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Thermal dynamics of silver clusters grown on rippled silica surfaces

Mukul Bhatnagar [a,b,*], Mukesh Ranjan [a,b], Kenny Jolley [c], Adam Lloyd [c], Roger Smith [c], Subroto Mukherjee [a,b]

[a] FCIPT, Institute for Plasma Research, Gandhinagar, Gujarat, India
[b] Nirma University, Ahmedabad, Gujarat, India
[c] Dept. of Mathematical Sciences, Loughborough University, Leicestershire LE11 3TU, UK

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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 500 K and 900 K. 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 ≈ 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.

1. Introduction

The wide tunability of Localised Surface Plasmon Resonance (LSPR) [1,2] shown by silver nanoparticles (np) in the visible and near infra-red spectrum has made them very useful in diverse applications including thermal applications [3], photovoltaics [4,5] and bio nanoscience [6]. 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. Refs. [13,14] consider the ripening process in detail after the deposition of individual atoms whereas reference [15] investigates the impact of clusters themselves onto a surface. Only few studies have focussed to understand the atomic interaction of silver with silica [16–18]. In a previous paper [19] we parametrised an interatomic potential function for the Ag–SiO_2 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 surfaces [17]. 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 model [17]. 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.

* Corresponding author at: FCIPT, Institute for Plasma Research, Gandhinagar, Gujarat, India.
E-mail address: mkbh10@gmail.com (M. Bhatnagar).

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2. 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 epipolised 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/cm^2 to generate rippled templates with periodicities of 20 nm, 35 nm and 45 nm. This generated rippled silicon structures with heights ≈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/s for 30 min 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 h and 4 h, respectively. The underlying ripple pattern was not observed to change even at temperatures of up to 1000 K.

3. Results

The top row of Fig. 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 nanometres [24]. 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 h 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 annealed for a time duration of 4 h. 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. Fig. 2 shows the histograms plotted from the micrographs for the samples annealed at 573 K for 1 h. 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–SiO_2 system and discuss the results in the following section.

4. Molecular dynamics simulations

We simulated the interaction between silver adatoms and a rippled silica template using molecular 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 impacts [26]. This works well when the diffusion

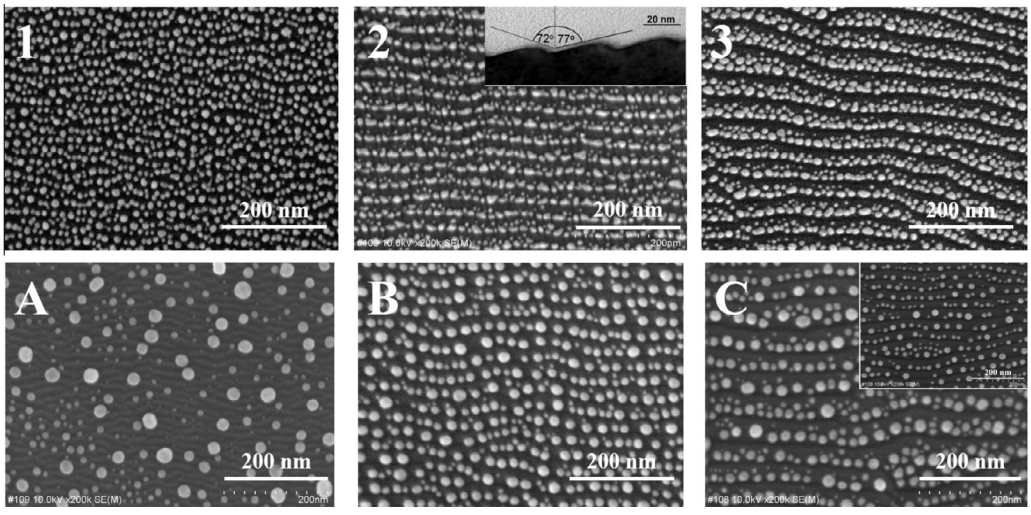

Fig. 1. Scanning electron micrographs (SEM) showing the deposited silver nanoparticles on rippled silica surfaces. Images 1, 2 and 3 show the silver nanoparticle morphology on the rippled template with periodicity $\lambda = 20$ nm, 35 nm and 45 nm, respectively. The inset in image 2 shows a cross sectional 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 573 K for a time duration of one hour. The inset in image C shows the morphology after annealing for 4 h.

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