

Building one- and two-dimensional nanostructures by diffusion-controlled aggregation at surfaces

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THE formation of nanometre-scale surface structures by atomic manipulation with the scanning tunnelling microscope has opened up opportunities for creating new metastable states of matter atom by atom¹. The technique allows the fabrication of arbitrary structures, but its application may be limited by considerations of speed, as only one nanostructure can be built at a time. Here we describe the simultaneous formation of many densely packed nanostructures of various morphologies using diffusion-controlled aggregation on surfaces. By exploiting the dependence of the mobility of adsorbed atoms on substrate crystal face and temperature, we are able to grow linear, two-dimensional or tenuous fractal aggregates of nanometre dimensions. The high number density (10^{11} – 10^{14} cm⁻²) of these structures means that their physical and chemical properties can be easily measured with conventional surface spectroscopies.

The deposition of atoms onto a substrate is a non-equilibrium process; the system tries to restore equilibrium by forming aggregates². The adatoms migrate on the surface and when meeting each other they can form critical nuclei, which subsequently can grow to clusters and islands by attachment of further adatoms. Nucleation and growth are competing processes. The outcome of this competition is determined by the surface diffusion (r.m.s. surface area migrated by an adatom in unit time) and the deposition flux (atoms deposited per unit time and unit surface)². The diffusion of an adatom stops when it hits a critical nucleus or a stable aggregate and condenses there. With increasing coverage, the density of stable nuclei increases until a saturation density is reached. After this, impinging atoms condense solely at existing aggregates. At this stage they are migrating the

average distance Λ_a . The average adatom diffusion length is temperature (and flux)-dependent. At low temperatures Λ_a is small, a high density of stable nuclei is formed and small clusters grow. With increasing temperature Λ_a increases, the saturation island density decreases and larger aggregates can grow. The shape of these aggregates is determined both by the directional anisotropy of Λ_a and by the average diffusion length of atoms adsorbed at the perimeter of the aggregate Λ_1 (refs 3, 4). At low temperatures $\Lambda_1 \approx 0$, that is, atoms attaching to an aggregate stick where they hit (the usual assumption in diffusion limited aggregation (DLA) simulations³). At elevated temperatures, however, atoms adsorbed on the edge of the aggregate can continue to migrate around the perimeter, that is $\Lambda_1 \gg 0$. Here we will demonstrate that by means of temperature control of Λ_a and Λ_1 , the size and shape of the aggregates formed can be manipulated specifically on an atomic level.

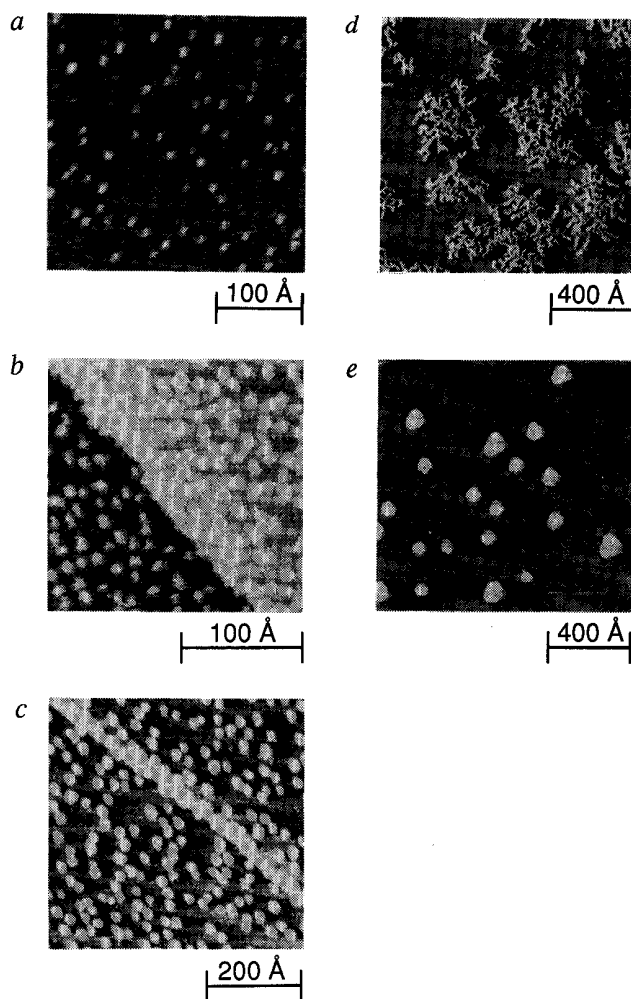


FIG. 1 Scanning tunnelling microscopy (STM) images of two-dimensional Ag aggregates grown on the Pt(111) surface. *a*, Ag dimers grown and imaged at 40 K. The total coverage of the surface (in monolayers, ML) by silver, $\theta_{Ag} = 0.012$ ML. *b* and *c*, Compact two-dimensional Ag clusters of average size $n = 6$ (*b*) and $n = 26$ (*c*) ($\theta_{Ag} = 0.12$ ML) synthesized by growing dimers at 40 K and successive annealing to 110 K and 150 K, respectively (these are also STM imaging temperatures). *d*, Large fractal Ag aggregates ($\theta_{Ag} = 0.12$ ML) grown and imaged at 110 K; the deposition flux was reduced here to 1 ML per 6×10^4 s. *e*, Two-dimensional equilibrium-shape Ag islands obtained by annealing dimers (such as shown in *a*) to a temperature of 280 K ($\theta_{Ag} = 0.12$ ML).

The experiments were performed with a variable-temperature scanning tunnelling microscope (STM) operating in ultra-high vacuum⁵. The accessible temperature range for *in situ* measurements is 25–600 K. The systems we have studied are Ag aggregates formed on the Pt (111) surface and Cu aggregates grown on Pd (110). The metal adsorbates were evaporated onto the substrates from molecular-beam-epitaxy Knudsen cells at rates of typically one monolayer per 900 s. All STM images have been acquired in a constant-current mode with tunnelling currents in the range 1.0–3.0 nA at sample voltages from –0.5 to –1.5 V.

At the very lowest temperatures, adatom migration is slow with respect to deposition resulting in small values of Λ_a (a few Å) and a high density of stable nuclei. An example of this regime is shown in Fig. 1a. Here 1.2% of a Ag monolayer has been deposited on the Pt (111) surface at 40 K. The migration barrier of Ag adatoms on Pt (111) being 140 ± 10 meV (ref. 5), the average diffusion length turns out to be only 9 Å at this temperature, giving rise to the exclusive aggregation of homogeneously distributed Ag dimers.

With increasing substrate temperature during deposition, Λ_a increases, the saturation island density decreases and larger clusters can grow (aggregates containing several atoms to thousands of atoms). The shape of these clusters, in the absence of directional anisotropies in Λ_a , is determined by the average diffusion length of atoms adsorbed at the perimeter of the aggregate, Λ_l . For small values of the perimeter diffusion length ($\Lambda_l \approx 0$ in DLA), the aggregates should grow in a ramified fashion, whereas for higher values the islands are expected to condense in compact shapes^{3,4}. An example in which the hindered perimeter diffusion leads to ramified growth is shown in Fig. 1d; large fractal Ag aggregates grow on the Pt (111) surface at 110 K. A detailed analysis reveals the expected mass-length scaling behaviour. The large aggregate size (~ 300 Å) has been tailored by reducing the flux to 1.7×10^{-5} monolayers per second, leading to a saturation island density of only 1.05×10^{11} cm⁻² as expected⁶. Under these conditions the free adatom mobility is sufficiently high ($\Lambda_a = 200$ Å) while the edge diffusion is still frozen. For self-diffusion on face-centred cubic transition metals, it has been found that migration barriers for edge diffusion (the channels on the (331) and (113) surfaces) are ~ 3 –4 times larger than for (111) terrace diffusion⁷.

The equilibrium island shape is formed by a brief anneal of kinetically determined aggregates to temperatures >250 K. The two-dimensional Ag islands shown in Fig. 1e, have been obtained by annealing dimers, such as those shown in Fig. 1a, to

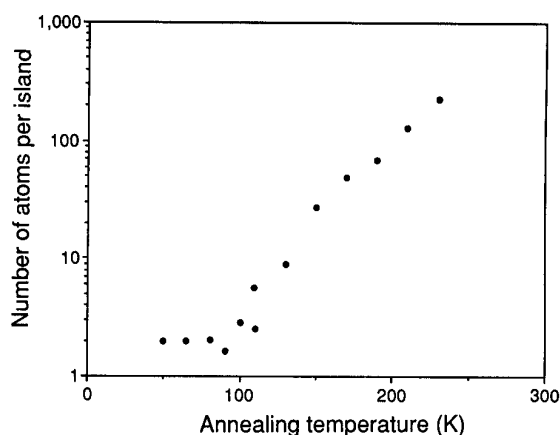


FIG. 2 Thermal stability of the Ag dimers synthesized by means of aggregation at 40 K. On annealing above 100 K, larger two-dimensional Ag clusters can be formed.

280 K. The observed hexagonal equilibrium shape with trigonal symmetry reflects the free energy ratio of the $\langle 1\bar{1}0 \rangle \{100\}$ and $\langle 1\bar{1}0 \rangle \{111\}$ ($\langle \text{direction} \rangle \{ \text{microfacet} \}$) island edges $\delta\{100\}/\delta\{111\} = 1.25$ (ref. 8).

Of particular importance is the intermediate range of cluster sizes, from a few atoms up to several hundred atoms. Many experimental and theoretical efforts are now exploring the evolution of physical and chemical properties as a function of the number of atoms involved⁹. The most dramatic effects are expected for small clusters with sizes up to several tens of atoms. Two-dimensional clusters of this size could in principle be nucleated on surfaces directly by diffusion-controlled aggregation, at an appropriate temperature, flux and coverage. According to nucleation theory⁶ the cluster-size distribution of these aggregates would, however, be rather broad. We have explored an alternative route that gives rise to narrow cluster-size distributions (Figs 1b, c, and Fig. 2). In the first step of this process; a homogeneous distribution of stable nuclei is grown on the Pt (111) surface. The clusters are formed in the second step by thermally activated coalescence of these nuclei. Two typical results are shown in Fig. 1b, c, where compact Ag clusters with an average number of atoms (n) of 6 and 26 have been aggre-

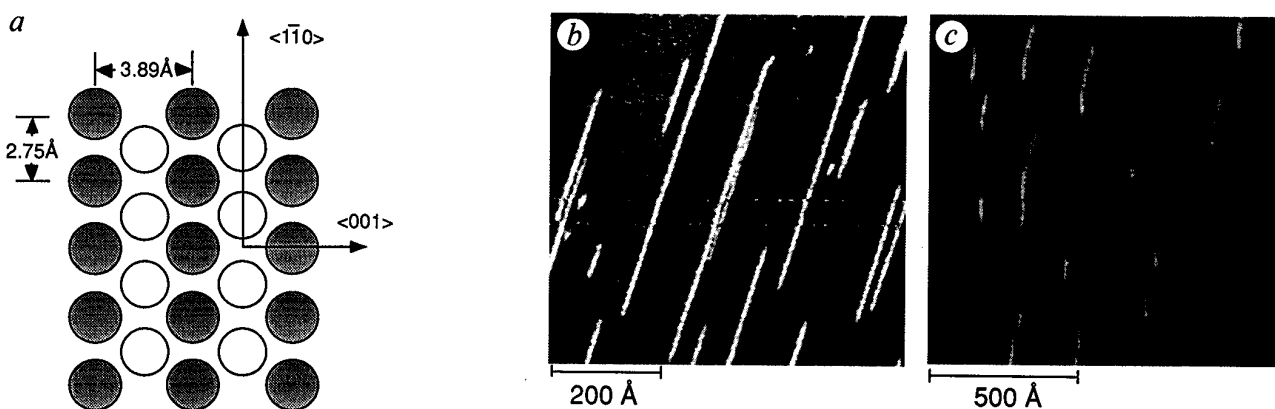


FIG. 3 Cu aggregates grown on the anisotropic Pd (110) surface. a, Surface geometry. b, STM image of monatomic Cu wires grown on the Pd (110) surface; the one-dimensional copper chains were grown and imaged at 300 K, the total coverage was $\theta_{\text{Cu}} = 0.05$ ML. c, The transition

from one-dimensional chains to two-dimensional islands upon growth at 350 K ($\theta_{\text{Cu}} = 0.1$ ML) demonstrates the kinetic origin of the monatomic wires.

gated via nucleation of dimers at 40 K and subsequent annealing to 110 K and 150 K respectively. The homogeneous spatial distribution and the narrow range of sizes are obvious in both STM images.

The diffusion barrier of the pre-nucleated dimers is twice as high as that of Ag adatoms¹⁰ and the dimers are stable over an extended temperature range (Fig. 2). On annealing the surface to temperatures >100 K, dimer diffusion and/or dissociation and subsequent adatom diffusion sets in, resulting in the formation of larger clusters by coalescence. The size of these clusters depends exponentially on the annealing temperature.

Diffusion-controlled aggregation can also be used to synthesize one-dimensional aggregates. One-dimensional systems have, indeed, been the focus of much interest because of their unique behaviour and the fact that certain problems can be solved exactly for these systems¹¹. The growth of one-dimensional aggregates makes use of the directional anisotropy of Λ_a (ref. 12). For surfaces with C_{2v} symmetry, there are two different migration barriers, representing two orthogonal directions. An example is the diffusion of Cu atoms on the Pd (110) surface, where the migration barriers are 0.76 and 0.51 eV for the orthogonal [001] and [110] directions, respectively¹³. The value of Λ_a [110] is thus larger than Λ_a [100] giving rise to a faster growth rate along the [110] channels. With decreasing deposition temperature, the ratio of the rate of diffusion along the close-packed direction to that in the perpendicular direction increases. It should therefore be possible to freeze out cross-channel diffusion along [100] while diffusion along the [110] channels is still sufficiently fast. Under such favourable conditions, exclusively one-dimensional chains of adatoms should grow along the [110] direction of the surface.

The experimental realization of such a situation is shown in Fig. 3b, in which Cu aggregates are grown and imaged on the Pd (110) surface at 300 K. At this temperature, the jump rate in the easy [110] direction is 10^4 times higher than that across the channel walls (assuming approximately equal prefactors¹⁴) and we observe the aggregation of long monatomic Cu chains with lengths up to several hundred Å. The average length of these one-dimensional Cu wires can be tailored, for example by varying the deposition temperature. Because diffusion along [100] is already negligible at 300 K, nucleation at temperatures <300 K will also result in the aggregation of one-dimensional chains, the average length of which will decrease with decreasing temperature (that is, decreasing Λ_a [110]). Whereas at 300 K for a total coverage of 0.05 ML the monatomic Cu chains consist of an average of 130 Cu atoms, at 180 K (at the same coverage) the average chain is composed of only 10 Cu atoms.

The monatomic Cu chains aggregated on the Pd (110) surface are metastable nanostructures. Upon a short anneal to, or direct growth at, 350 K, two-dimensional lens-shaped islands, several atomic rows wide, are formed. This is demonstrated in Fig. 3c, which shows the structure produced by growth at 350 K: two-dimensional Cu islands with an average aspect ratio of 15 are formed. The metastable character of the long one-dimensional Cu chains is not surprising. Field ion microscopy measurements¹⁵⁻¹⁷ and molecular dynamics calculations¹⁸ have revealed that in general the linear one-dimensional clusters constitute the equilibrium structure only at small sizes ($n < 10$). For Cu on Pd (110), however, recent molecular dynamics simulations¹⁹ reveal that at 0 K one-dimensional chains (which can be very long) are the energetically preferred structures. It appears to be the entropy gain associated with the transition from one to two dimensions that drives the Cu aggregates on Pd (110) to two-dimensional structures at elevated temperatures¹³.

This approach of diffusion-controlled aggregation for the synthesis of one- and two-dimensional matter is not restricted to the systems discussed, nor to metal aggregates on metal surfaces. Diffusion-controlled aggregation is applicable for all growth systems in the kinetic regime (including metals on semiconductors or insulators), and one should always be able to find a tempera-

ture window in which one- or two-dimensional aggregates (substrates with directionally anisotropic diffusion) can be produced by manipulating Λ_a and Λ_l . □

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