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Ordered Ag nanocluster structures by vapor deposition on pre-patterned SiO₂

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Abstract. Highly ordered Ag nanocluster structures have been grown on pre-patterned amorphous SiO₂ surfaces by oblique angle physical vapor deposition at room temperature. Despite the small undulation of the rippled surface, the stripe-like Ag nanoclusters are very pronounced, reproducible and well-separated. Computer modeling of the growth has been performed with a lattice-based kinetic Monte-Carlo (KMC) method using a combination of a simplified inter-atomic potential and experimental transition barriers taken from the literature. An effective transition event classification method is introduced which allows a boost factor of several thousand compared to a traditional KMC approach, thus allowing experimental time scales to be modeled. The simulation predicts a low sticking probability for the arriving atoms, millisecond order lifetimes for single Ag adatoms and ≈ 1 nm square surface migration ranges of Ag adatoms. It is also shown that metal nucleations can trigger even on defect free surfaces. The simulations give excellent reproduction of the experimentally observed nanocluster growth patterns.

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FIG. 1. (a) Atomic force micrograph image of a rippled, v-SiO₂ surface. (b) Scanning electron micrograph (SEM) of the rippled surface after Ag deposition for 75 minutes at RT. The average thickness and width of the rods are ~ 10 nm estimated from the mean coverage 5.8 ML and Ag area fraction. The incidence angle is 70° from the mean surface normal and perpendicular to the ripples.

The study of functional nanostructures such as quantum dots, nanoparticles and nanowires is of special interest in materials science [1, 2, 3, 4]. In particular, well-aligned metallic nanoparticles and nanowires provide novel electromagnetic, optical properties and are promising candidates for transparent conductive electrodes in advanced semiconductor devices [5, 6]. As a bottom-up technique for the manufacture of templates for functional metallic nanostructures, low energy (≤ 1 keV) ion bombardment is a well established method [7, 8, 2], which can be used to produce adjustable ripple structures with respect to height and wavelength. Oates *et al* [2] made self-organized arrays of Ag and Co nanoparticles by utilizing rf magnetron sputtering on oxidized, rippled Si templates. Camelio *et al* [3] reported long-range ordered Ag nanoparticles produced by shadow deposition using ion-beam sputtering on BN (or Si₃N₄) doped, rippled Al₂O₃. Oxidized, amorphous substrates are often utilized as templates of such metal deposition since their weak interaction promotes the Volmer-Weber (VW) type growth of nanoclusters (NCs) and the weak adsorption of metals on vitreous silica (v-SiO₂) results in an extremely low initial sticking probability [9]. Metals generally possess high adsorption energies at defect sites [10] and therefore trigger heteronucleations which is the dominant mechanism for metal nucleations on v-SiO₂. Energetic metal deposition using sputtering [2, 3] induces scattered heteronucleations since the energetic process itself can form surface defects. It would therefore be expected that a more accurate control of metal nucleation could be achieved if the surface were kept defect free. In recent experiments employing electron (e)-beam evaporation instead of sputtering, where the deposition energy is much lower, Ni nanowire formation on rippled SiO₂ surface was reported [11]. With even slower e-beam evaporation, (growth rate 2.6×10^{-4} nm/s compared to 0.1 nm/s reported in Ref.[11]) highly ordered Ag nanorod arrays were successfully produced from self-organized Ag NC's of diameter ~ 10 nm.

In this rapid communication, we examine the problem both experimentally and computationally and present a new atomistic three dimensional lattice-based kinetic Monte-Carlo (KMC) simulation [13] which allows simulations to be performed over experimental time scales. It will be shown that this method not only gives excellent agreement with experiment but also establishes a metal nucleation mechanism on regular v-SiO₂ surfaces which is somewhat contrary to traditional belief [9, 14, 10, 15].

The rippled templates are fabricated by 500 eV Ar⁺ beam sputtering of Si(100) at an angle of 67° to the surface normal [8]. An oxidized layer ~ 2 nm then forms

immediately after exposure to the natural environment. The ripples are highly ordered and perpendicular to the ion beam (Fig.1 (a)). Cross-sectional electron microscopy images demonstrate the asymmetry of the ripples which have a periodicity of 30-40 nm and a height of 1-3 nm (see also Fig.2 (a)). Silver was deposited using an e-beam evaporator under ultra high vacuum condition (2.0×10^{-6} Pa) at room temperature (RT) with the source aligned at 70° to the surface normal. The deposition time was 75 minutes and the average Ag accumulation was 5.8 mono-layers (ML) calibrated by Rutherford Back Scattering. After deposition, silver nanorods with a mean length 20-120 nm, height and width ~ 10 nm as well as small NCs with diameter up to 5 nm were obtained (Fig.1 (b)). At the 70° incidence angle, almost all of the rippled template was exposed to the incoming Ag vapor. Despite the non-shadowed deposition, the observed Ag NCs grow preferentially along the slope whose normal points towards the evaporation source. Only a few small NCs at various growth stages are observed on other parts of the surface.

Although KMC is a well-established technique [16], we introduce some innovations to simulate the process considered above in a reasonable computing time. The model system is constructed as a face centered cubic (fcc) grid with (100)-symmetry embedded in a simple cubic lattice of size $512 \times 512 \times 128$ with periodic boundary conditions. The unit length of the fcc grid is consistent with the inter-atomic distance of silver in the perfect fcc crystal structure, i.e. 1 lattice unit (l.u.) corresponds to 0.204 nm. Various escape paths in this fcc grid network and associated transition rate constants are estimated effectively as follows. The fcc grid is divided into a substrate and vacuum region. Depositing and diffusing Ag atoms are only allowed to occupy fcc sites regarded as local energy minima within a perfect cubic overlayer of the vacuum region. Since no significant change is observed experimentally, the topography of substrate region is held fixed and assumed defect free. The saw-like asymmetric rippled substrate formed in the experiment (Fig.2 (a)) is modeled by an fitting function with periodicity 33 nm and height 2.4 nm (Fig.2 (b)). The local Ag atom arrival rate (*local flux*) f_{loc} is given as $f_{loc} = \vec{f} \cdot \vec{n}$ where f is the Ag flux from the evaporator, \vec{n} is the surface normal and \vec{f} is the flux vector oriented to the evaporation source. The incident angle is 70° to the mean surface normal and perpendicular to the ripple direction.

In order to estimate various migration barriers quickly, a relatively simple many-body potential is chosen, the RGL potential [17], together with migration values taken from the literature. The RGL potential is widely utilized in molecular dynamics simulations describing especially well the Ag facet properties [19, 18, 20, 22, 21, 23, 24, 25, 26]. For a silver atom i , let n_i^{Ag} and $n_i^{SiO_2}$ be the number of the nearest neighbor (NN) positions occupied by Ag and the positions belonging to the substrate region respectively. The configuration energy E_i of i is then defined by $E_i = -\zeta \sqrt{n_i^{Ag}} + A n_i^{Ag} + E_i^{Ag-SiO_2}(n_i^{SiO_2})$, where the first two terms are determined from the RGL-potential with parameters $\zeta = 1.1663$ eV, $A = 0.09982$ eV [27] exhibiting the *nonlinear dependency* on NN atoms and $E_i^{Ag-SiO_2}(n_i^{SiO_2})$ is the Ag-SiO₂ interaction term defined by $E_i^{Ag-SiO_2}(n_i^{SiO_2}) = 0$ for $n_i^{SiO_2} = 0$, or the adsorption energy $E_{ad}^{Ag-SiO_2}$ otherwise. The movement of atoms is handled by single atomistic jumps to the NN

empty position. The barrier is determined by the local configuration of the initial and final site of the jumping atom.

For transitions with a negative potential energy change, the jump attempt, usually involving an increase in NN's, occurs instantaneously. For transitions with a positive energy change, the barrier is estimated from the RGL potential. Otherwise, for transitions which conserve the number of NN's, migration barriers taken from the literature are utilized. For example, the Ag ad-monomer (adatom) migration barriers on the (111), (100) and in-channel(110) oriented Ag surfaces are estimated as 0.10 eV, 0.38 eV, and 0.28 eV from the calculations in Ref. [20, 28, 19] respectively. For Ag adatom migration on the bare substrate, the barrier $E_m^{Ag/SiO_2} = 0.20$ eV and the adsorption energy $E_{ad}^{Ag/SiO_2} = 0.245-0.300$ eV are employed. The variation of these energies $\Delta E \equiv E_{ad}^{Ag/SiO_2} - E_m^{Ag/SiO_2}$, together with the Boltzmann factor $e^{-\Delta E/kT}$ determines the probability of desorption or adatom jump on the substrate. The simulation temperature is held fixed at 300 K.

A particular feature of this model is that all transition barriers are measured relative to the migration barrier E_m^{Ag/SiO_2} . Each jump attempt of an Ag atom is accepted with probability determined from the Boltzmann factor with this renormalized transition barrier. Every transition event is therefore classified from the level originating from this migration barrier. Each migration with a barrier under 0.2 eV is assumed as an unstable transition and exhibits free migrations without any appropriation for the simulation time step. Thus, most of the simulation steps distinguish metastable level transitions with barriers above 0.2 eV. We term this the boost energy. A fuller description of the migration barrier estimation as well as details of the rate-based optimization method is presented elsewhere [13].

In this rate-based (RB) KMC model, the depositing atoms are set in the positions exposed to the trajectories and only the kinetics of Ag atoms are considered. The atoms detaching from Ag NCs or the substrate including desorbent ad-dimers are eliminated from the simulation immediately. Concerted motions, grain boundaries, reflection and surface drifting on impact are excluded. Under this scenario the migration barrier of Ag adatoms on the substrate is close to the desorption energy and arriving Ag adatoms are easily released to the vacuum and thus a short adatom-lifetime (AL) is expected. The boost energy 0.2 eV accelerates the simulation speed with a factor of $e^{0.2/kT} \sim 2290$. A typical growth process takes two or three CPU days on a modern single processor machine whereas a traditional KMC simulation might require some decades of computation time to obtain a similar surface coverage!

The local flux, f_{loc} , ranges from 20% to 75% of the flux f from the evaporator (Fig.2 (c)) due to the surface slope and the 70° deposition angle. In the experiment, nucleation is mostly observed in narrow stripe-like regions where the local flux is highest. Rapidly growing NCs in the high local flux region coalesce and become nanorods. The more slowly growing NCs located in the lower flux region remain as satellite clusters but there is some evidence of incomplete nanorod formation close to the well-formed nanorods where the flux is not quite so high (see Fig.1 (b)). Fig.2 (d) and (e) show the

FIG. 2. (a) Cross-sectional TEM image of a rippled v-SiO₂ surface. (b) The rippled surface used in the model and a schematic description of the Ag deposition. The Ag flux f , the vectors of incident angle \vec{i} and the surface normal \vec{n} are shown. (c) The local incident angle dependent Ag arrival rate f_{loc}/f (%) as a function of surface topography \vec{n} and flux \vec{i} . (d) Micrograph of the deposited Ag nanorods and NCs. (e) The simulation result from the Ag PVD model with a mean coverage of 4 ML. (f) Atomic scale NC growth process at the simulation time 10% (i), 50% (ii) and 100% (iii) of the growth stage indicated by the rectangle in (e). Arrows in (e), (f)-i exhibit the azimuthal direction of the incoming Ag flux.

direct comparison (top views) between the magnified SEM image (d) and the model (e). A similar formation of Ag nanorods and satellite NCs is obtained from the RB-KMC simulations with $E_{ad}^{Ag/SiO_2} = 0.26$ eV, i.e. $\Delta E = 0.06$ eV. Xu and Goodman [9] reported $\Delta E^{Cu/SiO_2} = 0.10 \pm 0.02$ eV as the difference of activation- and adsorption energies of Cu adatom on v-SiO₂ based on the precursor model [29]. DFT calculations show that the adsorption energy Ag-SiO₂ is generally about 70% of Cu-SiO₂ [15], thus the obtained value agrees well with the report of Ref. [9].

Fig. 2 (f) shows three different growth stages of NCs. In the early stages, nucleation is concentrated on the slopes facing the incoming atoms. Two small Ag particles with the diameter 2 nm and the height 1.2 nm (6 layers) are observed (i). Less nucleation occurs in low local flux regions due to a high re-emission rate. Further deposition promotes VW growth preferentially along the ripple due to NC coalescence (ii). The height is around 4.1 nm, the width and length are 5 nm and 12 nm respectively. Various growth stages of the Ag NCs can be seen due to the time difference between nucleations. As more Ag is deposited, the KMC algorithm minimizes the surface free energy of the NCs and their shapes attain a form that would be expected from purely thermodynamic considerations (iii). The top of the NC is 5.4 nm high from the substrate; the width is 10 nm. A round shape appears typically on the deposition side of the NC whereas the other side is faceted.

Although ad-dimer desorption occurs in the simulation, this is less than of ad-monomers due to the model restriction of concerted motions. However, the adhesion energy of an Ag dimer on SiO₂, calculated by DFT, is lower than the Ag monomer even on a defect site [15]. Thus, ΔE can be a little larger than suggested here due to a high desorption rate of ad-dimers. Desorption of larger NCs is not observed and in any case a high adhesion energy of trimers is also predicted by DFT [15].

The total simulation time is 1.2×10^7 t for 6 ML Ag accumulation where 1 t corresponds to the time for one jump attempt. In total, Ag atoms equivalent to 17.1 ML of Ag atoms are deposited with 35% remaining on the surface. Comparing the experimental duration of 75 min with the total simulation time of 1.2×10^7 t yields $1 t = 3.75 \times 10^{-4}$ s, giving a consistent simulation flux of $f = 0.0038$ ML/s.

The initial nucleation distribution and subsequent growth patterns are sensitive to

FIG. 3. Top Figure: The adatom lifetime as a function of the mean migration area of an Ag adatom and the Ag NC growth modes of three examples are shown. The circles (○) indicate data obtained from the simulations with parameters $\Delta E = 0.045\text{--}0.100$ eV at 300 K. The insets show typical traces of surface adatom random-walks with the color scale indicating the sequence of atomistic movements; **a**, **b** and **c** are with parameters $\Delta E = 0.045$ eV, 0.060 eV and 0.100 eV respectively. Lower Figure: The corresponding Ag surface morphology after a mean coverage 6 ML with three different viewpoints for each case.

the rate of arrival and the difference between the migration and desorption energies of the Ag adatom on SiO₂. Due to this sensitivity, the growth is studied by varying these parameters. Because the flux was not known experimentally we investigated the influence of the AL on the nucleation density distribution under the presumed flux of $f = 0.0038$ ML/s. Due to the discretized pathways in the fcc grid, the probability of desorption of an Ag adatom P_d is $P_d = e^{-\Delta E/kT} w_d/w_{tot}$ where w_d and $w_{tot} = 12$ are the number of directions for detaching from the substrate and total jump directions respectively. The factor w_d/w_{tot} is determined by the geometrical configuration of the jumping atom. The mean AL T_{AL} is given by $T_{AL} = P_d^{-1}$. Here, the migration area exhibiting the trace of single adatom random-walks on the *flat* surface is considered. Thus the geometrical factor w_d/w_{tot} is held fixed at 1/3 due to the (100) orientation of the surface.

The probability existence distribution $C(t, x, y)$ of a single adatom deposited at the origin may evolve via the reaction-diffusion equation $\partial_t C - D (\partial_{xx} C + \partial_{yy} C) = -T_{AL}^{-1} C$ with the initial condition $C(0, x, y) = \delta(x)\delta(y)$, where δ is the Dirac delta function, D is the surface diffusion coefficient. Integrating the equation yields $C(t, x, y) = \exp[-(x^2 + y^2)/4Dt - t/T_{AL}]/4\pi Dt$. The surface diffusion coefficient D for the (100) oriented surface is $D = 0.167$ l.u.²/t corresponding to 1.85×10^{-17} m²/s.

Fig. 3 shows the average migration area of a single adatom on the flat substrate as a function of mean AL. Each plot exhibits the average migration area of 100,000 samples. The mean migration area separates from the mean propagation (solid line) significantly with increasing AL since the overlapping area of the migration trace for a long AL, (which does not contribute to the enlargement of migration area but to the existence probability), is not negligible. The insets in the upper diagram of Fig. 3 show typical migration traces of adatom random-walks and the lower diagram shows three dimensional views of a 6 ML Ag cluster distribution for $\Delta E = 0.045$ eV (**a**), 0.060 eV (**b**), and 0.100 eV (**c**) respectively.

a is the shortest AL sample. The mean AL is 17.1 t $\sim 6.41 \times 10^{-3}$ s and the mean migration area is 0.41 nm². This shows that a large number of Ag NCs with the VW growth mode is observed only in high deposition regions and that the NCs tend to grow in the direction of deposition. Ag accumulation therefore strongly enhances the small surface topography variation.

The parameters corresponding to Fig. 3 **b** give the best fitting to the SEM picture.

These are the same as in Fig. 2 (e) with a different random number seed. The mean AL is 30.6 t \sim 1.15 \times 10⁻² s and the mean migration area is 0.62 nm². Nucleations occur frequently in the peak deposition region and coalescence of NCs is promoted there. **c** is the longest AL sample and here the mean AL and migration area are 143.6 t \sim 5.39 \times 10⁻² s and 2.14 nm² respectively. Nucleations occur everywhere on the substrate and the distribution of Ag NCs follows closely the local flux distribution shown in Fig. 2 (c). The sticking probabilities of **a**, **b** and **c** are 0.18, 0.35 and 0.82 respectively.

These results predict that the type of NC growth can be tuned by controlling the substrate temperature, the incident angle and flux to promote an effective coalescence along the surface topography due to the AL of metal adatoms. Indeed, for Co, which possesses a much higher adsorption energy to v-SiO₂ than of Ag, we observed selective nucleation of type **b** after heating pre-patterned substrates up to 1200 K, while overall nucleations similar to type **c** were observed at RT. Under a high flux the tendency of nucleations shifts **a** \rightarrow **b**, **b** \rightarrow **c** and vice versa. From the graph of Fig. 3, a linear flux dependency of nucleation pattern is expected for a long AL while a striking amplification of the underlying surface topography is observed for a short AL.

In summary, we have reproduced experimentally observed Ag NCs grown on rippled templates by the introduction of a new type of KMC simulation method, the RB-KMC method. The coalescence of NCs is promoted mainly in high flux regions and less nucleation occurs in low flux regions due to re-evaporation from the substrate. Contrary to traditional belief, millisecond order lifetimes, and \approx 1 nm square surface migration ranges of Ag adatoms can trigger metal nucleations even on defect free surfaces. The nucleation density is influenced strongly by the AL of metal adatoms on templates as well as the flux, especially for a short AL and the amplification of the initial pre-patterned surface is drastically pronounced in a certain low flux regime.

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