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# Tailoring Low-Dimensional Structures by Diffusion Controlled Aggregation.

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We demonstrate a novel technique for the synthesis of densely packed planar nanostructures: diffusion controlled aggregation at surfaces. Through appropriate control of the surface mobility and substrate symmetry well defined distributions of one-dimensional (1D) or two-dimensional (2D) metastable nanostructures can be built. Due to the high number density of these structures ($10^{11}$–$10^{14}$ cm$^{-2}$) the physical and chemical properties are easily accessible with conventional surface spectroscopies.

The physical properties of heteroepitaxial structures are ultimately determined by the growth process. Conceptually, heteroepitaxial growth has been widely studied by means of the thermodynamic approach which is essentially based on the idea that the surface free energy must be minimized [1]. The conditions for this to happen in practice are only fulfilled at sufficiently high substrate temperature at which immediate rearrangements of the diffusing adatoms at preexisting island perimeters are possible. In many experiments, however, metastable structures that reflect the kinetic behavior are the common rule. Far from equilibrium, a variety of metastable low-dimensional structures can be tailored by controlling the deposition temperature, deposition rate, the symmetry of the substrate and the atomic nature of the aggregate-substrate system [2].

The evaporation of adatoms onto a substrate drives the system into nonequilibrium, which tries to restore equilibrium by forming aggregates [1]. 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 and the migration barrier of adatoms together with the deposition rate determine the outcome of this competition [2]. The diffusion of an adatom is terminated 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. From there on impinging atoms condense solely at existing aggregates. At this stage they are migrating the average distance $\Lambda_a$. The average adatom diffusion length is temperature (and flux) dependent. At low temperatures $\Lambda_a$ is small, a high density of stable nuclei is formed and clusters grow. With increasing temperature $\Lambda_a$ increases, the saturation island density decreases and larger aggregates can grow. The shape of these aggregates is determined by directional anisotropy of $\Lambda_a$ and by the average diffusion length of atoms adsorbed at the perimeter of the aggregate $\Lambda_l$ [3,4]. Here we will demonstrate that via temperature control of $\Lambda_a$ and $\Lambda_l$ the size and the shape of the formed aggregates can be manipulated specifically on an atomic level.

The experiments were performed with a variable temperature scanning tunneling microscope (STM) operating in ultra-high-vacuum [5]. The accessible temperature range for in-situ measurements is between 25K and 600K. The systems we have studied are Ag aggregates formed on Pt(111) surface and Cu-aggregates grown on Pd(110). The metal adsorbates were evaporated onto the substrates from MBE-Knudsen cells at rates of typically 1 monolayer (ML) per 900 s. All STM images have been acquired in a constant current mode with tunneling current from $I = 1.0$ nA to 3.0 nA at sample voltage from $V = -0.5$ V to -1.5 V.

At very lowest temperatures, adatom migration is slow with respect to deposition resulting in small values of $\Lambda_a$ (a few Å) and a high density of stable nuclei. An example for such a situation is shown in Fig.1a. Here 1.2% of a Ag monolayer have been deposited on the Pt(111) surface at 50K. The migration barrier of Ag adatoms on Pt(111) being 140±10 meV [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, $\Lambda_a$, the saturation island density decreases and larger clusters can grow (aggregates containing several atoms to thousands of atoms), the shape of which, in the absence of directional anisotropies in $\Lambda_a$ . is determined by the average diffusion length of atoms adsorbed at the perimeter of the aggregate. $\Lambda_l$. For small values of the perimeter diffusion length the aggregates should grow ramified, while for higher values the islands are expected to condense in compact shapes [3.4]. An example where the hindered perimeter diffusion leads to ramified growth is shown in Fig.1d: large fractal Ag-aggregates grow on Pt(111) at 110K. The large aggregate size has been tailored by reducing the flux to $1.7\text{x}10^{-5}$ML/s leading to saturation island density of only $1.05\text{x}10^{1}$1cm$^{-2}$ in agreement with the expectation [9]. Under these conditions the free adatom mobility is already sufficiently high ($\Lambda_a = 200$Å) while the edge diffusion is still frozen [6], giving rise highly ramified Ag islands with lateral dimensions of more than 300Å.

The equilibrium island shape is formed upon a brief anneal of kinetically determined aggregates to temperatures above 250K. The 2D Ag islands shown in Fig.1e have been obtained by annealing of dimers, such as shown in Fig.1a, to 280K. The observed hexagonal equilibrium shape with trigonal symmetry reflects the free energy ratio of the $\langle 110\rangle\{100\}$ and $\langle 110\rangle\{111\}$ ($\langle \mathit{directional}\rangle\{\text{microfacet}\}$) island edges $\partial\{100\}/\partial\{111\}=1.25$ [7].

Of particular importance is, however, the intermediate range of cluster sizes from a few atoms up to several hundred atoms. Many experimental and theoretical efforts are currently underway to explore the evolution of the physical and chemical properties from the single atom to the bulk as a function of atoms involved [8]; the most dramatic effects being expected for small clusters composed of only a few 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 chosen temperature, flux and coverage. According to nucleation theory [9] the cluster size distribution of this aggregates would,

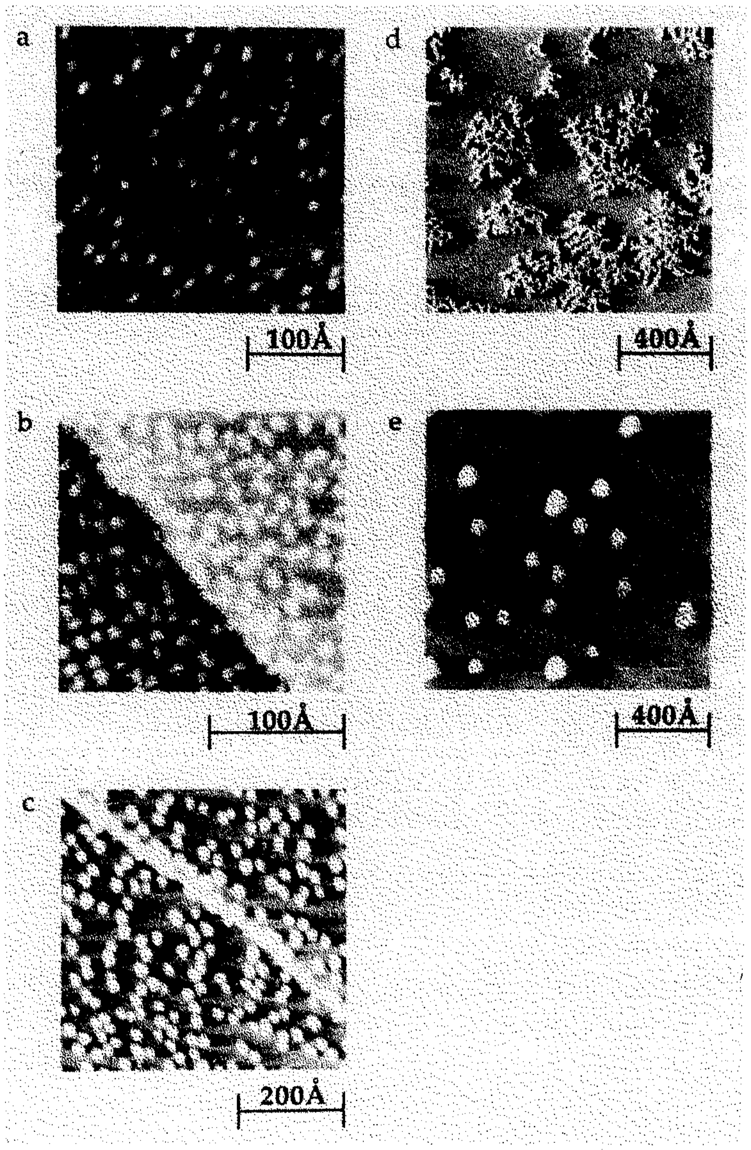

**Figure 1.** STM-images of two-dimensional Ag-aggregates grown on the Pt(111) surface. a)Ag-dimers ($\Theta_{Ag}$=0.012ML) grown and imaged at 40K. b) and c) Compact 2D Ag clusters of average size n=6 (b) and n=26 (c) ($\Theta_{Ag}$=0.12ML) synthesized by growing dimers at 40K and successive annealing to 110K and 150K, respectively (also STM imaging temperatures). d)Large fractal Ag aggregates ($\Theta_{Ag}$=0.12ML) grown and imaged at 110K; the deposition flux was reduced here to 1ML per $6\text{x}10^4$s. e) 2D equilibrium shape Ag islands obtained by annealing dimers such as in image a) to a temperature of 280K ($\Theta_{Ag}$=0.12ML).

however, be rather broad.

We have explored an alternative route which gives rise to narrow cluster size distributions (Fig.1b,c). In a first step a homogeneous distribution of stable nuclei is grown on the Pt(111) surface, followed by a second step, in which the clusters are formed by thermally activated coalescence of the nuclei. Two typical results are shown in Figs.1b and 1c, where compact Ag clusters with an average size of atoms (n) 6 and 26 have been aggregated via nucleation of dimers at 40K and subsequent annealing to 110K and 150K respectively. The homogeneous spatial and narrow distribution is obvious in both STM images.

The diffusion barrier of the prenucleated dimers is twice as high as that of Ag adatoms [10] and the dimers are stable in an extended temperature range up to 100K. Annealing the surface to temperatures above 100K, dimer diffusion and/or dissosiation 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 according to $n(T_a) \approx (1/16)\exp(T_a/26)$.

Diffusion controlled aggregation can also be used to synthesize one-dimensional aggregates. 1D-systems have, indeed, been the focus of much interest because of the unique behavior and the fact that certain problems can be solved exactly for these systems [11]. The growth of 1D-aggregates makes use of the directional anisotropy of $\Lambda_a$ [12]. For surfaces with $C_{2v}$ symmetry there are two different migration barriers, representative of two orthogonal directions. An example is the Cu diffusion on the Pd(110) surface, where the migration barrier are 0.76 eV and 0.51 eV for the orthogonal [001] and $[1\bar{1}0]$ directions, respectively (see below). $\Lambda_a$ $[1\bar{1}0]$ is thus larger then $\Lambda_a[001]$ giving rise to a large growth speed along the $[1\bar{1}0]$ channels. With decreasing deposition temperature the ration of diffusion along the close-packed direction to that perpendicular increases. Therefore it should be possible to freeze out cross-channel diffusion along [001] while diffusion along the $[1\bar{1}0]$ channels is still sufficiently high. Under such favorable conditions exclusively one-dimensional chains of adatoms should grow along the $[1\bar{1}0]$ direction of the surface.

Figure 2 shows STM images of submonolayer Cu islands grown on Pd(110) at various temperatures T and low Cu coverages ($\Theta_{Cu} \leq 0.1$ML). Cu islands have high aspect ratios at all temperatures and are oriented along the $[1\bar{1}0]$ direction. At temperature of 300K and below (Fig.2a and b) linear chains **monoatomic** in width are formed. At $T = 300$K the monoatomic Cu-wires can reach length up to 1000Åcorresponding to aspect ratios as large as A=300. Above about 300K, 2D-islands that are still elongated in the $[1\bar{1}0]$ direction start to form (see Fig.2c and d). As is clear from Fig.2, the surface density of islands drops as a function of temperature. This illustrates that a set of images taken at different deposition temperatures contains information on the adatom diffusion length on the surface.

The diffusion analysis of this data can be done by analyzing the density of islands as a function of the substrate temperature as outlined in recent papers [5,13,14]. At constant deposition rate and coverage, the island density N is found to be proportional to $D^{-d/2(d+1)}$ where $D$ is the diffusion coefficient of adatoms. In the case of isotropic 2D diffusion $d = 2$, while in the case of 1D diffusion $d = 1$. Fig.3a) and b) show log-in plots of the overall surface density of islands and of the linear density of islands in the [001] direction as a

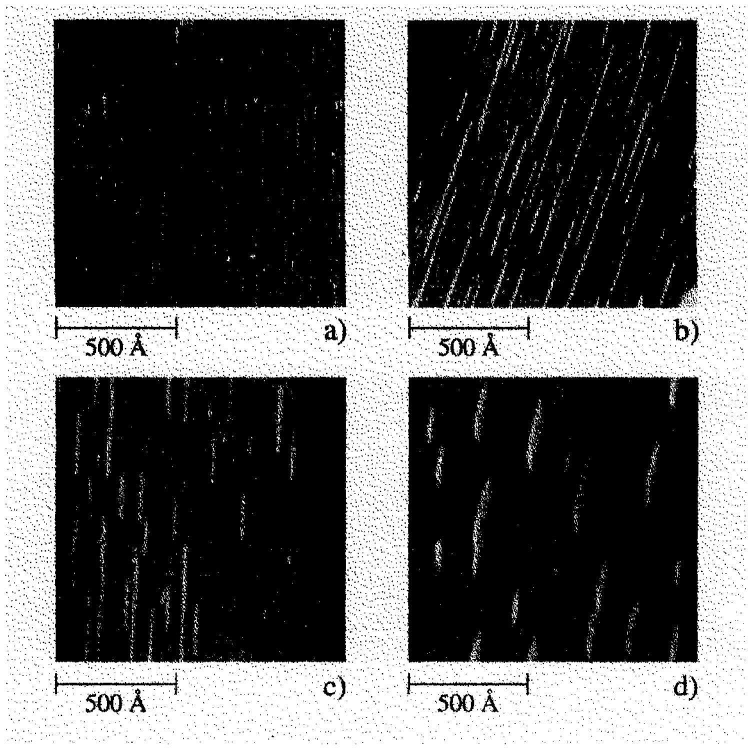

**Figure 2.** Cu aggregates grown on the anisotropic Pd(110) surface at four different temperatures and nearly the same Cu coverage of $\Theta_{Cu}$=0.1ML except for b) where $\Theta_{Cu}$=0.07ML. Temperatures are: a) 265K, b) 300K, c) 320K and d) 350K.

function of $1/T$. As long as the transverse diffusion is not activated, the overall density of islands (Fig.3b) determines the diffusion barrier in the easy direction while the linear density of islands perpendicular to the channel walls (Fig.3a) essentially determines the diffusion barrier in the [001] direction. In order to avoid accidental coalescence, the experimental data focus on the low coverage regime below 0.1ML. Possible island coarsening due to growth of bigger islands at the expense of smaller ones through reevaporation of atoms from the edges has only been observed for $T > 400$K. The island densities in Fig.3 nicely reflect the transition from 1D to 2D growth. The overall density shows Arhenius behavior in the entire range from 350K to 180K demonstrating that the longitudinal diffusion is active in the entire range down to the lowest measured temperatures. The atoms move along the $[1\bar{1}0]$ channels without any transverse migrations and the island formation is a true 1D problem. In this case the analysis that consists in considering the island density to be proportional to $D^{-1/4}$ is justified. The diffusion barrier that can be obtained from the truly 1D regime through the overall density is $E_{[1\bar{1}0]} = 0.51 \pm 0.05$ eV. On the other hand, the linear island density along [001] (determining the cross channel barrier), shows Arhenius behavior only above 300K and is constant at temperatures below. This indicates that below 300K transverse diffusion of Cu adatoms is frozen. It is only above this

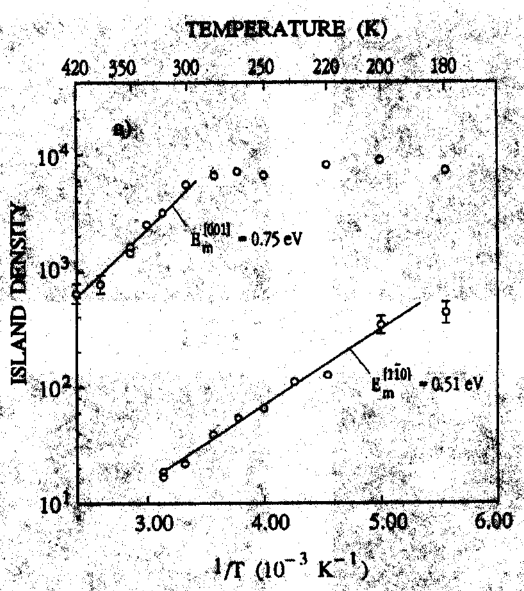

**Figure 3.** Arhenius plot of the linear transverse density (a) and overall density (b) of Cu islands on Pd(110) as a function of $1/T$. The island densities are in arbitrary units.

temperature that cross channel diffusion is active and contributes to 2D island formation. The diffusion barrier is determined to be $E_{[1\bar{1}0]} = 0.75 \pm 0.07$ eV.

The average length of the one-dimensional Cu-wires can be tailored for example by varying the deposition temperature. Diffusion along [100] being negligible already at 300K the nucleation at temperatures $T < 300$K, will also result in the aggregation of 1D-chains, the average length of which will decrease with decreasing temperature (i.e. decreasing $\Lambda_a[1\bar{1}0]$). While for 300K at a total coverage of 0.05ML the monoatomic Cu-chains consist in average of 130 Cu-atoms, at 180K (at the same coverage) the average chain is composed of only 10 Cu-atoms.

We would like to conclude by stressing, that the approach of diffusion controlled aggregation for the synthesis of 1D- and 2D-matter outlined here is neither restricted to the systems discussed nor restricted 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 temperature window in which 2D- or 1D-aggregates (substrates with directionally anisotropic diffusion) can be tailored via the manipulation of $\Lambda_a$ and $\Lambda_l$.

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