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Variable-temperature scanning tunneling microscopy was used to study the effect of kinetic cluster energy and rare-gas buffer layers on the deposition process of size-selected silver nanoclusters on a platinum(111) surface. Clusters with impact energies of ≤1 electron volt per atom could be landed nondestructively on the bare substrate, whereas at higher kinetic energies fragmentation and substrate damage were observed. Clusters with elevated impact energy could be soft-landed via an argon buffer layer on the platinum substrate, which efficiently dissipated the kinetic energy. Nondestructive cluster deposition represents a promising method to produce monodispersed nanostructures at surfaces.

Nanostructure formation at surfaces has been studied extensively both because of the intrinsic interest in structures with reduced dimensions and because of potential technological applications. The most advanced techniques for the synthesis of nanostructured surfaces are atomic manipulation with scanning-probe methods (*1*, *2*) and self-organized growth (*3*). A promising alternative route is the controlled deposition of nanoclusters from the gas phase (*4*, *5*). The deposition of clusters on a solid substrate is characterized by a number of important physical phenomena. When a cluster impinges on the surface, it must transfer its kinetic energy and the energy of condensation to the substrate crystal lattice to ensure efficient sticking. The energy dissipation depends primarily on the relation between cluster surface and internal cluster binding strength and on the cluster impact energy. At high impact energies, the condensation energy is negligible, and a large amount of energy can be delivered to a localized region of the surface during the collision, resulting in substantial cluster fragmentation, substrate damage, and even implantation. The extreme nonequilibrium conditions in energetic cluster surface collisions have been exploited to grow smooth films at low temperatures (*6*). In contrast, the synthesis of nanostructured surfaces requires low kinetic energies to be released during the impact to ensure a nondestructive deposition in which the nanoclusters maintain their individual characteristics.

Despite considerable recent effort in studying cluster surface interactions (*5*, *7–12*), the effect of the impact parameters on the result of the deposition process has not been characterized in situ on the microscopic scale to date. We now report the investigation of the deposition of size-selected Ag_n clusters (n = 1, 7, and 19) of varying kinetic energy (1 to 14 eV per cluster atom) onto a Pt(111) substrate in ultrahigh vacuum (UHV). Deposition took place either onto the bare surface at 80 or 90 K or into a preadsorbed Ar buffer layer at 26 K, which was subsequently evaporated at 90 K (*13*). The surface and cluster morphologies were characterized in situ in the same UHV chamber by variable-temperature scanning tunneling microscopy (STM) (Fig. 1) before and after annealing to 300 K. Our study was motivated by the hope of obtaining controlled soft landing through

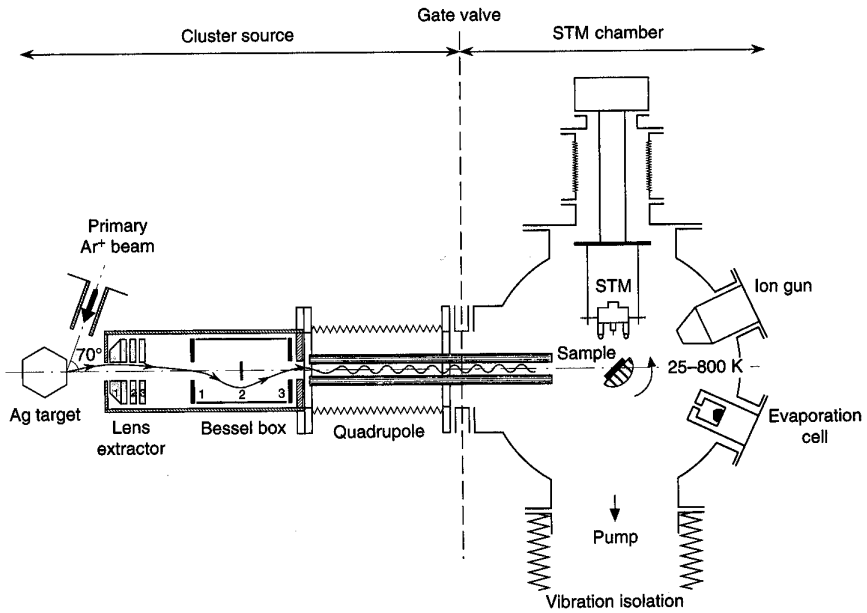

Fig. 1. The apparatus for the cluster deposition experiment consists of two UHV chambers separated by a gate valve. The Ag clusters were produced by sputtering of a Ag target in a differentially pumped secondary ion source, energy-filtered (Bessel box), and mass-selected by a quadrupole (*5*). During deposition, the non–rare gas background pressure was held in the 10^{-10} mbar range. Cluster current densities were on the order of several 10^{11} atoms cm^{-2} s^{-1}, the equivalent to deposition of 0.1 monolayer in about 10 min. After deposition onto the Pt(111) crystal, the resulting structures can be examined by variable-temperature STM (25 to 800 K) (*25*). All STM images were measured in constant-current mode, with a typical tunneling resistance of 10^8 ohm.

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energy dissipation in a rare-gas buffer layer. This possibility was suggested by recent matrix deposition experiments which demonstrated that size-selected Ag clusters codeposited with rare gases do not fragment (*14*, *15*), and by the molecular dynamics simulations of Cheng and Landman (*16*), who studied in detail the deposition dynamics of Cu nanoclusters on bare and rare gas–covered Cu(111).

A useful reference experiment for the cluster deposition is the "thermal" condensation of vapor-deposited Ag atoms onto the clean Pt(111) surface under otherwise identical conditions, that is, a typical molecular beam epitaxy (MBE) experiment. During thermal growth of 0.1 monolayer (ML) of Ag on Pt(111) at 80 K (Fig. 2A), small ramified Ag clusters of monoatomic height were formed in a nucleation and aggregation process that has been analyzed in detail (*17*, *18*). The average island size was ~100 atoms, and the island size distribution showed the expected scaling (*19*) with a rather large normalized standard deviation $\sigma^* = 0.55$. Here, $\sigma^* = \sigma/\langle s \rangle$ is defined as the standard deviation over all island areas, normalized to the mean island area. Upon annealing of the islands to 300 K, the Ag clusters decayed as a result of Ostwald ripening, that is, by vaporization of single atoms from the island edges into a two-dimensional (2D) gas phase, and the Ag condensed at preexistent Pt step edges, leaving behind clean substrate terraces (Fig. 2B) (*20*).

The aggregates that formed after deposition of size-selected nanoclusters showed markedly different structures, exhibiting compact forms (Fig. 3). Further, the islands created by deposition of 3D clusters were always observed to be 2D on the surface, that is, of monoatomic height, implying that the 2D structure is energetically favored. This finding can be rationalized by means of simple bond-counting arguments. For small clusters, a 2D structure permits an increased number of metal-metal bonds (*21*).

In a deposition experiment, the kinetic energy released during the impact might cause even a more substantial reorganization of the atomic structure, which can include cluster fragmentation or substrate

Table 1. Analysis of the size distribution of Ag aggregates formed upon low-temperature deposition of size-selected Ag_n clusters on Pt(111). 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 rather the uncertainty of its center position. In the case of MBE-grown Ag islands, the average island size is a function of temperature and coverage. In the two soft-landing cases, the σ^* values are resolution-limited.

Cluster size n	Kinetic energy (eV)	Kinetic energy per cluster atom	Average size	Width σ^*
		Thermal atoms		
1	0.2	0.2	$f(T, \theta)$	0.55
		Clusters/bare substrate		
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
		Clusters/Ar buffer layer/substrate		
7	20	2.9	7 ± 2	0.35

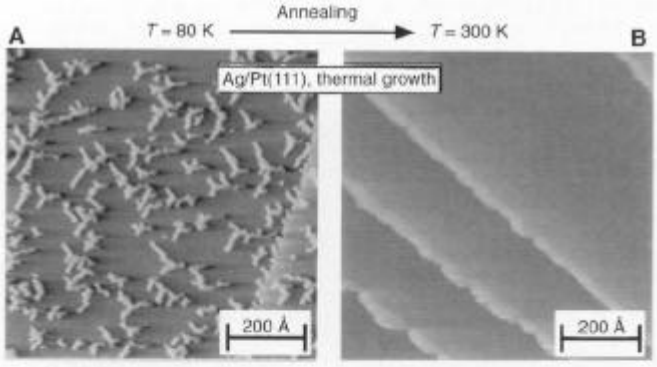
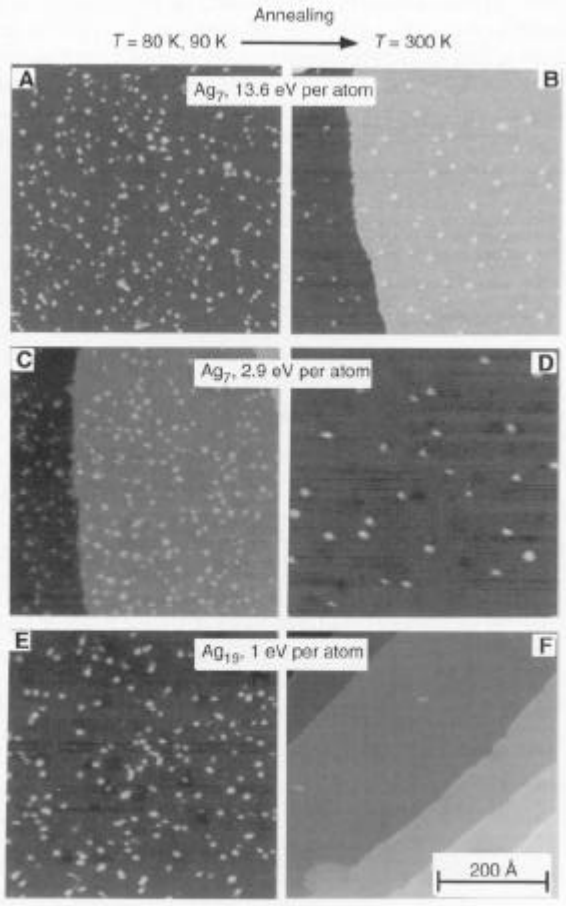


Fig. 2 (left). (**A**) Growth of ramified Ag clusters upon deposition of thermal Ag atoms onto Pt(111) at 80 K. Coverage $\Theta = 0.1$ ML, deposition flux $R = 2 \times 10^{-5}$ ML/s. (**B**) The MBE-grown Ag islands decay by Ostwald ripening upon annealing to 300 K. **Fig. 3 (right).** Destructive and nondestructive deposition of Ag_7 and Ag_{19} clusters at 80 K [90 K for (E)] onto the bare Pt(111) surface. The kinetic energy per cluster atom was 13.6 eV (**A**), 2.9 eV (**C**), and 1 eV (**E**). (**B**, **D**, and **F**) The surfaces after annealing to 300 K. Because of the thermal drift during the annealing procedure, the STM does not picture exactly the same spot. By lowering the kinetic energy of the clusters to 1 eV per atom, the deposition process became nondestructive. The size of all images is 500 Å by 500 Å.



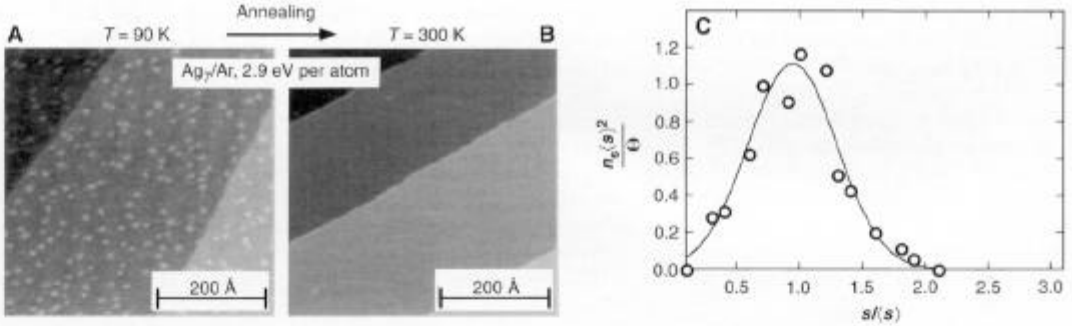


Fig. 4. Soft landing of Ag_7 clusters (2.9 eV per atom) through energy dissipation in an Ar buffer layer (10 ML) on Pt(111) at 26 K. The surface is imaged after desorption of the Ar layer at 90 K (**A**) and after further annealing to 300 K (**B**). (**C**) The normalized island size distribution of the aggregates at 90 K. With n_s being the density of clusters of area s, $\langle s \rangle$ the average cluster area, and Θ the total Ag coverage, $n_s\langle s \rangle^2/\Theta$ is the normalized density of clusters of relative size $s/\langle s \rangle$. The standard deviation σ^* as a fraction of mean island size is 0.35, compared to $\sigma^* = 0.49$ for landing on the bare substrate. The line is a Gaussian fit that serves as a guide to the eye.

damage. These effects were observed for the "harder" landing conditions investigated. After the low-temperature ($T = 80$ K) deposition of Ag_7 clusters onto the bare substrate with an impact energy of 95 eV (that is, 13.6 eV per atom) and subsequent annealing to 300 K, there were still small islands found on the terraces (Fig. 3, A and B). As explained above, small MBE-grown Ag islands on Pt(111) decay under these conditions by Ostwald ripening. Hence, the cluster deposition process must have created surface defects that now act as pinning centers for the diffusing atoms up to temperatures of at least 300 K. It is likely that these defects are either Pt adatoms or Ag substitutional atoms in the substrate that are created in an exchange process during the energetic impact. Above 600 K, Ag forms a surface alloy with the Pt(111) surface (*22*, *23*). Locally, this temperature can be reached upon an energetic cluster 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 four to six deposited clusters in the energy range investigated (that is, up to 13.6 eV per cluster atom). In the case of Ag_7 clusters deposited with 2.9 eV per atom, for example, only one pinning center per ≈10 deposited clusters was created (Fig. 3, C and D). This dependency shows the way toward a nondestructive deposition of clusters onto bare substrates: Lowering the kinetic energy per cluster atom should drive the system toward a soft-landing behavior. Indeed, for Ag_{19} clusters with a kinetic energy of 20 eV (that is ≈1 eV per atom), no pinning centers were found, and all the deposited material had condensed at the step edges of the substrate crystal after annealing to 300 K (Fig. 3, E and F).

The absence of any surface defects does not necessarily imply that the deposition process is nondestructive for the clusters themselves. The released energy might be sufficient to disintegrate the clusters without creating any substrate damage. To investigate this possibility, we examined quantitatively the island size distributions (Table 1). As expected, the normalized width σ^* was sharpest for the nondestructive landing and increased with harder landing conditions, indicating substantial fragmentation during the deposition process in the latter cases. The mean island size in the nondestructive landing case corresponded 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 does not exceed that seen in an MBE-growth experiment. This result indicates that 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.

To study the effect of a rare-gas buffer layer on the deposition process, we compared two similar experiments: the landing of Ag_7 with kinetic energy $E_{kin} = 20$ eV on the clean surface (see above) and via an Ar buffer layer. In the latter case, the clusters were deposited at $T = 26$ K into a preadsorbed Ar layer of about 10 ML (*24*). By subsequent annealing to 90 K, the Ar was desorbed, and the clusters could be imaged on the Pt surface (Fig. 4A). In contrast to the bare substrate case, this landing procedure did not create any pinning centers (Fig. 4B). Furthermore, the small relative width of $\sigma^* = 0.35$ indicates a sharp size distribution (Fig. 4C).

Our experiments illustrate the possibility of soft landing of nanoclusters through energy dissipation into a rare-gas buffer layer. Clusters, which under otherwise identical conditions decay during the deposition process and create substrate defects, were landed nondestructively by the use of such layers. The opposite case of a hard landing also provides interesting potential for the nanostructuring of surfaces. In our experiments, otherwise thermally unstable structures could be stabilized by the use of defects that were created in the violent deposition process.

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