

Decorated Ag₁₉ on Pt(111) or the “Rare Gas Necklace”

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Ag₁₉ cluster ions are mass selected and deposited on a Pt(111) surface covered by five monolayers of Kr. Almost monodispersed hexagonal shaped Ag islands are observed after Kr evaporation at 125 K. The identification of the island shape and the exact number of atoms has been successful by decorating the clusters with Kr atoms which can be counted by high resolution scanning tunneling microscopy.

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Clusters bridge the gap between solid state properties on one side and the world of atomic and molecular physics on the other. Their geometrical structure, electronic and magnetic properties, catalytic activity, etc. depend on their size [1]. This has been evidenced by a large amount of gas phase experiments, where the number of atoms per cluster can be precisely controlled. In particular, for clusters containing less than 100 atoms it has been shown that every atom counts.

Experimental evidence for the importance of the precise size of clusters deposited on a solid substrate has been found, for example, in the catalytic activity of gold clusters on oxide substrates [2] and the minimum number of silver atoms to form an image speck [3]. This shows that the cluster size plays also a crucial role in the properties of the ad-cluster system, especially for small aggregates.

It is difficult to obtain on a surface clusters with a well-defined number of atoms. One way, followed by an increasing number of research groups, is to produce clusters in a beam, size select them prior to deposition, and try to softland them at low kinetic energy on the substrate [4]. Alternatively, softlanding can be achieved by depositing some monolayers of rare gas on top of the surface, deposit the clusters in the rare gas matrix which plays the role of a buffer layer, and bring them into contact with the substrate by evaporating the rare gas. Such a technique has been used with success for Ag clusters deposited on Pt(111) [5].

In all cases, a crucial step is the determination of the cluster size after deposition, since in the deposition process the clusters may well fragment and/or implant. Optical methods like absorption, fluorescence, and Raman spectroscopy are adequate when clusters are deposited into weakly interacting matrices like rare gases or nitrogen. Such studies have shown that softlanding into and onto these substrates is feasible and that almost monodispersed samples are produced [6–8]. These methods are, however, not applicable when the clusters are deposited on strongly interacting surfaces like metals. Scanning tunneling microscopy (STM) has been used to image the adclusters, but the precise determination of the size is difficult because of tip convolution problems. Atomic resolution, which allows us to count the atoms, has been achieved so far only in a few selected cases for clusters grown on weakly inter-

acting surfaces. Piednoir *et al.* [9] report on an atomically resolved Pd₂₇ cluster, grown on MoS₂ imaged at room temperature. Hansen *et al.* [10] report on the smallest island to be imaged with atomic resolution which has a diameter of approximately 40 Å. This corresponds to about 250 atoms for an island of monoatomic height. However, atomic resolution for small clusters on strongly interacting surfaces, like metals, has not been reported so far.

We show in this Letter that it is possible to obtain a precise determination of the size and the shape of a metal cluster deposited on a metal surface by decorating it with rare gas atoms. This is due to the large corrugation of rare gas atoms, which can be atomically resolved. More specifically, we determine the size and shape of Ag₁₉ aggregates deposited at low temperature on Pt(111), using the rare gas buffer layer technique.

Ag₁₉ clusters have been deposited and imaged using a new experimental setup which combines size selected cluster deposition with thermal energy atom scattering (TEAS) and low temperature ($T = 8$ K) STM. A detailed description is given elsewhere [11]. We grow 5 monolayer (ML) of Kr on Pt(111) at $T_s = 25$ K, before starting the cluster deposition. Ag₁₉ clusters are deposited at 30 eV kinetic energy for about 5 min at a current density of 800 pA/cm². Finally we add 1 ML of Kr on top to protect the sample which is then transferred to the STM keeping the low temperature. The clusters are imaged at $T_s = 8$ K. Annealing is performed by raising the sample to the desired temperature and subsequent cooling to the measurement temperature.

Figure 1a gives an STM image of the surface morphology after deposition at 25 K, Figs. 1b and 1c have been obtained after annealing at, respectively, 60 and 125 K. On the same figure we have also drawn the corresponding cartoonlike models. In order to discuss more fully our results, we plot in Fig. 2 the height distribution for the three situations reported in Fig. 1 and the height distribution obtained after annealing at 140 K, followed by deposition of 1 ML of Kr (see later). STM measures electronic density, and thus the “electronic height” is different from the physical height of a structure. For further discussion we compile in Fig. 2 both electronic and physical heights of relevant adstructures. Notice that Ag and Pt adlayers can

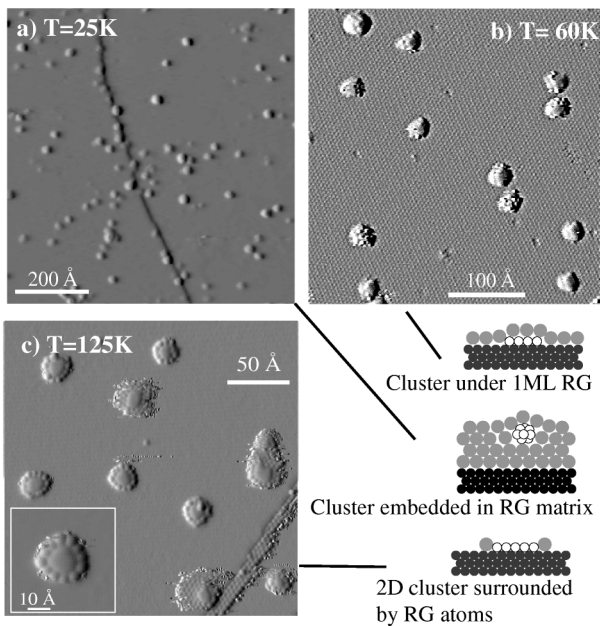


FIG. 1. Cluster-substrate morphology with the corresponding STM images for $\text{Ag}_{19}/\text{Kr}/\text{Pt}(111)$ at different annealing temperatures. Also given are cartoons illustrating the proposed morphologies.

be readily distinguished. All our measurements indicate that we measure heights related to silver adatoms. We do not expect implantation and ejection of Pt substrate atoms into the adlayer.

After deposition and before annealing (see Fig. 1a and the corresponding model), we expect the clusters to keep their identity and to be three dimensional. This is inferred from optical experiments on matrix isolated clusters [12], where size specific absorption spectra have been measured. Figure 2a shows a broad height distribution. This is not surprising since the particles can penetrate at different depths into the rare gas layer. However, molecular dynamic calculations show that the penetration depth at the energies we use is very shallow [13,14], so that we do not expect the clusters to reach the Pt substrate.

For further investigations we make use of the different binding energies of krypton atoms placed in different environments. This allows us to desorb them selectively. At an annealing temperature ($T_s = 60$ K) the Kr atoms which are bound to other Kr atoms desorb (heat of adsorption: $E_{\text{Kr-Kr}} = 120$ meV [15]), while the Kr atoms in contact with the Pt terraces, steps, or Ag clusters do not (heat of adsorption: $E_{\text{Kr-Pt}} = 158$ meV [16]). This situation is shown in Fig. 1b, where the Pt terraces and clusters are covered with 1 ML of Kr. It is imaged on Pt(111) with atomic resolution. A detailed analysis [17] shows very good agreement with already published data [18,19]. The Ag_{19} clusters are imaged as protrusions (Fig. 1b) with lateral dimensions which correspond well to a rare gas covered 2D or 3D cluster as depicted in the cartoon in Fig. 1b. Further information is obtained from the height distribu-

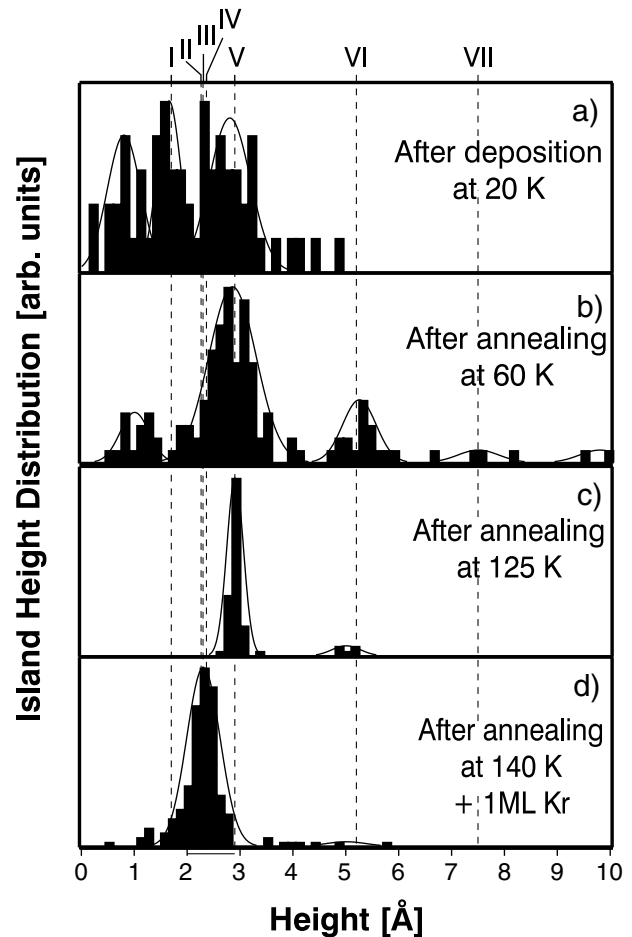


FIG. 2. Height distribution as measured with the STM for $\text{Ag}_{19}/\text{Kr}/\text{Pt}(111)$ at different annealing temperatures. Also given on the top axis are the physical and electronic heights of relevant adstructures: I: 1.7 Å, 1 ML Kr island electronic height; II: 2.27 Å, 1 ML Pt(111) physical step height; III: 2.3 Å, 1 ML Pt(111) electronic height; IV: 2.36 Å, 1 ML Ag island physical height; V: 2.9 Å, 1 ML Ag island electronic height; VI: 5.2 Å, 2 ML Ag island electronic height; VII: 7.5 Å, 3 ML Ag island electronic height.

tion (Fig. 2b). One clearly distinguishes 2 broad peaks whose positions correspond to islands one and two layers high. The smaller peak centered at 1 Å is assigned to Kr ad-atoms. The most intense peak at ~ 3 Å indicates that at this annealing temperature most of the clusters have already transformed into flat islands.

Further annealing results in evaporation from the terraces leaving only higher coordinated Kr atoms at steps and adsorbates on the surface (heat of adsorption on Pt(997): $E_{\text{step}} = 210$ meV [19]). This implies that the Kr atoms form a chain along the step edges and a ring around the adsorbed clusters. The same situation is obtained by desorbing completely the Kr overlayer and redepositing a small amount of Kr, just sufficient to decorate the step edges and the clusters. This is the situation measured in Fig. 2c for $T_s = 125$ K during redeposition of Kr atoms. The monoatomic steps of the Pt(111) surface as well as the

adclusters are decorated by Kr atoms. Notice that we observe both mono row and multiple row structures. The height distribution of the Ag aggregates (see Fig. 2c) is very sharp and corresponds exactly to the electronic height of 1 ML of silver, as expected from the model shown.

Figure 3 gives more detailed information for the Ag cluster decorated by a ring of Kr atoms shown in the inset of Fig. 1c. Figure 3a is a high resolution STM image of this cluster, clearly showing that it is surrounded by 12 Kr atoms. This typical situation is found with an abundance of approximately 70%. Figure 3b measures the height of this particle along the line scan drawn in Fig. 3a. The center of the scan shows the electronic height of Ag on Pt. Krypton atoms decorating the silver steps are imaged 1.9 Å high, compared to 1.7 Å for Kr islands on Pt(111). It is unfortunately not possible to find atomic resolution for the Ag atoms themselves; however, we show below that the Kr decoration allows us to find in an indirect way the size and shape of the Ag island.

We first assume that the number of Ag atoms is equal to 19, i.e., to the number of atoms in each deposited cluster. This is reasonable given the gentle deposition process of our technique. We also assume that during the passage from 3D to 2D the Ag atoms within an island can move to find their minimum energy position, the atoms being in epitaxy with the underlying Pt substrate [20]. The minimum energy configuration, which maximizes the coordination number of a 19 atom Ag island is a regular hexagon. A considerable energy increase is, e.g., calculated ($\Delta E = 313$ meV [21]) when a Ag atom is taken out of a fourfold coordinated site and placed on a twofold site

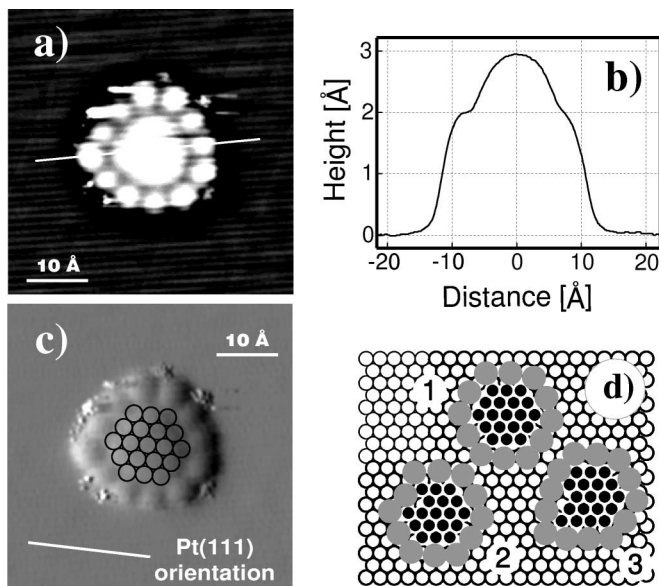


FIG. 3. Ag_{19} cluster on Pt(111) surrounded by 12 Kr atoms. (a) $I = 380$ pA, $V_{\text{bias}} = -200$ mV; the image has been filtered to artificially increase the contrast; (b) line scan across the cluster; (c) model superposed to the image; (d) models for different adcluster morphologies.

(only in plane coordination is counted). To build the decorated cluster, we choose the diameter of the Kr atoms equal to 4.0 Å, corresponding to the Kr lattice constant of a monolayer. This is a reasonable assumption, since we found that the lattice constant of the Kr atoms on step edges changes only very slightly compared to that of islands on terraces. Within these assumptions, which correspond to model 1 in Fig. 3d, we need 12 Kr atoms to decorate the cluster. This model fits nicely the STM image shown in Fig. 3a. See also Fig. 3c, where we have superposed a 19 atom regular hexagon in epitaxy with the Pt(111) underlying substrate.

However, the resolution of the STM image cannot exclude model 2 in Fig. 3d, i.e., a regular hexagon with one atom missing. We show below (see Fig. 4) that this case can be excluded by redepositing Kr on top of the cluster. The Kr necklace is sensitive to the shape of the island. For example, model 3 corresponds to a 19 atom island with an irregular shape: 13 Kr atoms are needed. The observation that most clusters reach an equilibrium shape means that either the energy barrier for a transition from an irregular to a regular shape is small, or that the “shape energy” which is released when the cluster comes into contact with the surface [22] allows the cluster to transform immediately into its energetically favorable form. We believe that the latter is true since it has been shown [20] that a structural change of the cluster by edge diffusion is frozen at the temperatures considered. That only about 70% of the clusters show a 12 atom ring arises from uncompleted dressing of the cluster and from fragmentation into smaller clusters.

The hexagonal morphology of a 19 Ag atom island is further supported by the following experiment. We first raise the temperature of the substrate to 140 K, in order to evaporate all Kr atoms, and then redeposit Kr during cooldown. We expect that during redeposition the rare gas atoms move freely on the Pt surface, first attach to the

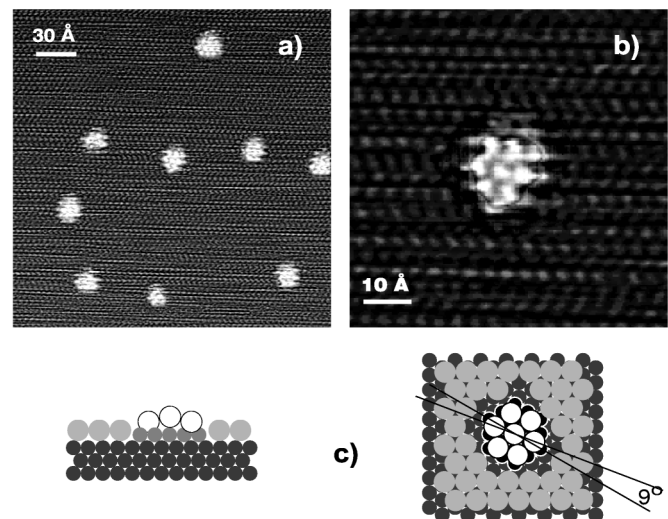


FIG. 4. Kr redeposited on top of Ag_{19} : (a) overview $I = 430$ pA, $V_{\text{bias}} = -210$ mV; (b) zoom in; (c) model proposed.

metallic step edges (this is the situation of Fig. 2c), and when these are saturated attach to the step edges formed by the condensed rare gas and gradually build a full monolayer. At the same time Kr atoms condense on top of the 2D silver islands, adjusting themselves in a minimum energy configuration. This is the experiment described in Fig. 4. The Kr monolayer on top of Pt(111) together with some Ag clusters is shown in Fig. 4a; a magnification of one of the clusters is given in Fig. 4b. 7 Kr atoms forming a centered hexagon are accommodated on top of a Ag island. We also observe that the hexagon is rotated by about 7° compared to the crystallographic direction of Pt(111). Notice also that the height distribution (see Fig. 2d) has a maximum at the physical height of a 2D silver island. These observations can be nicely explained within a simple hard sphere model. We assume that the 19 atom island has the shape of a regular hexagon and place the Kr atoms at the minimum energy position on top of the island. One then easily realizes that the hexagon can accommodate only 7 Kr atoms, and that the Kr overlayer should be rotated by approximately 10° with respect to the substrate. Such a model is shown in Fig. 4c. Notice that the center Kr atom has a slightly higher position than the other 6 atoms. This model would also explain the observation of a maximum of the height distribution at the physical height, if we admit that the tunnel current is dominated by the Kr overlayer, whose density of state is smaller than that of the Ag island. If we remove an atom from the Ag hexagon, as was depicted in Fig. 3d(2), the Kr heptamer on the Ag₁₉ terrace becomes very unlikely, since one of the 7 Kr atoms would not be in a stable configuration. This removes the ambiguity between the configurations of Figs. 3d(1) and 3d(2).

In conclusion, imaging of small metal clusters on metal surfaces with atomic resolution has not been achieved up to now, and seems very difficult. We show in this paper that rare gas atoms can be used as a very sensitive probe to determine the morphology of metal adclusters on metal surfaces, circumventing thus the difficulties of a direct observation of the atom position. More specifically we show that by decorating with Kr atoms Ag islands deposited on Pt(111), the Ag atoms in most cases form a 19 atom regular hexagonal island. This opens the possibility to study in detail the deposition process of mass selected clusters in thin rare gas layers, and the transition from very weak to strong cluster surface interaction.

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