

## Magic Clusters in Two Dimensions?

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The initial stages of growth of Pt on Pt(111) have been investigated as a function of the substrate temperature. The main result is that, while between 200 and 400 K the cluster density decreases with increasing temperature in accordance with nucleation theory, in the range of 400–500 K the density *increases* by more than 1 order of magnitude in obvious contradiction to expectations. At coverages below 0.1 we find at temperatures above 500 K a high density of small clusters (possibly heptamers) which appear to be stable with respect both to decomposition and to further growth.

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One of the striking features of small metal *gas phase* clusters is the existence of magic numbers, i.e., the enhanced stability of clusters of a certain size. At least for simple metals like the alkali or noble metals, magic numbers for small clusters could be explained in terms of an *electronic* shell structure with high stability corresponding to closed electron shells [1,2]. For larger clusters *geometric* structures (e.g., closed atomic shells) were found to be responsible for particularly stable cluster sizes [3].

In this paper we focus on small metal clusters grown on a surface of the same material. Here, the clusters are expected to be two dimensional with the cluster atoms sitting at the surface lattice sites [4]. Therefore, in contrast to the gas phase, where the geometrical configuration of the atoms in the cluster does not necessarily follow the corresponding three-dimensional bulk structure, the two-dimensional structure of the surface is imposed on the 2D cluster. The geometrical structure will therefore serve as an organizing principle even for the stability of small 2D clusters, although it has to be borne in mind that electronic effects may compete with these considerations.

In our present study of the initial stages of growth of Pt on Pt(111), clusters are formed under *growth conditions*, i.e., while continuously depositing Pt atoms onto the surface at a low rate. Under these circumstances, the observation of small stable clusters as majority species can only be expected if the growth of the clusters beyond a certain (magic) size by accommodation of adatoms is hampered. In other words, it does *not* suffice that these clusters do not decompose thermally, but in addition their further growth to larger stable structures must be less probable than their creation. From the measurements reported in this paper, we conclude that this is indeed the case at low coverages for substrate temperatures above 500 K. The consequence is the formation of a high density of small stable clusters during deposition of the first 10% of a monolayer (ML).

The experiments are performed in an UHV molecular-beam scattering apparatus described in more detail elsewhere [5,6]. The monitoring of the cluster sizes relies on the attenuation of the specularly reflected He beam due

to diffuse scattering from small adatom structures and steps present on the surface [7]. During deposition of Pt atoms onto the Pt surface at a sufficiently low temperature, 2D nucleation takes place and small clusters are formed which, under usual conditions, grow continuously to larger islands. If the cross section for diffuse scattering from these structures is known, the total amount of diffuse scattering at a given coverage can be used to determine the cluster or island size. Small clusters scatter perfectly diffusively, and the cross section for diffuse scattering can be approximated by the geometrical overlap of the single adatom cross sections [7]. For larger islands, only the step edges surrounding the islands contribute to diffuse scattering. At a given coverage, the total amount of diffuse scattering is the higher the smaller the adatom structures on the surface are. The cross section of single Pt adatoms on Pt(111) has not been measured yet. We will assume here that it is similar to that measured for a number of adsorbed molecules and for vacancies, i.e., about  $120 \text{ \AA}^2$  for a room-temperature He beam incident at  $\vartheta_i = 40^\circ$  [7].

Figure 1 shows the evolution of the normalized intensi-

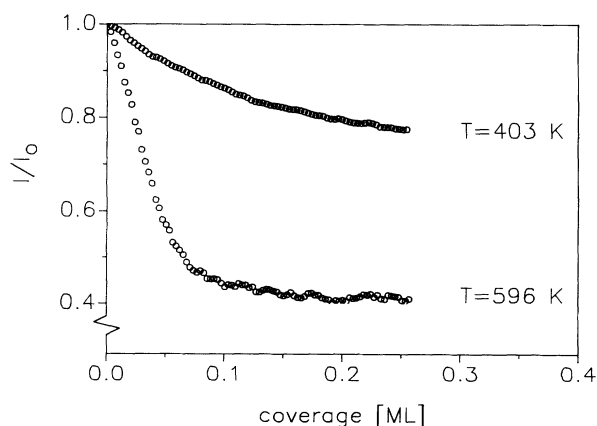


FIG. 1. Normalized in-phase He specular peak height as a function of coverage during deposition of Pt onto Pt(111) at two different substrate temperatures as indicated and a deposition rate of 0.002 ML/s.

ty of the specularly reflected He beam ( $E_{\text{He}}=67$  meV) during deposition of Pt at a rate of 0.002 ML/s as a function of the coverage  $\theta$  for two different substrate temperatures. The angle of incidence is  $\vartheta_i=68.5^\circ$  corresponding to *in-phase* conditions: scattering contributions from adjacent terraces interfere constructively. Since there is no variation of the He intensity in the absence of Pt deposition, as we have checked carefully, the attenuation of the reflected He intensity directly measures the total amount of diffuse scattering due to deposited material [8]. Surprisingly, the curve recorded at 600 K lies below that recorded at 400 K, revealing that the diffuse scattering, i.e.,  $1-I/I_0$  is stronger and thus the structures formed during deposition are *smaller* at 600 K compared to the situation at 400 K. This feature is at variance with the common picture derived from nucleation theory in which the size of grown structures at a given coverage *increases* with increasing temperature [9]. Also the shape of the two curves is different. The curve at 400 K has a concave shape consistent with the continuous growth of a constant number of larger islands, i.e., the total amount of diffuse scattering increases with the step length as  $\sqrt{\theta}$  [10,11]. In contrast, the high-temperature curve shows a steep, almost linear decrease before leveling off at a coverage between 5% and 10%. This steep initial decay is characteristic for the continuous formation of a high density of isolated, perfectly diffuse scatterers. In order to investigate this phenomenon systematically, deposition curves like those shown in Fig. 1 have been measured over an extended temperature range. Their initial slope  $\Sigma'n_s$ , defined by the relation [7]

$$I/I_0 \approx 1 - \Sigma'n_s\theta, \text{ for } \theta \rightarrow 0,$$

has been evaluated;  $I_0$  is the He specular peak height at a given temperature in the absence of Pt deposition,  $n_s$  the number of lattice sites per unit area, and  $\Sigma'$  the effective

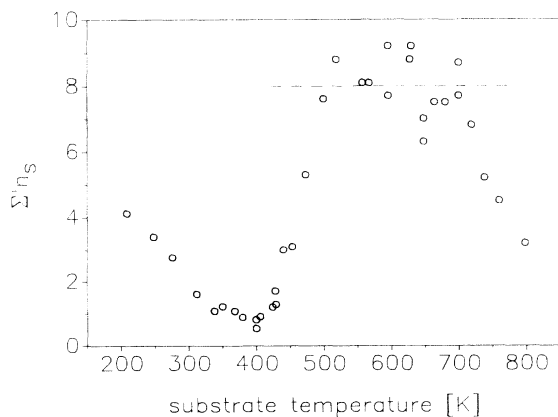


FIG. 2. Initial slope of deposition curves as a function of the substrate temperature. Deposition rates of 0.0018–0.0023 ML/s. The dashed line corresponds to a situation where all clusters are heptamers.

cross section for diffuse scattering per deposited atom. The result is shown in Fig. 2.

Starting at low temperatures, the value of the initial slope  $\Sigma'n_s$  decreases with increasing temperature up to 400 K; i.e., the total amount of diffuse scattering at fixed coverage decreases showing that the average number of islands decreases with rising temperature. This is in line with nucleation theory [9]. However, above 400 K a sudden increase in diffuse scattering by approximately 1 order of magnitude is observed. At higher temperatures, the initial slope retains its high value until it eventually starts to decrease above 700 K. The absolute value of the initial slope indicates that the small structures grown above 500 K consist of only a few atoms. Indeed, these clusters can be shown to be perfect diffuse scatterers and one obtains under the assumption that all the clusters are hexagonal heptamers a value of  $\Sigma'n_s \approx 8$  as indicated by the dashed line in Fig. 2.

The stability of these diffuse scatterers was investigated by stopping the deposition of Pt atoms at a coverage of 5%, i.e., within the steep part of the 600-K deposition curve (cf. Fig. 1). The He intensity was further recorded while the substrate was held at the growth temperature. As seen in Fig. 3, hardly any annealing is observed for at least 350 s showing that the small structures formed on the surface are stable.

A possible contribution of non-negligible density of free Pt adatoms to the high diffuse scattering observed above 500 K could be ruled out by continuing to monitor the He intensity while cooling the sample (right part of Fig. 3). If the adatom density had a measurable contribution, the He intensity should increase significantly because adatoms would condense as the temperature is decreased. The Debye-Waller corrected data in Fig. 3 (right part) demonstrate that this is not the case.

From the experimental observations reported so far, it is clear that we are dealing with a high density of small stable clusters formed during deposition at high tempera-

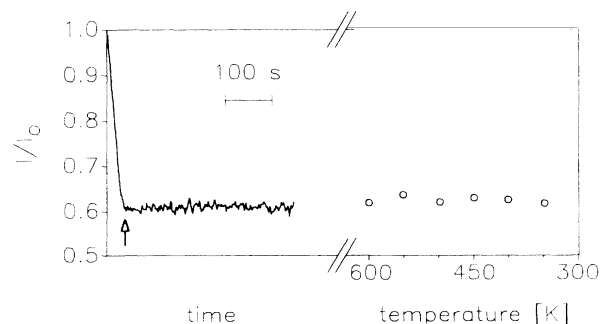


FIG. 3. Annealing behavior after deposition of 0.05 ML (arrow) at 600 K. Left part: He intensity as a function of time while the substrate is held at 600 K. Right part: He intensity, corrected for Debye-Waller effects, while the substrate is cooled from 600 to 350 K. Note that He reflectivity behaves completely reversibly with temperature.

tures. Therefore, at high temperatures, the further growth of small clusters above a certain size is hampered. In order to understand this phenomenon, it is worthwhile to consider the stability of clusters as a function of their size. This is most easily done in the framework of a nearest-neighbor model, i.e., by describing the binding energy of a cluster in terms of effective nearest-neighbor bonds.

Counting the in-plane nearest-neighbor bonds that have to be broken to remove an atom from a small compact cluster, no significant stability variations with size are expected if the probability of simultaneously breaking two bonds is low. Indeed, if a triangular trimer is a stable cluster, clusters of more than three atoms are stable, too, because each of the cluster atoms has at least two nearest neighbors (see Fig. 4). Thus, once a trimer is built, it will steadily accommodate further adatoms and grow to a large island. The situation is different if the temperature is raised to a value where two bonds can easily be broken but the probability of breaking simultaneously three bonds is small. The smallest stable configuration then is a hexagonal heptamer, as shown in Fig. 4. In this case the further growth of the heptamer is not at all obvious: adding one or two atoms to this cluster leads to less stable configurations with atoms having only two nearest neighbors (see Fig. 4). A stable configuration, i.e., a compact decamer, is reached only after addition of *three* atoms.

From these considerations it appears attractive to relate the sudden increase in diffuse scattering around 450 K in Fig. 2 to the probability of simultaneously breaking two bonds becoming significant. Heptamers formed by nucleation of adatoms would be hindered from growing to larger clusters by the "stability gap" between heptamers and decamers while the further deposition of atoms would result in the production of new heptamers. A high density of heptamers would build up, in line with the steep decrease of the He intensity in the high-temperature deposition curves (cf. Fig. 1) and the measured value of their

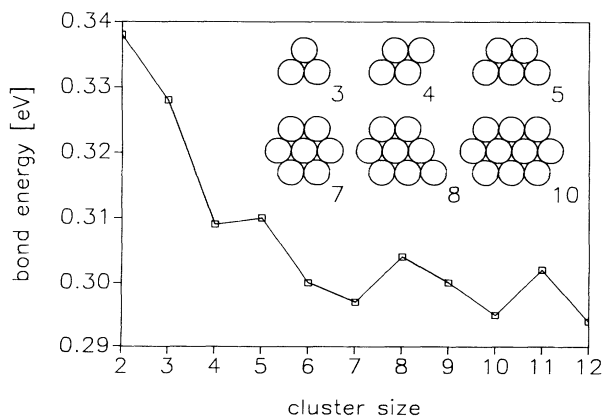


FIG. 4. Effective dissociation energy per bond for Pt clusters on Pt(111) calculated in the effective-medium theory [12]. Inset: 2D clusters on a hexagonal lattice.

initial slope,  $\Sigma'n_s \approx 8$  (cf. Fig. 2). However, with the number of heptamers increasing, the collision rate with adatoms also increases and the creation rate of new heptamers decreases, correspondingly. Eventually, some of them will succeed in overcoming the stability gap and grow to larger clusters. Adatoms newly arrived at the surface will now accumulate at these large clusters stopping the production of new heptamers completely. This point would correspond to the coverage at which the sudden change of slope in the deposition curves is observed (see Fig. 1).

The application of this simple model requires that the probability of simultaneously breaking two bonds becomes important in the temperature range of 400–500 K. This will be shown to be the case on the base of a simple estimate outlined below. A real crystal surface consists of terraces bounded by monatomic steps, which for the freshly prepared Pt(111) surface have a size of about  $1000 \text{ \AA} \times 1000 \text{ \AA}$ . An intrinsic time scale for atomic processes on a terrace during deposition of Pt atoms is given by the mean time between two deposition events onto a terrace. The impingement rate of Pt atoms corresponds to 0.002 ML/s, equivalent to one Pt atom on a terrace per  $3.3 \times 10^{-3} \text{ s}$ . Roughly speaking, the simultaneous breaking of two nearest-neighbor bonds becomes significant, if the residence time of an atom in a configuration with two nearest neighbors is equal to or less than this time unit. This allows the estimation of an upper limit for the strength per nearest-neighbor bond. For a temperature of 450 K and an activation barrier for diffusion of 0.23 eV [12], the result is 0.35 eV. This value is in agreement with recent calculations made by Hansen *et al.* [13]; see Fig. 4.

From the mobility argument it also follows that, at 450 K, an atom impinging near the center of a terrace reaches a step within less than  $10^{-3} \text{ s}$ . However, step propagation is only observed above 900 K [14]. The conclusion is that the probability of incorporation of an adatom into a step is very low for temperatures above 450 K. This confirms the basic assumption of our model that, above 450 K, the probability of simultaneously breaking two bonds is very high. Indeed, the lifetime of a ledge adatom (held by a double bond at the ledge) becomes too short to reach a kink position, where it would be more stably incorporated by a triple bond.

However, it is quite clear that our simple model does not work if the strength per nearest-neighbor bond is the same for all the clusters from dimers to decamers. Indeed, with a fixed bond strength, the probability of forming a heptamer is smaller than the probability of a heptamer growing to a decamer, because all the clusters smaller than the heptamer are as unstable as the octamer and eniomer. This failure could be avoided by making the nearest-neighbor interaction dependent on the cluster size. For instance, a twofold bound atom in a trimer should be attached more strongly than a likewise twofold bound atom in a octamer. Recent calculations by Hansen

*et al.* show indeed that the effective nearest-neighbor bond strength *decreases* with *increasing* cluster size [13]; see Fig. 4. We have introduced this feature into simple rate equations similar to those used by Venables, Spiller, and Hanbücken [9]. In this Letter we mention only a few characteristics. The atom-atom interactions are modeled as effective nearest-neighbor interactions and dimers and larger clusters are assumed to be immobile. Using a bond strength decreasing with increasing cluster size, we could obtain a narrow cluster size distribution peaked around heptamers up to coverages of a few percent. Although the rate equations require a stronger cluster size dependence than in the results of Hansen *et al.*, we feel that this result is quite satisfactory in view of the crudeness of the rate equation approach.

In summary, we report the discovery of a new phenomenon during the first stages of growth of Pt on Pt(111) at temperatures above 500 K. Below coverages of 10% of a monolayer, small clusters are continuously formed by nucleation of adatoms but do not grow beyond a certain size. Instead, a high density of these clusters, which are stable at the growth temperature, builds up. Based on the size of the cross section for diffuse scattering of these clusters and on geometrical arguments concerning the stability of small clusters, we propose that these clusters are hexagonal heptamers.

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