to the accumulation of silver adatoms. Some final configurations were then annealed at different temperatures. Figure 3 shows the radial distribution function (rdf) for Si-O atomic pair. The rdf has broadened peaks and goes to 1 as the distance increases which should be the case for an amorphous or glassy substrate. Similar plots were obtained for other atomic pairs of the substrate. The image on the right shows the side view of the silica substrate with both planes of the rippled surface explicitly marked. The normal of the exposed plane lies in the direction of the incoming silver atoms

while that of the opposite plane points away.

In a typical electron beam evaporation experiment, the kinetic energy of the evaporated atoms from the crucible containing the material has an energy much less than 1.0 eV^{34,35} with a narrow energy distribution³⁶. Therefore, we fixed $E_{Ag} = 0.1$ eV as the kinetic energy for the Ag adatom. The bottom 3 layers of the substrate were fixed and periodic boundary conditions were applied in the X and Z directions of the substrate. Each simulation was continued until the system equilibrated or the Ag atom was found to evaporate from the surface and reach a distance of more than 0.5 nm from the topmost atom of the surface (the interaction range for Ag-Ag = 0.5 nm, Ag-SiO₂ = 0.35 nm). The equilibration time was around 20 ps in all cases after which the substrate temperature settled down to the heat bath level and the next Ag atom was deposited. Cumulative depositions were performed at AOI = 0° , 20° , 40° , 60° and 70° with the substrate coupled to the thermostat fixed at a temperature of 300 K. A total of 132 deposition events were simulated for each angle of incidence. Figure 4 shows the final snapshots for these angles of incidence. The strong ionic nature of the substrate did not result in any broken Si-O bonds and substrate atoms only oscillated around their initial positions after a deposition event. The results from the cumulative depositions clearly show that the angle of incidence plays a crucial role in the formation of silver clusters on the rippled surface. The effect of angle can be understood

Figure 4: Final snapshots from the cumulative deposition of silver on the rippled silica surface at different AOI. The left column shows the side view whereas the right column shows the corresponding top view. It is seen that as the AOI increases from the surface normal, the number of silver atoms present on the more exposed plane is greater than the opposite plane of the rippled surface. Here $E_{Ag} = 0.1 \text{ eV}$ and $T = 300 \text{ K}$.

in terms of the apparent area of the surface visible to the incoming adatom. We discuss the effect for the case of 0° and 70° .

Due to the asymmetric nature of the rippled surface, the angle made by the vector of the Ag adatom (incident at 70° w.r.t the surface normal) with the exposed plane is 57° while that with the opposite plane is 88° . Previously¹⁹ the variation of the sticking probability with incidence angle was determined. For an AOI = 70° the silver clusters stick preferentially on the exposed plane with a reduced sticking probability on the other plane whereas one does not observe much difference for the AOI 0° case. The observed growth of the clusters is in fair agreement with the current experimental results as well as with the earlier reported investigations on the observed self-assembly of silver np for AOI 70° ³⁷.

To study the temperature dependent behaviour of the deposited clusters, we heat treated all the systems with final temperatures from T

= 500 K to $T = 900$ K in steps of 100 K. For all the simulation runs, the system was coupled to the thermostat to maintain the system at the desired temperature. The length of the simulation was 1 nanosecond (ns). A movie file was created for all simulation runs to understand the dynamical behaviour of the clusters. As the temperature was increased to 900 K, concerted motions by clusters take place on the silica surface. This also occurs at lower temperatures but over much longer time scales. This behaviour confirms that the silver clusters form through cluster migration on the surface and not just by adatom attachment as was assumed in the previous KMC model. Other studies have also confirmed the observed coalescence behaviour³⁸.

Fig. 5 shows a cluster coalescence event observed for an AOI = 0° . Image 1 shows the cluster configuration after 132 deposition events. After 12 picoseconds (image 2), it is seen that the cluster B joins the cluster on the ridge and at $t = 24$ ps (image 3) we only see a single cluster present on the top portion of the rippled surface. Although the two small clusters merge together, the nearby isolated adatom has only moved 1 step. This is because diffusion on an amorphous surface is site dependent, the value of $E_b = 0.2$ eV being only an average value with some adatoms being more strongly bound than others. With the formation of a close-packed Ag structure, the height of the cluster also increases which is in agreement with the experimental results³⁹.

These simulations also shed light on the observed ordered coalescence of the silver np (see Fig. 1) which is not observed when silver np are deposited and annealed on a flat silica surface. This property of silver np to form an ordered chain on the rippled surface is particularly favourable when silver is deposited at an AOI = 70° . To gain insight to the observed coalescence of silver np, we searched for clusters that performed a crossing over the ridge made by the asymmetric tilt of the two planes. Table II shows this behaviour of the deposited clusters for different angles of incidence. The cluster mobility over the ridge was found to be negligible at 500 K. For 600 K onwards, it was ob-

Figure 5: Snapshots showing the migration of silver clusters on the rippled silica surface for an AOI = 0° at $T = 600$ K. The cluster present on the ridge of the rippled surface is marked blue (A) while that present on the slope is marked black (B). The two clusters merge together within a time scale of tens of picoseconds.

Table 2: Observed crossover of the silver clusters on the rippled surface for different angles of incidence at different temperatures. X - cluster migration across the ridge does not occur. $\checkmark$ - cluster migration present across the ridge. In all the cases, $E_{Ag} = 0.1 \text{ eV}$ with the number of deposition events = 132

AOI\Temp.	500 K	600 K	700 K	800 K	900 K
0°	X	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
20°	X	X	X	$\checkmark$	X
40°	X	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
60°	X	X	$\checkmark$	$\checkmark$	$\checkmark$
70°	X	X	X	X	$\checkmark$

Figure 6: Image 1-3: Snapshots showing the migration of the silver cluster (purple) over the ridge portion of the rippled silica surface deposited with an AOI = 0° and $T=600 \text{ K}$. Image 4 shows the system configuration at time $t = 1 \text{ ns}$.

served that the crossover was present for AOI 0° . As an example, we show in figure 6 the snapshots of crossover of a silver cluster from one plane to the other.

The purple marked silver cluster moves from one plane to the other within a span of 18 ps and merges into the larger cluster present on the corner of the surface during the time scale of the simulation. Thus in our case, there are three key parameters which play an important role to understand the observed motion of silver clusters; 1.) the site where the cluster is bonded to the surface; a deeper potential well causes reduced cluster mobility. 2.) the size of the cluster; bigger the cluster, the lesser the mo-

bility. 3.) the temperature to which the system is heat treated; a higher temperature leads to increased mobility along with the evaporation from the surface.

It was observed from figure 1 that silver np deposited at AOI = 70° ($\lambda \approx 35 \text{ nm}$) show an ordered coalescence when annealed at a temperature of 573 K. This behaviour is also observed through the MD simulations of heat treatment of the silver clusters deposited at an AOI = 70° (see table II). Fig 7. gives an example of the dynamical behaviour of the silver clusters when heat treated at 600 K.

It is seen from images 1, 2 and 3 in figure 7 that the two clusters coalesce (at time $t =$

Figure 7: Snapshots showing the coalescence of the silver clusters at specified time for $T = 600$ K. The two clusters are marked as green and blue. The deposition parameters are $E_{Ag} = 0.1$ eV, $AOI = 70^\circ$ and $T = 300$ K.

574 ps) and remain on the exposed plane of the rippled surface until the end of the simulation. At an $AOI = 70^\circ$, the deposited clusters are present only on the exposed plane of the surface. When the temperature of the system is raised, the clusters, depending upon their size and the substrate site to which they are bonded, move on the surface which in turn increases the probability to interact with a nearby cluster, an event more favourable for the clusters present on the same plane of the rippled surface. This behaviour indicates towards the experimentally observed patterns of silver np, although our system suffers from the limitation of a lower periodicity (≈ 5.84 nm) than experiment.

An important observation from SEM images of annealed silver np on ripple structure with periodicity ≈ 20 nm (fig. 1, image A) is that the np are found to be present all over the template (no ordered pattern) as against the case for $\lambda = 35$ nm or $\lambda = 45$ nm. To understand this experimental observation, we performed cumulative deposition of silver on a different rippled surface. The dimensions in X and Z directions were same as the previous rippled surface but the angle of inclination was reduced by 5° for the two planes. This leads to an inclination of 8° for the exposed plane and 13° for the opposite plane from the surface horizontal. We name this surface R2. As before, the number

of deposition events was fixed to 132 with a time interval of 20 ps between each deposition event. The AOI for deposition was 70° with $E_{Ag} = 0.1$ eV. Fig. 8 (image A and image B) shows the results from this simulation.

On comparing the simulation results of the cumulative deposition between the two rippled surfaces [R1 (figure 4) v/s R2], it is seen that the silver clusters grow on the exposed plane only for R1 whereas clusters are present on the both planes for R2. This is due to the reduction in the angle of the inclination of the planes for R2 as this leads to apparent angles of 62° and 83° for the exposed plane and the opposite plane thereby leading to an increase in the sticking probability on the Ag atom on the opposite plane of the surface. The above result supports our experimental results (fig. 1, image 1) which shows that the deposited silver np are present on the rippled structure ($\lambda = 20$ nm) without any global alignment as observed for the other two periodicities.

We now compare the results from the heat treatment of the deposited clusters on the two surfaces. The deposited clusters on R2 were heat treated at $T = 600$ K for a time period of 1 ns. The clusters deposited on R1 show a distinct patterns (fig. 7) whereas for the case of R2, snapshots 1, 2 and 3 (fig. 8) show that the cluster migration is present across the ridge

Figure 8: Images A and B show the side view and the top view of the deposited silver on the rippled surface. The total number of deposition events is 132, $T = 300$ K, $\text{AOI} = 70^\circ$. Images 1, 2 and 3 show the snapshots at specific time intervals from the heat treatment simulation at $T = 600$ K. The two clusters marked green and blue are seen to coalesce with cluster migration from one plane to the other. Image 3 shows that only two clusters are present with no further coalescence until the end of the simulation.

formed by the two planes. In particular, the green marked cluster migrates from the exposed plane towards the blue marked cluster present on the opposite plane within a timescale of 300 ps. This behaviour was not observed for R1 as the opposite plane was devoid of clusters during the cumulative deposition. These observations are in good agreement with our experimental results for silver np deposited on a rippled template with $\lambda = 20$ nm which does not show the ordered patterning as compared to $\lambda = 35$ nm and $\lambda = 45$ nm.

Conclusion

Self-alignment due to temperature induced coalescence is observed for silver np deposited on the rippled template with periodicity 35 nm and 45 nm. For the ripple periodicity of 20 nm, we do not observe self-alignment of silver

np as the np are found to be distributed in a random manner over the substrate identical to the coalescence behaviour on a flat substrate. This feature is also reflected through the histograms for the measured size of the silver np which show a narrow distribution for $\lambda = 35$ nm and $\lambda = 45$ nm.

The results from MD simulations of the cumulative deposition of silver on the rippled surface show that the angle of incidence plays a crucial role to obtain a configuration of self-aligned silver np. In particular, the observed growth of silver clusters for the AOI of 70° takes place on the exposed plane of the rippled surface. The simulation results from the heat treatment of the deposited silver clusters show that cluster migration across the ridge of the rippled surface is present only for $\text{AOI} < 70^\circ$ in the temperature range 600 K to 800 K which is in agreement

with the experimental observations.

Acknowledgement This work was supported by the DST - British Council Exchanges with India scheme, UKIERI Grant: IND/CONT/E/13-14/642.

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