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Sub-monolayer growth of Ag on flat and nanorippled SiO$_2$ surfaces

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In-situ Rutherford Backscattering Spectrometry (RBS) and Molecular Dynamics (MD) simulations have been used to investigate the growth dynamics of silver on a flat and the rippled silica surface. The calculated sticking coefficient of silver over a range of incidence angles shows a similar behaviour to the experimental results for an average surface binding energy of a silver adatom of 0.2 eV. This value was used to parameterise the MD model of the cumulative deposition of silver in order to understand the growth mechanisms. Both the model and the RBS results show marginal difference between the atomic concentration of silver on the flat and the rippled silica surface, for the same growth conditions. For oblique incidence, cluster growth occurs mainly on the leading edge of the rippled structure.

Silver nanoparticles have widespread application in nanotechnology and are being used in diverse applications ranging from bio nanoscience, thermal applications and photovoltaics. Our interest arises from their optical properties due to the interaction of the conduction electron cloud of a nanoparticle with incident electromagnetic radiation. This characteristic optical signature known as Localised Surface Plasmon Resonance has been a well studied topic. However, the growth of metallic nanoparticles on flat oxidised surfaces is not yet fully understood. For some surfaces and growth conditions, there is a Volmer Weber mode that leads to the formation of separated clusters until the thickness of the film reaches around 100 nm. However layer by layer growth can also occur, e.g. on ZnO. Recently, studies were undertaken using lattice-based Kinetic Monte Carlo (KMC) to model the growth of Ag nanoparticles on a rippled SiO$_2$ surface. The model used simplified assumptions such as no reflection of Ag, no cluster migration and no energy nor angle of incidence dependence of the incident Ag. In addition the underlying lattice was assumed to be face-centred cubic (fcc) so it was not clear if the predicted growth patterns were affected by this. Here, we perform in-situ RBS to measure the dependency of atomic concentration on the angle of incidence (AOI) of the silver flux for the flat SiO$_2$ surface and compare it with a rippled silica surface. We use MD to understand the dependency of the sticking coefficient on the binding energy ($E_b$) of the silver to the surface and the kinetic energy (K.E.) of the incident Ag for multiple AOIs. A potential parameterisation using the optimum value of $E_b$ is then used in the simulation to deposit silver successively.

The modification of a crystalline silicon surface to a rippled structure is a well studied topic. We report in brief the fabrication process of a ripple pattern on silicon and the subsequent deposition of silver on the flat and the rippled surface. An epi-polished silicon wafer (100) was bombarded by a 500 eV broad beam of Ar$^+$ ions at an AOI = 67° to the surface normal. The generated rippled silicon (periodicity = 35 nm, amplitude $\approx$ 2 nm) has an asymmetric nature where two planar surfaces sub-

tend different angles to the average surface normal (see Fig. 1, image (d)). This substrate was then exposed to atmosphere which leads to the formation of a native oxide layer on the surface. Subsequent deposition of silver was performed using an electron beam evaporation system at a pressure of $10^{-8}$ mbar. The PVD system is mounted directly on the RBS beam line for performing in-situ measurements to monitor the growth of silver clusters on both the flat silica surface and rippled silica surface simultaneously. The deposition rate was tuned through RBS and fixed at 0.1 ML/minute, where 1 ML for a fcc silver lattice corresponds to the surface density of $1.2x10^{15}$ atoms/cm$^2$. The direction of the incident vapour flux was varied from 0° to 85° to the surface normal. The RBS beam line generates an incident beam of He$^{2+}$ ions with kinetic energy 1.7 MeV. The system uses a geometry, where the incident angle of the He$^{2+}$ ions is 40°; the exit angle is 50° and scattering angle is 170°. The raw RBS data was fitted using the SIMNRA software to extract the atomic density of the silver present on the silica surface at a constant time interval of one minute. The deposition of silver and the in-situ RBS measurements were done at room temperature.

We prepared a special sample (1 cm$^2$) which was partly flat and partly rippled (Fig 1, image (b)). Plot (a) of fig. 1 shows the distribution of the incident atomic flux from the evaporator onto this substrate. It is seen that the incident flux is constant for a width of 14 mm. Image (b) shows the topology of both the flat surface and the rippled surface with a schematic of the points of measurement for in-situ RBS. A separation of 5 mm was kept to avoid variation of deposited silver over the measurement region. All our experimental results are from the deposition of silver on this substrate as this makes the RBS measurements independent of the deviation of the atomic flux in the two different regions. Image (c) and image (d) show the SEM images of the deposited silver at an AOI of 70°. It is clearly visible from both the images that the deposited silver nanoparticles grow by the Volmer Weber mode and in the case of the rippled surface, silver nanoparticles follow the topology of the underlying template as previously observed.
The flat surface is the two substrates show that the RMS surface roughness for surface normal. Atomic force microscope (AFM) analysis of to the oxygen atoms and the yellow spheres silicon. Geometry on the rippled surface. The red spheres correspond to the Ag atoms. The inset in image (d) shows the deposition of silver. The inset in image (c) shows the direction of the incidence Ag at 70° w.r.t the surface normal of the flat silica surface.

To understand the results obtained from RBS measurements, we used MD\textsuperscript{15} to simulate the interaction of a silver atom with the silica surface. The detailed description of the potentials used in this work is given in the supplementary material Si\textsuperscript{16}. Since there is a lack of experimental or ab initio data that gives a value for the average binding energy of Ag to SiO\textsubscript{2}, we fit a simple pairwise Morse potential for the Ag-Si and Ag-O interactions. We chose two sets of parameters that gave average binding energies of 0.2 and 0.6 eV. The former value is consistent with previous lattice-based KMC simulations\textsuperscript{17}.

Initially, 800 independent impact events (incident Ag atom energy, $E_{Ag} = 1.0\, eV$) were performed on a rectangular silica substrate. The procedure to create an amorphous silica surface was as follows: A charge neutral SiO\textsubscript{2} substrate was generated with random positions of silicon and oxygen atoms. A total of 999 atoms was chosen so as to create a big enough surface to simulate the silver-silica interaction. The simulation box was generated by calculating the volume of the box required to hold 333 atoms of silicon and 666 atoms of oxygen with the density of silica taken as 2.65 g/cm\textsuperscript{3}. The dimensions of the box were $X = 2.92$ nm, $Y = 1.46$ nm and $Z = 2.92$ nm and initially periodic boundary conditions (PBC) in all cartesian directions were used. The structure was then relaxed using a quench process\textsuperscript{17} until the system temperature was below 100K. The system was finally minimised using damped MD to remove excess energy. To create a free surface for SiO\textsubscript{2}, the box size was increased in the Y direction to 2.92 nm. The bottom 3 layers of the solid were kept fixed so as to avoid wrapping the lowest layer of atoms with the top of the vacuum region above the SiO\textsubscript{2} surface. As the atoms present on the surface need to be relaxed within the new box size ($X = 2.92$ nm, $Y = 2.92$ nm and $Z = 2.92$ nm), the system was damped again for $t = 10$ ps. Thus the average surface normal lies in the Y direction with PBC operating in the X and Z directions. The incident Ag atom was projected from a distance of 0.8 nm above the highest atom on the silica surface at different incidence angles and positions to generate the data. Each impact event was carried out for a time period of 10 ps which gives enough time to decide if the Ag atom is captured by the surface. After each impact, the surface was reinitialised to be silver-free and the process repeated. Some simulations were carried out with substrates quenched from different random initial configurations.

Fig. 2 shows a comparison of the observed atomic density of silver on the flat silica surface and the rippled silica surface for an AOI = 70°. It is seen that there is minimal difference in the atomic concentration of silver on both the surfaces. A similar trend was observed in several such experiments. Since the growth was performed only up to the equivalent of a few monolayers, the atomic density does not show any saturation before the completion of the experiment.

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FIG. 1. (Colour online) (a): RBS measurement of atomic flux over a width of 14 mm on a partly flat and partly rippled surface. (b): Images showing the sites for RBS measurements. The angle of incidence was kept fixed at 70° to the average surface normal. Atomic force microscope (AFM) analysis of the two substrates show that the RMS surface roughness for the flat surface is $\approx 0.2$ nm whereas the amplitude modulation on the rippled surface is $\approx 2$ nm. Images (c) and (d) show scanning electron micrographs (SEM) after cross deposition of silver. The inset in image (c) shows the direction of the incidence Ag atoms. The inset in image (d) shows the deposition geometry on the rippled surface. The red spheres correspond to the oxygen atoms and the yellow spheres silicon.

FIG. 2. (Colour online) Plot shows the atomic concentration of the silver on the flat and the rippled silica surface obtained through in-situ RBS. The angle of deposition was kept fixed at 70° w.r.t the surface normal of the flat silica surface.
energy barriers for diffusion are low then the time acceleration movement only occurs as series of rare events. If the 21 model diffusion between particle impacts time scales followed by an off-lattice KMC approach to complications associated with these diffusion barriers are generally not accessible by MD alone. Recently a 21 atom impacts. MD simulations are limited to time scales much more computing power than modelling individual 21 events such as Ag dimer/cluster evaporation increase 21 for a partially covered surface could reduce further 21 as the simulation results show a trend similar to the 21 and above is more than that observed in 21 or above is quite high when 21 was based on the fact that \( E_{ Ag} = 0.5 \text{ eV} \) and \( E_{ Ag} = 0.5 \text{ eV} \) was cut at two different angles from the surface normal consistent with those shown in image (a) of Fig. 4. Having cut the structure, the system was relaxed using damped MD. During the relaxation, the angles of the two planes did not change greatly although there was some flattening at the top of the crest. The temperature of the substrate was kept at 300K by a heat bath of atoms located above the fixed layers in the system. The time period of each simulation was kept fixed at 20 ps which was too long to allow for temperature equilibration and for the silver to diffuse over the surface. Each new simulation was started from a random position in the X-Z plane but at a fixed height. We used the model with \( E_{ Ag} = 0.5 \text{ eV} \) as the simulation results show a trend similar to the reported experimental observations 23 and for comparison with the previous KMC model 9 . The choice of incident adatom K.E. \( E_{ Ag} = 0.5 \text{ eV} \) was based on the fact that \( E_{ Ag} = 1.0 \text{ eV} \) and above is more than that observed in evaporation experiments 19 and \( E_{ Ag} = 0.1 \text{ eV} \) shows negligible variation of mean sticking coefficient with change in the incident angle of incidence. The evaporation rate for \( E_{ Ag} = 1.0 \text{ eV} \) or above is quite high when \( E_{b} = 0.2 \text{ eV} \) and we could observe Ag clusters of up to 7 atoms being dislodged from the surface by impacting Ag.

The main growth mechanisms seen in the simulations are the diffusion of adatoms and small clusters over the surface to join existing larger clusters, the direct attachment of incoming silver atoms to a cluster and the coalescence of large clusters when they come within a certain interaction range.

Images (a) and (c) in Fig. 4 show typical results from the cumulative deposition of Ag on the rippled surface
and the flat surface at an AOI of 70°. It is seen from Fig.
4 (a) and (b), that the Ag atoms form clusters on the face of the rippled surface more exposed to the incident atomic flux. The opposite face contains less Ag. This is because at an AOI = 70°, the average normal on the exposed face (A_e) makes an angle of 57° with the incident vector of the incoming Ag atom whereas the opposite face (A_o) of the rippled surface subtends an apparent angle of 88°. This leads to a decrease in the sticking coefficient for A_o. This is reflected through the plot (b) of Fig 3. which shows a change of 15% in Ag coverage when the AOI changes from 57° to 70° and the difference will further increase for an AOI = 88°. The observed cluster formation on the rippled silica surface and the flat silica corresponds well with the experimental observations (Fig. 1, image (c) and image (d)) with the clusters being randomly distributed on the flat surface but with gaps on that part of the rippled surface where the incidence angle is around 88°. In addition, the rippled surface contains about 19% more silver than the flat surface for the same incidence flux. However, more runs and better statistics are required to determine if this is a repeatable observation.

Image (a) and image (b) of fig. 5 show the comparison for surface coverage of silver on the rippled silica surface and the flat silica surface for the AOI = 20°, respectively. It is seen from the final snapshots that the difference in surface coverage between the two surfaces is minimal. The model gives no Ag nanoparticle arrays for AOs close to the surface normal, consistent with the experimental results.

In conclusion, the atomic density of silver is observed to be marginally different for the flat surface and the rippled surface as measured through in-situ RBS. A similar result is obtained from MD after cumulative deposition of silver for an AOI = 70°. MD simulation shows that the sticking coefficient reduces with angle of incidence for $E_b = 0.2\ eV$ in a manner consistent with the experimental results except near grazing incidence. MD was also able to identify growth mechanisms due to the low energy barriers for small Ag cluster diffusion over the surface. The cluster patterns predicted by MD are also in agreement with the observations from SEM.

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16. See supplemental material at for description of the interatomic potentials used to simulate the SiO2 substrate and Ag-SiO2 interaction.