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Hard and soft landing of mass selected Ag clusters on Pt(111)

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Abstract

Mass selected Ag_n clusters ($n=1,7,19$) from a secondary ion source have been deposited onto a Pt(111) substrate at low temperature. The surface and resulting cluster morphology have subsequently been characterized within the same UHV chamber by variable temperature STM as a function of cluster size, kinetic impact energy, and substrate temperature. The kinetic energy per cluster atom was found to be the decisive parameter for a controlled deposition. Noble gas buffer layers (≈ 10 ML Ar), which were pre-adsorbed onto the surface at low temperatures, were found to efficiently dissipate the impact energy opening up the possibility of soft landing clusters with elevated kinetic energy.

Keywords: Clusters; Epitaxy; Low index single crystal surfaces; Platinum; Scanning tunneling microscopy; Silver; Surface structure, morphology, roughness, and topography

1. Introduction

A central goal in nanostructuring of surfaces is the creation of well defined island populations. In molecular beam epitaxy (MBE), the standard growth technique for nanosized features on crystal surfaces, the island nucleation- and growth process is basically determined by statistic events. This yields island populations with relatively large size distributions [1]. A promising alternative is the deposition of size selected nanoclusters [2–10]. One can hope that the aggregates which form upon deposition of such objects from the gas phase will maintain their sharp size distribution. In a normal cluster deposition experiment, however, the energy which is released during the impact is sufficient to disintegrate at least parts of the clus-

ters or to create even substrate damage or implantation. One has thus to ensure a nondestructive soft landing in order to ensure that the nanoclusters maintain their individual characteristics. A promising way to do so has been proposed by Cheng and Landman [11] who studied in detail the deposition dynamics of Cu nanoclusters on Cu(111) by molecular-dynamics simulations and predicted controlled soft landing via energy dissipation in a rare gas buffer layer. We performed the first in situ STM study to test this important prediction.

2. Experimental

The experiments were performed with a variable temperature STM operating in UHV (Fig. 1). The accessible temperature range for in situ

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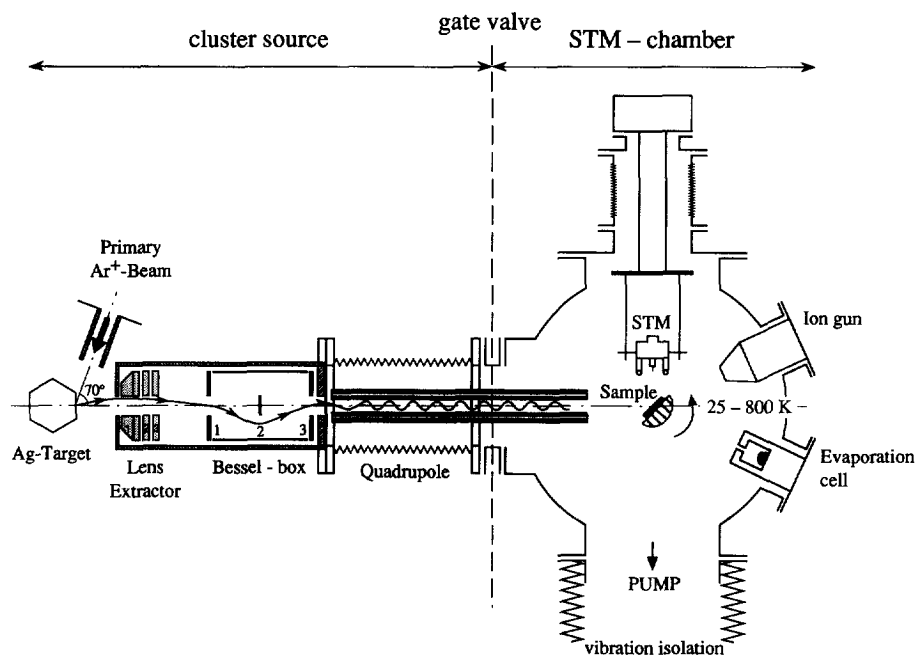


Fig. 1. The setup of the cluster deposition experiment consists of two UHV chambers which are separated by a gate valve. The Ag clusters are produced by sputtering of a Ag target. The charged clusters pass two differential pumping stages (not shown in the image), a Bessel-box (energy filter) and a quadrupole mass filter in which only clusters of a selected mass are transported to the sample. After deposition of the clusters onto the Pt(111) crystal the resulting structures can be examined by variable temperature STM.

measurements is 25–800 K [12]. The size-selected Ag_n clusters are produced by sputtering in a differentially pumped secondary ion cluster source with quadrupole mass separation [7], which is directly attached to the STM chamber. Particular attention has been paid to provide ultraclean deposition conditions; during deposition the non-rare gas background pressure stays in the 10^{-10} mbar range. Cluster current densities are on the order of several 10^{11} atoms $\text{cm}^{-2} \text{s}^{-1}$; i.e. the equivalent of 0.1 atomic monolayer (ML) is deposited in about 10 min. All STM images have been measured in constant current mode.

In the experiments the size-selected silver clusters were deposited either onto the bare Pt(111) surface at 80 or 90 K or into a pre-adsorbed Ar buffer layer at $T \approx 25$ K. Immediately after deposition the surface was imaged by STM at $T = 80\text{--}90$ K. At this temperature the Ar layers have desorbed, and the clusters can be imaged on the Pt crystal. Further, at this low temperature, silver dimers and larger clusters are stable on the Pt(111) surface

[13]. This ensures to measure the surface as it evolves in the deposition process. The surface morphology is then further followed in situ as a function of temperature in annealing experiments.

3. Results and discussion

A useful reference for the cluster deposition experiment is the MBE growth of Ag on a Pt(111) substrate under otherwise identical conditions (i.e. deposition flux, coverage, and sample temperature having the same values). In such an experiment single Ag atoms with thermal energies (i.e. ≈ 0.2 eV) are deposited onto the substrate. The corresponding result of the thermal growth of 0.1 monolayers (ML) of Ag on Pt(111) at 80 K is shown in Fig. 2a. Small ramified Ag clusters of monoatomic height are formed in a nucleation and aggregation process which has been analyzed in detail in Refs. [13,14]. The average island size is ≈ 100 atoms and the distribution of island sizes

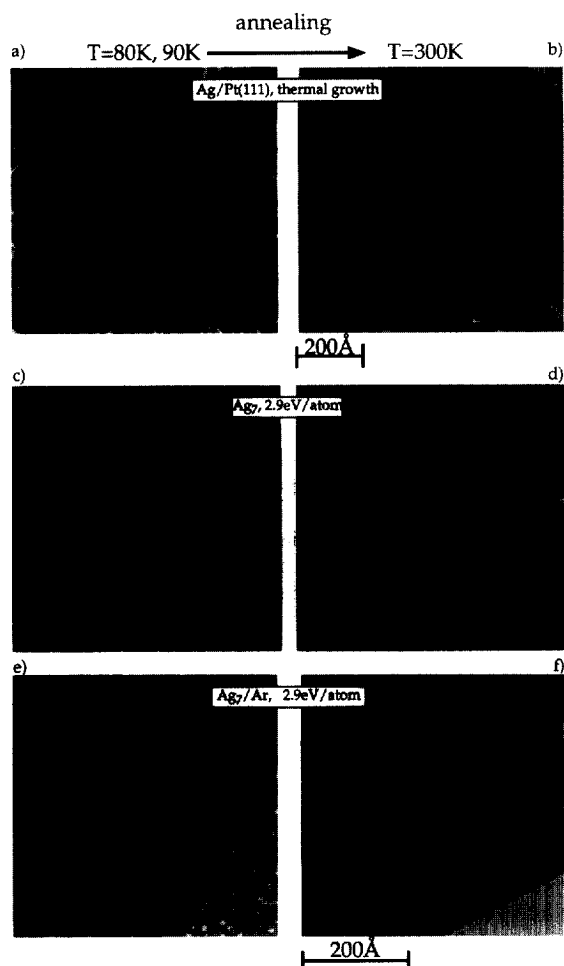


Fig. 2. (a) Growth of ramified Ag clusters upon deposition of thermal Ag atoms onto Pt(111) at 80 K. Coverage $\theta = 0.1$ ML, deposition flux $R = 2 \times 10^{-5}$ ML s^{-1} . (b) The MBE grown Ag islands decay by Ostwald ripening upon annealing to 300 K. The deposited material condenses at the pre-existent Pt substrate step edges and manifests itself as a bright rim. (c) Deposition of Ag_7 clusters on the bare Pt(111) crystal. Despite similar deposition flux, coverage and substrate temperature as in (a), the resulting morphology is remarkably different. Compact Ag islands are imaged at low temperature. (d) After annealing to room temperature still some islands are found on the Pt(111) terraces. This indicates that surface defects were created during the deposition process which now stabilize the islands against thermal decay. (e) Cluster deposition under the same conditions as in (c), but at $T = 25$ K into a 10 ML thick Ar buffer layer which was pre-adsorbed on the Pt crystal. The size distribution of the resulting islands becomes much sharper. Further, the buffer layer protects the crystal surface against sputter damage induced by the cluster deposition process. No pinning centers are found in the annealing experiment (f).

shows the expected scaling [1] with a rather large normalized standard deviation of $\sigma^* = 0.55$. Here, $\sigma^* = \sigma / \langle s \rangle$ is defined as the standard deviation over all island areas, normalized to the mean island area. These islands, being stable at 80 K (only Ag adatoms are mobile at 80 K and Ag dimers on Pt(111) start to decay only at 110 K [13]), decay due to Ostwald ripening upon annealing to 300 K, and the Ag condenses at pre-existent Pt step edges, leaving behind clean substrate terraces [15] (Fig. 2b).

The aggregates which form after deposition of size-selected nanoclusters show remarkably different structures, exhibiting compact forms (Figs. 2c and e). Interestingly, the islands created by deposition of three-dimensional (3D) clusters are always observed to be two-dimensional (2D) on the surface, i.e. of monoatomic height. This transition necessarily implies that the 2D structure is energetically favored, which can be rationalized on hand of simple bond counting arguments. A Ag_7 cluster (pentagonal bipyramid) oriented with 3 atoms towards the Pt substrate can at most have 15 Ag–Ag and 9 Ag–Pt bonds. A close packed 2D heptamer has 12 Ag–Ag and 21 Ag–Pt bonds, which obviously has a lower total energy. This simple picture is corroborated by effective-medium calculations [16]. We calculate an energy difference of 2.7 eV in favor of the flat 2D Ag-heptamer in the above system $Ag_7/Pt(111)$. Further, this transition is hardly kinetically hindered for small clusters. In the calculations the energy of adsorption is sufficient as activation energy since this transformation takes place at 0 K for clusters with zero kinetic energy.

In a real deposition experiment, the kinetic energy released during the impact might cause cluster fragmentation or substrate damage. These effects occur indeed for the “harder” landing conditions investigated. After the low-temperature ($T = 80$ K) deposition of Ag_7 clusters with an impact energy of 20 eV, i.e. 2.9 eV per atom, and subsequent annealing to 300 K, there are still small islands found on the terraces (Fig. 2d). As explained above, small MBE-grown Ag islands on Pt(111) decay under these conditions. Hence, the cluster deposition process must have created surface defects which now act as pinning centers for

the diffusing atoms up to temperatures of 300 K. It is likely that these defects are either Pt adatoms or Ag substitutional atoms in the substrate which are created in an exchange process during the energetic impact. The density of the pinning centers was found to increase with the kinetic energy per atom of the impinging clusters, saturating at about one pinning center per 4–6 deposited clusters (in the energy range investigated, i.e. up to 13.6 eV per cluster atom). For Ag₇ clusters with 2.9 eV per atom (Fig. 2d) one pinning center per 10 deposited clusters was created.

The behavior upon annealing of clusters which have been deposited into a Ar buffer layer of about 10 monolayers thickness is very different. Figs. 2e and f show the surface after deposition of Ag₇ with kinetic energy of 20 eV (the same landing conditions as in Figs. 2c and d) into such a layer. The buffer layer was pre-adsorbed on the Pt crystal and the clusters deposited at $T=25$ K. By annealing to $T=90$ K the Ar was desorbed and the surface was imaged at this temperature. Though the clusters are as well two-dimensional (Fig. 2e), they now decay at room temperature (Fig. 2f) like “normal” Ag islands created by MBE growth. This shows that a rare gas buffer layer can indeed protect the surface from defect creation induced by the cluster deposition.

It is now interesting to investigate the effect of the rare gas buffer layer on the clusters themselves. We examined the size distribution of the aggregates which had formed after the low-temperature deposition (Table 1). The width of the size distribution is again characterized by the normalized standard deviation σ^* . As expected, the width of the island size distribution increases with harder landing conditions (i.e. towards higher impact energies per cluster atom), indicating strong fragmentation and reorganization of the deposited material during the landing process. As a direct effect of the Ar buffer, for Ag₇ with $E_{\text{kin}}=20$ eV, the measured σ^* decreases from 0.49 to 0.35 when the clusters are deposited into the gas matrix. The latter value is already substantially influenced by the resolution limit of the STM measurement in which the convolution of the real structure with the STM tip is pictured. For very small structures this convolution error, together with vibrational

Table 1

Analysis of the size distribution of Ag aggregates formed upon low temperature deposition of size selected Ag_n clusters on Pt(111)

Cluster size n	Kinetic energy (eV)	Kinetic energy per cluster atom	Average size	Width σ^*
7	95	13.6	7 ± 2	0.54
19	95	5.0	13 ± 3	0.48
7	20	2.9	8 ± 2	0.49
19	20	1.0	16 ± 4	0.37
Thermal atoms	0.2	0.2	$f(T, \theta)$	0.55
With Ar buffer layer				
7	20	2.9	7 ± 2	0.35

The data are arranged in order of decreasing impact energies per cluster atom. The width σ^* of the size distribution is described by the standard deviation over all island areas, normalized to the average island area. The error in the average island size does not describe the width of the distribution, but the uncertainty of its center position. In the case of MBE-growth, the average island size is a function of temperature and coverage.

disturbances of the STM, results in a different imaging of clusters of same size but dissimilar form and hence increases the relative error of the measurement. In the case of isolated Ag adatoms, deposited at low coverages and at temperatures where diffusion is frozen in ($T=35$ K), $\sigma^*=0.28$ is found. The residual width of $\sigma^*=0.35$ indicates thus a sharp size distribution. The mean island size in the nondestructive landing case corresponds within the experimental error with the number of atoms in the deposited clusters. But even after a hard landing the average island size on the surface equals the original cluster size, and the width of the size distribution is still comparable to a MBE growth experiment. This indicates that under hard landing conditions parts of the clusters stay together in the fragmentation process and act as effective nucleation sites for released adatoms. The overall island density on the surface is thus determined by the number of deposited clusters, yielding a mean island size which equals the number of atoms in the original clusters.

As can be seen in Table 1, for cluster deposition on the bare substrate, there is a trend towards sharper island size distributions when the kinetic

energy per cluster atom is lowered. The width of this distribution after deposition of Ag_{19} with $E_{\text{kin}}=20$ eV becomes nearly as sharp as after deposition into a buffer layer, $\sigma^*=0.37$. Here again, the clusters imaged on the surface at low temperature decay upon annealing to 300 K. This behavior indicates another possibility of a controlled landing of nanosized metallic clusters: If the kinetic energy per cluster atom as the decisive parameter is lowered to ≈ 1 eV per atom the aggregates can be deposited nondestructively even on the bare metallic surface.

4. Conclusion

Our experiments support the hypothesis of a soft landing of nanoclusters via energy dissipation into a rare gas buffer layer. Clusters, which under otherwise identical conditions decay during the deposition process and create substrate defects, could be landed nondestructively by the help of such layers. But it is worth mentioning that the opposite case of a hard landing provides as well interesting potentials for the nanostructuring of surfaces. In our experiment, otherwise thermally unstable structures could be stabilized by the help of just those defects which were created in the violent deposition process.

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