



# Controlled growth of uniform silver clusters on HOPG

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## Abstract

We have investigated growth of silver clusters on three different, i.e. normally cleaved, thermally oxidized and Ar<sup>+</sup> ion sputtered highly oriented pyrolytic graphite (HOPG), surfaces. Scanning tunneling microscopy (STM) observations reveal that uniformly sized and spaced Ag clusters only form on the sputtered surface. Ar<sup>+</sup> sputtering introduces relatively uniform surface defects compared to other methods. These defects are found to serve as preferential sites for Ag cluster nucleation, which leads to the formation of uniform clusters.

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## 1. Introduction

Ag clusters have many unique characteristics such as fluorescence and enhanced Raman scattering [1,2]. A single Ag cluster formed by thermal vacuum evaporation exhibits fluorescence in visible light region under either blue (450–480 nm) or green (510–550 nm) light excitation [1]. When irradiated with fluorescent light, spherical Ag particles can reform into triangular nano-prisms, which could be used for multicolor diagnostic labeling [2]. In terms of its easy preparation, stable

and well-defined structure, as well as its weak interactions with metals, highly oriented pyrolytic graphite (HOPG) surface has been extensively used as substrate for growth of Ag clusters (particles) from different forms of Ag [3–8], as driven by their great application potential in industrial chemical catalysis.

In most vapor deposition methods, Ag growth on HOPG usually proceeds via the three-dimensional Volmer–Weber mode, as established by STM [3,5,6,10] and SEM [4] observations, and by molecular dynamics simulations [9]. Small clusters are nucleated randomly on the substrate and then coalesced into large islands, due to high mobility of Ag atoms and stronger interaction among them (compared to the Ag–substrate interaction). If the

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terraces are wide enough, cluster grouping could happen which creates small irregularly shaped groups of clusters. To avoid these problems, low-temperature growth technique was also tested, but this usually leads to some fractal patterns [6]. The situation is further complicated by presence of surface steps. Ag clusters were observed to preferentially nucleate at the steps with high reactivity. The reduced mobility along the steps could suppress the cluster coalescence, providing a promising way to achieve uniform clusters. However, steps of different heights have different electronic properties, and thus affect the size uniformity of clusters [4]. Under this context, control of surface steps and structure becomes very crucial for achieving uniform and high-density Ag clusters on HOPG.

In this work, we modified the HOPG surface by either thermal oxidizing or  $\text{Ar}^+$  sputtering, and tried to improve the size uniformity of nanoclusters on it. The surface oxidation in air creates overlapping pits, and the majority of Ag clusters nucleates at the boundaries of the pits. Since it is difficult to control the diameter and depth of these pits, the obtained Ag clusters are not evenly spaced. On the other hand, the  $\text{Ar}^+$  sputtering produces fairly uniform defects for nucleation of Ag clusters, leading to formation of narrow-sized Ag clusters.

## 2. Experimental details

The experiments, except for the oxidation process, were performed in an ultrahigh vacuum system (the base pressure  $< 1.0 \times 10^{-10}$  mbar) where a Park STM chamber and a preparation chamber are housed. HOPG samples were cleaved with adhesive tape and immediately loaded into the preparation chamber. Sample oxidation was done in air at  $750^\circ\text{C}$ .  $\text{Ar}^+$  bombardment was performed in the preparation chamber with an Ar pressure of  $5.0 \times 10^{-5}$  mbar and an ion energy of 1.5 keV. During the sputtering, the angle and distance between the  $\text{Ar}^+$  beam and sample surface were approximately  $70^\circ$  and 10 cm, respectively.

Ag (99.999%) was evaporated from a tantalum boat at a rate of  $\sim 0.25$  ML/s onto the HOPG

substrate at room temperature. During deposition, the chamber pressure was kept below  $1.0 \times 10^{-9}$  mbar. Surface morphology before and after Ag deposition was examined by STM in the constant current mode at room temperature. The typical tunneling current was 1 nA and the sample bias was 1 V. The tungsten STM tip was prepared by electrochemical etching in a 5 M KOH solution.

## 3. Results and discussion

### 3.1. Ag growth on flat HOPG

The nucleation and growth of Ag on flat HOPG have been reported before [4,6]. The steps were found to act as effective sinks, and the Ag clusters form quasi-one-dimensional chains along steps. With increasing coverage, clusters diffuse across the surface and coalesce to small stable islands on terraces [6].

In our experiment, both fractal and compact Ag clusters were observed, depending on the depositing rates. At low deposition rate, quasi-one-dimensional Ag cluster chains form along steps, while fractal islands form on terraces, probably due to increasing diffusion length of Ag adatoms on the HOPG terraces [6,10]. On the other hand, high depositing rate leads to compact Ag clusters. This is not surprising since the island density is proportional to the flux-to-mobility ratio [11]. That is, the probability for two mobile particles to meet and nucleate a new island increases, and the effect of steps becomes relatively insignificant at high depositing rate.

### 3.2. Ag growth on oxidized HOPG

Reaction of  $\text{O}_2$  with HOPG induces oxidation pits, and creates many steps on the surface [12]. Fig. 1(a) shows a typical STM image of the surface after oxidization at  $750^\circ\text{C}$  for 2 min. We can clearly observe that multiplayer etching takes place and annular pits with diameters from a few nanometers to several hundred nanometers are created on the terraces. The step heights alongside the pits are  $\sim 3$ – $4$  nm. During the etching process,

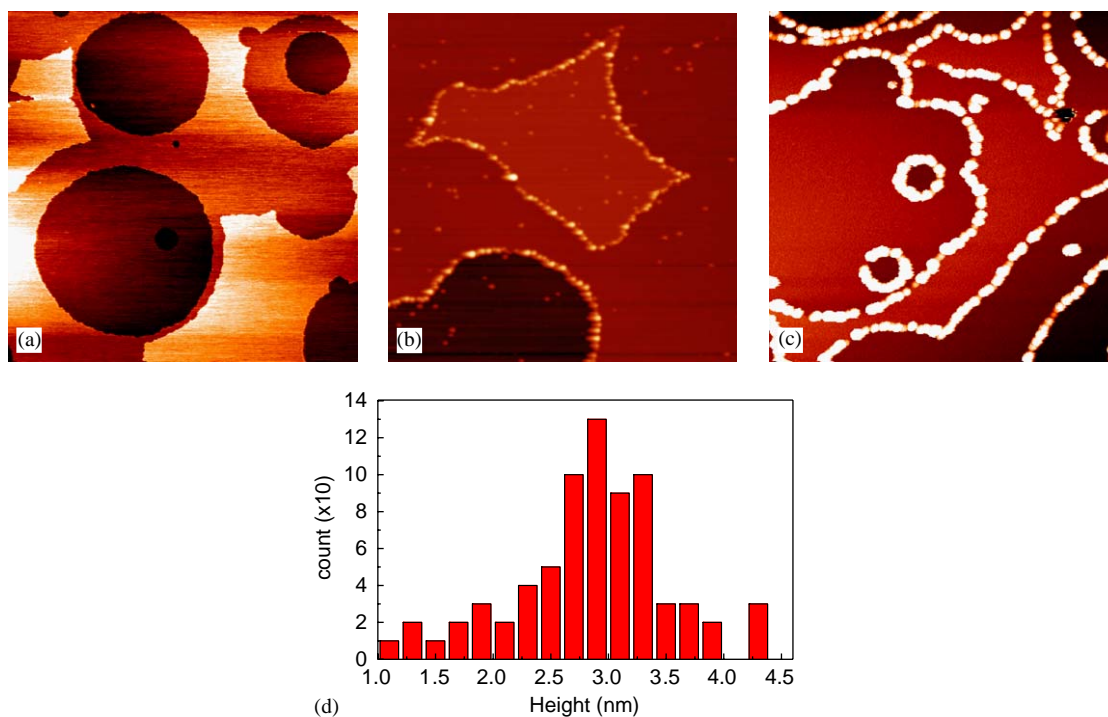


Fig. 1. STM images of the HOPG surface after (a) ( $1\ \mu\text{m} \times 1\ \mu\text{m}$ ) oxidation at  $750\ ^\circ\text{C}$  for 2 min, (b) 0.8 ML Ag deposition on the oxidized surface ( $500\ \text{nm} \times 500\ \text{nm}$ ), and (c) ( $1\ \mu\text{m} \times 1\ \mu\text{m}$ ) 0.8 ML Ag deposition on the oxidized HOPG with additional annealing at  $60\ ^\circ\text{C}$  for 7 min. (d) the height distribution histogram of the Ag clusters shown in (c).

$\text{O}_2$  molecules exothermally dissociate and chemisorb at the top or bridge site of a vacancy, or form a precursor state of molecular oxygen at the bridge site. CO and  $\text{CO}_2$  are produced by thermal activated reaction between the dissociated  $\text{O}_2$  molecules and some hydrocarbons in air, and are desorbed from the surface, producing surface atomic vacancies [13].

After deposition of 0.8 ML silver on the oxidized HOPG, clusters form. Majority of the clusters appears near the edge of the pits, with very few on the flat terraces (see Fig. 1(b)). Annealing at  $60\ ^\circ\text{C}$  for several minutes not only improves the size uniformity of the clusters, but also removes the clusters on the terraces via cluster diffusion and/or desorption, as seen in Fig. 1(c). Because the clusters are of spherical in nature, to remove the tip convolution effect we used the cluster heights rather than cluster diameters for size measurement of the clusters [14]. Fig. 1(d) shows the height

distribution of the clusters. A very broad size distribution is observed, which is most likely caused by different heights of the pit steps. Regardless of some size uniformity improvement by annealing, it is difficult to achieve high-density clusters on the oxidized surface due to the preferential nucleation at the pit edges.

### 3.3. Ag growth on $\text{Ar}^+$ sputtered HOPG

Ion bombardment can create protrusions on the HOPG surface, and these defects might act as nucleating sites in the subsequent deposition process [15,16]. We modified the HOPG surface by  $\text{Ar}^+$  sputtering. Figs. 2(a) and (b), respectively, show the STM image and the corresponding line profile of the HOPG surface after  $\text{Ar}^+$  sputtering. Uniform protrusions with height of  $0.33 \pm 0.13\ \text{nm}$  are formed on the surface. The surface root mean square roughness is about  $0.095\ \text{nm}$ . Figs. 2(c), (e)

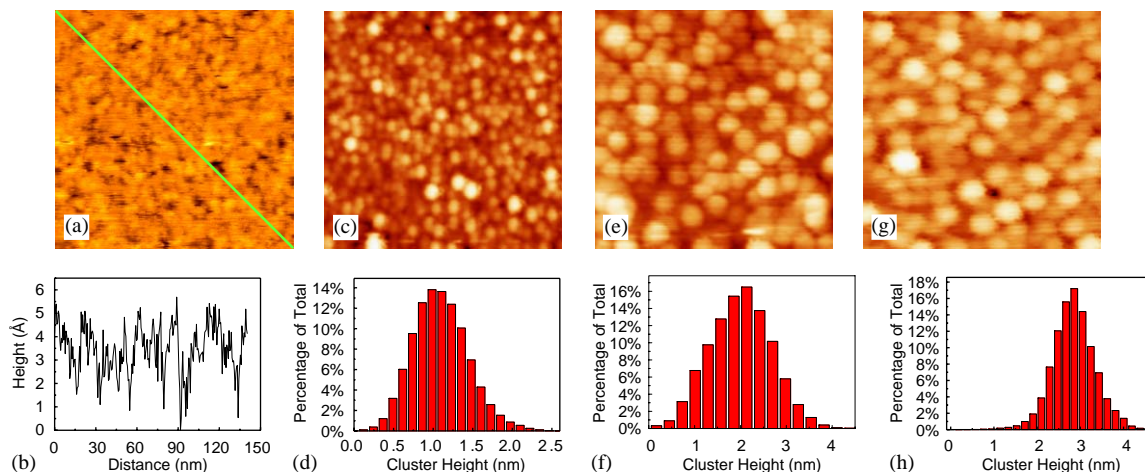


Fig. 2. (a) and (b) the topographic STM image and the corresponding line profile of the HOPG surface after  $\text{Ar}^+$  sputtering. (c), (e) and (g) the STM topographic images ( $100 \text{ nm} \times 100 \text{ nm}$ ) of the sputtered HOPG surface deposited with 2.5 ML, 5 ML and 7.5 ML Ag, respectively. (d), (f) and (h) are the corresponding height distribution histograms.

and (g) show the surface morphologies after 2.5, 5 and 7.5 ML Ag deposition, respectively. The corresponding histograms of cluster height distribution are shown in Figs. 2(d), (f) and (h). There is an overall trend of increasing size (from 1.1 to 2.9 nm) with increasing coverage. It can be clearly seen that most clusters appear spherical and are of uniform size.

It is known that cluster nucleation and diffusion often depend on intrinsic or extrinsic surface defects. For example, previous experimental studies have revealed that for Cu deposited on the  $\text{Ar}^+$  sputtered HOPG surface, both average size and density of the Cu clusters were well correlated with the surface defect density. The nucleation of Cu clusters takes place at these defect sites, and the Cu clusters must overcome an energy barrier to diffuse and coalesce. This energy barrier was influenced by the interaction between cluster and substrate surface and strongly depends on the surface defect density [17].

In our case, the uniformly distributed defects induced by  $\text{Ar}^+$  sputtering act as the nucleation centers and limit the diffusion of initially formed Ag clusters. The high-density and uniform distribution of defects increase the nucleation density and overrule the tendency to preferential nucleation at steps, leading to a high island density and

small island size. With increasing Ag coverage some islands grow larger at expense of some others, namely, “Ostwald ripening” [18] takes place. The surviving islands whose sizes are beyond the critical island size continue to grow with increasing coverage. Therefore, when the formation of Ag at the initial stage is closely correlated with the surface defects, the increased cluster size at higher coverage should be a result of the Ostwald ripening. Compared with previous study [4], the clusters obtained with our method are more uniformly spaced and sized. Such high-density and uniform clusters not only make them promising for applications, but also enable us study their properties by macroscopic techniques such as Raman spectroscopy.

#### 4. Summary

We have investigated growth of Ag clusters on flat, oxidized and sputtered HOPG surfaces by using STM. High-density and uniform clusters are obtained on the  $\text{Ar}^+$  sputtered surfaces. The results consistently demonstrate that due to the inert nature of the graphite surface, the surface defects and steps play the most important role in formation of Ag clusters/islands.

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