Molecular dynamics simulation of metal nanoislands growth

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Abstract. We present the atomistic model and the simulation of a self-assembled growth of a silver nanoisland film and small groups of nanoislands on a glass substrate after thermal poling of the glass with a profiled electrode. The calculations were performed in molecular dynamics simulator LAMMPS taking into account the diffusion of the metal atoms towards and along the glass surface and their clustering. Lennard-Jones potential was used to describe metal-metal and metal-glass interaction. The potential parameters were determined to provide qualitative coincidence of the simulated configurations of the metal nanostructures and the experimental ones, such as an isolated nanoisland, a pair and a set of three nanoislands and a “plasmonic molecule”.

1. Introduction

Metal nanostructures such as a nanoisland film and small groups of metal nanoislands are in particular of interest for optics due to wide applications of surface plasmon resonance (SPR) phenomenon. The SPR excitation at the resonant wavelength results in an effective absorption of the corresponding electromagnetic wave and high enhancement of local electric field nearby metal surface [1]. These optical properties of metal films have been employed in surface-enhanced Raman spectroscopy [2] providing 8-9 orders of magnitude enhancement, biosensing [3], photovoltaics [4], and photocatalysis [5].

One of the perspective ways of nanoisland film fabrication is an out-diffusion of reduced silver and self-assembled growth of silver nanoislands on the surface of a silver-to-sodium ion-exchanged glass [6]. Moreover, modulation of silver ions distribution within the glass via an additional thermal poling treatment with a profiled anodic electrode allows fabricating isolated nanostructures [7]. Optical properties of the isolated nanostructures highly depend on their size and morphology including spatial configuration of small groups of the nanoislands. Hence, understanding of nanoisland growth mechanisms would allow one to control the morphology and resonant characteristics of fabricated structure [8]. It is hard to deduce the final configuration of the nanostructures with an analytical approach, especially in case of non-uniform initial silver distribution in glass; therefore, we used a molecular dynamics simulation, which allows simulating nanoislands growth on the base of interparticle interactions calculations.
2. Object and model
An effective technique of the isolated nanostructures fabrication has recently been reported [7, 9]. A soda-lime glass slide is processed in following sequence: an enrichment of glass subsurface layer with silver ions by ion-exchange in AgNO$_3$/NaNO$_3$ melt, a modulation of silver ions distribution with a profiled anodic electrode (“thermal poling”) under DC field and annealing in hydrogen atmosphere resulted in silver clustering in the glass bulk and nanoisland formation on the surface. The mode of annealing and the pattern of the electrode, which in our case is a net of square and rectangular hollows, determine a configuration of nanoisland groups [9]. The silver shifted to the glass bulk in the region of contact glass-electrode (“poled region”) cannot reach the surface in the course of annealing contrary to non-poled areas under hollows in the electrode. Thus, the formation of silver nanoislands appears in non-poled regions only. The annealing in reducing atmosphere along with the ion exchange of the glass is a way to fabricate a self-assembled nanoisland film with randomly distributed nanoislands [6]. We used molecular dynamics method to simulate formation of the nanoislands and determine the set of parameters, which provide a qualitative match of simulated configurations with the experimental ones, registered with atomic force microscopy (AFM) and presented in Ref. 10.

3. Molecular Dynamics
Molecular dynamics is a computer simulation method for studying physical movements of atoms and molecules. The particles are allowed to interact for a fixed period giving a view of the dynamical evolution of the system. Trajectories of the atoms are determined by numerical solving of Newton’s equations of motion for a system of interacting particles. The forces between the particles and their potential energies are calculated using interatomic potentials. We used molecular dynamics simulator LAMMPS [11] for calculations and atomistic simulation data visualizer OVITO [12] to render the system configuration at a certain time step.

We simulated diffusion of reduced silver atoms along the surface of the glass and their clustering into nanoislands by depositing a fixed flux of $N$ number of neutral atoms on an $L$ x $W$ immobile substrate surface. This is valid for early stages of nanoislands growth, when the majority of reduced silver atoms comes to free surface of the glass, not to already formed nanoislands. All atomic interactions were approximated by a standard 12/6 Lennard-Jones (LJ) potential but its parameters (bond energy, $\epsilon$, and zero-crossing distance, $\sigma$) were determined considering different strength of interaction silver with silver / fused quartz (the poled region of the glass [14,15]) / non-poled glass. We established LJ potential parameters of the substrate atoms interaction as reference value (1, 1) to reduce the number of unknown parameters of the system, and performed all calculations in LJ units system for convenience. Thus, one can restore real bond energy and zero-crossing distance from the scaled values. A Langevin thermostat was applied to the system for temperature control, generic system trajectory was consistent with the microcanonical ensemble. If an atom approached the substrate borderline, it was removed from further computations.

![Figure 1. Initial configuration of the modeled system “Ag atoms – poled glass – non-poled glass”.](image)
For the simulation of the thermal poling, we limited the area of silver atoms deposition to the $L_1 \times L_2$ non-poled region in the center of the poled substrate (see Figure 1). The flux density corresponded to analytically calculated one appeared after the thermal poling with the profiled electrode [10]. We varied $(L_1, L_2)$ pair to obtain different possible configurations of the isolated nanostructures, such as a nanoisland, a pair, a set of three nanoislands and a “plasmonic molecule” [13].

It should be noted that a typical diameter of an isolated nanoisland is $\sim 100$ nm, which corresponds to $\sim 50$ million of atoms in case of, e.g. hemispherical nanoisland. Thus, we had to make scaling to reduce computation time and simulate nanoislands consisted of $\sim 1000$ atoms only instead of a real number of the atoms.

4. Results and discussion

4.1. Nanoisland structures

The parameters of Ag – Ag and Ag – non-poled glass interactions were established to provide formation of randomly distributed nanoisland film under uniform flux of silver atoms. The image of simulated film is presented in Figure 2 together with the scanning electron microscopy (SEM) image of a typical nanoisland film grown by the out-diffusion technique.

![Figure 2. A spatial configuration of a simulated film (left) and SEM image (right) of a nanoisland film grown by out-diffusion technique.](image)

We started with spatially modulated silver flux density according to the analytical model to simulate the formation of isolated nanostructures in course of thermal poling treatment of ion-exchanged glass. However, simple introduction of concentration gradient in the simulation did not result in the appearance of individual nanostructures, whereas the addition of slight difference in surface tension at the interfaces silver – non-poled and silver – poled glass resulted in matching calculated nanoisland configurations with ones experimentally observed. Difference in LJ potential parameters of Ag – poled glass and Ag – non-poled glass interactions is illustrated in Table 1.

|          | Ag – Ag | Ag – non-poled glass | Ag – poled glass | glass – glass |
|----------|---------|----------------------|-----------------|---------------|
| $\varepsilon$ | 2.25    | 2.1                  | 2.0             | 1             |
| $\sigma$   | 0.95    | 0.945                | 0.9             | 1             |

The selection of parameters was based on the best statistics of qualitative coincidence of simulated nanostructures and experimental nanoisland configurations. Deviations of $\varepsilon$ about 0.1 and $\sigma$ about 0.01
resulted in essential disagreement of these configurations. Unfortunately, direct comparison of the values from Table 1 with literary data is hardly possible because of the shortage of information concerning Ag – glass and Ag – poled glass (fused quartz) interaction potentials. Nevertheless slightly stronger interaction of silver with multicomponent glass than with silica follows from earlier performed diffusion and wetting experiments, and this corresponds to the established relation of LJ parameters.

The set of parameters allowed simulating plasmonic structures, such as an isolated nanoisland, a pair and a set of three nanoislands. Spatial configurations of the nanostructures strongly depend on the aspect ratio of width to height of the hollow in the profiled electrode, and the simulations were in coincidence with the experimental results for the same aspect ratios, as it is shown in Figure 3.

![Figure 3](image)

**Figure 3.** Experimental (top row) and simulated (bottom row) spatial configurations of small group of nanoislands: (a) an isolated nanoisland, (b) a pair of nanoislands and (c) a set of three nanoislands. The dashed outlines correspond to the non-poled regions of the glass.

When the size of the square hollow in the electrode was slightly less than one micron, the nanoparticles tended to grow along the perimeter of the non-poled region on the glass [13]. The same behaviour was observed in the simulations (Figure 4). The atoms that diffused to the glass surface at the very end of the annealing rapidly lost kinetic energy, became low-mobile, and were not able to reach nanoislands placed along the perimeter. These atoms formed smaller clusters in the center of the non-poled glass region.

![Figure 4](image)

**Figure 4.** The AFM image (left) and simulated spatial configuration (right) of “plasmonic molecule”.
Statistically 60% of simulations with specified LJ potential parameters but varied initial spatial
distribution of silver atoms resulted in the formation of certain configuration (an isolated nanoisland,
two and more nanoislands etc.). A similar statistic is observed in the experimental data.

4.2. Dynamical evolution of the system
Molecular dynamics simulation gives one an opportunity to investigate time evolution of the
nanoislands formation and growth. During the annealing of an ion-exchanged glass atoms diffuse
according to the concentration gradient, hence they move towards the boundaries of the non-polled
region of the glass, where clustering into nanoislands occurs (Figure 5a, 5b). While annealed glass is
being cooled at the end of the process (the income silver atoms flux is null), individual atoms join the
closest nanoparticle along the perimeter of the non-polled region, thus final configuration includes
mainly atom clusters and is almost free of single atoms (see Figure 5c). Simulation of the cooling
process corresponds to a sample cooling at room temperature after it has been pulled out from the
annealing setup. Typically, the annealing treatment lasts 10 minutes and the cooling time is about 5-8
minutes. The optimal simulation cooling duration is about 50% of the annealing time. The slight
difference may be explained by the difference in silver atoms fluxes: the flux is immediately reset to
zero after the simulation cooling begin, while the flux slowly fades in course of the real cooling.

![Figure 5](image-url)

**Figure 5.** Dynamical evolution of the simulated system “Ag atoms – poled glass – non-polled glass”.

It is worth to note that in the simulation we used number of atoms about five orders of magnitude less
than the real quantity of atoms in a nanoparticle. Thus modeled structures, being similar with
experimental ones differs with the latter in both temporal and spatial scale.

5. Conclusion
The processes of the formation of silver nanoisland film and their groups under the annealing of an
ion-exchanged glass in hydrogen atmosphere were studied and simulated by means of molecular
dynamics. Spatial configurations of the nanoisland films grown under a given set of experimental
conditions were analyzed, and corresponding parameters of the silver-glass interaction potential,
which provide qualitative reproducing of experimentally observed configurations of the
nanostructures, were revealed. Temporal evolution of the silver distribution on the surface of the glass
during annealing was studied. We studied and simulated specific nanostructures grown on the glass
surface after thermal poling with the profiled electrode: the isolated nanoisland, the pair, the set of
three nanoislands and the “plasmonic molecule”. The simulation showed good qualitative agreement
with experimental data.
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