



# Crystalline structure and orientation of gold clusters grown in preformed nanometer-sized pits

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## Abstract

Gold clusters were produced by condensing evaporated gold in nanometer-sized preformed pits on the surface of highly oriented pyrolytic graphite (HOPG). The height of the clusters was  $6.7 \pm 0.7$  nm as measured with scanning tunneling microscopy in ultrahigh vacuum, the lateral width was  $10.1 \pm 1.9$  nm as determined with transmission electron microscopy (TEM). Using TEM for electron diffraction, we obtained information on the crystalline structure of the clusters. The intensity of the observed diffraction rings shows the preferential orientation of the clusters with the (111) plane of the gold lattice parallel to the (0001) surface of HOPG. This was compared to the diffraction pattern of gold clusters produced in the gas phase by inert-gas evaporation and deposited on a flat HOPG surface at room temperature as complete units which showed no preferential orientation. The directional alignment in the surface plane as it is described in the literature for larger gold crystallites grown on a flat HOPG surface is not observed for the nanometer-sized clusters grown in pits.

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## 1. Introduction

The properties of clusters, i.e. small particles with a size of a few nanometers, generally differ from the corresponding bulk properties. One feature which is different from the bulk is the crystalline structure of

the clusters. For example, one observes an icosahedral structure for small rare gas clusters, which does not exist as a bulk structure because of its fivefold symmetry, and which finally changes into the fcc structure of the bulk rare gas solid [1]. For metal clusters, both the metallic bond of the free electrons and the lattice of the ion cores determine the cluster structure [2]. If one considers clusters on a substrate, the crystalline structure of the clusters can be strongly influenced by the interaction with the substrate. Effects like preferential orientation or epitaxial growth of the clusters on the substrate may be observed. This can be compared to the corresponding thin film

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deposition of the cluster material on the same substrate. In addition to a dependence on the deposition parameters (like e.g. temperature) there will be a dependence on cluster size for the cluster–substrate interaction. Also it may be an important difference whether the clusters are deposited as complete units or whether they are grown by the condensation of atoms on the substrate.

Using a surface of highly oriented pyrolytic graphite (HOPG) with preformed nanometer-sized pits we were able to produce metal clusters by condensation of the evaporated cluster material in the pits. The three-dimensional shape of the clusters could be measured with a combination of scanning tunneling microscopy in ultrahigh vacuum (UHV-STM) and transmission electron microscopy (TEM). The cluster size proved to be very uniform [3].

Because the sample surface was covered homogeneously with about  $5 \times 10^{10}$  clusters/cm<sup>2</sup> we were able to use TEM also for electron diffraction. Thus, we obtained information on the crystalline structure of the clusters and their orientation relative to the substrate. We compared the findings with the electron diffraction pattern of gold clusters which were produced by inert-gas evaporation [4] and deposited as complete units on a HOPG surface.

## 2. Results and discussion

The preparation of the cluster samples is described in detail elsewhere [3], so we will give only a short summary of the preparation method. On a freshly tape-cleaved HOPG surface we produced about  $5 \times 10^2$  surface defects per  $\mu\text{m}^2$  by sputtering with Ne ions of 1 keV kinetic energy. Then we heated the samples in air at a temperature of 530°C for 20 min. In this way we oxidized the defects to small pits with diameters of  $5 \pm 2$  nm and a depth of one monolayer [5]. The evaporation of gold on this nanostructured surface at a substrate temperature of 600°C resulted in the condensation of gold clusters in the pits. Cluster production by evaporation of the cluster material onto the HOPG surface with preformed pits is compatible with UHV conditions. This should allow the use of a broad range of cluster materials. We have hitherto been restricted to the noble metals silver and gold [3] only because we

evaporated the metal in the load-lock chamber of our system, which had a base pressure of about  $10^{-6}$  mbar. The fixation of the clusters to the pits enabled to image the clusters using a UHV-STM without displacing them by the STM-tip (Fig. 1). In the STM image we evaluated the height distribution of the clusters, which proved to be very uniform. The mean height and its standard deviation is  $6.7 \pm 0.7$  nm. The width of the clusters measured with STM is influenced by the convolution with the tip shape, as proved by TEM which could be performed on the same cluster sample, after thinning the HOPG from the backside to a thickness of about 100 nm. The TEM image (Fig. 2) shows the lateral size of the clusters, which also proved to be rather uniform with a mean cluster diameter of  $10.1 \pm 1.9$  nm. We have indicated the mean cluster diameter measured with TEM in the line profile of the STM image (Fig. 1),

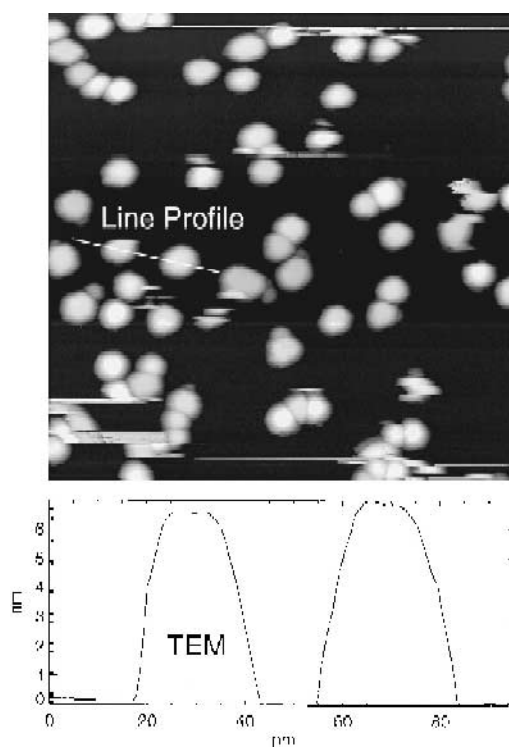


Fig. 1. Gold clusters produced by the condensation of the evaporated metal in preformed nanometer-sized pits on the surface of HOPG. Topology ( $300 \times 300 \text{ nm}^2$ ) and line profile were measured with UHV-STM. The horizontal bar inserted into the line profile indicates the mean lateral diameter as measured with TEM (Fig. 2) to illustrate the influence of the tip shape.

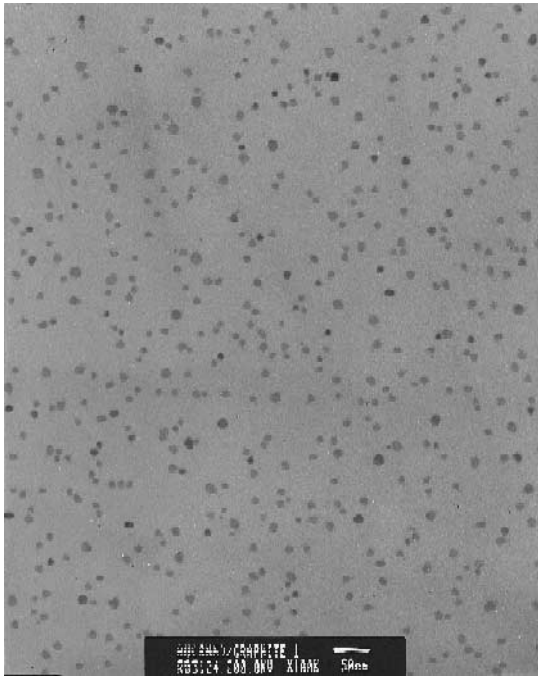


Fig. 2. TEM image of the same sample with gold clusters as in Fig. 1 taken after thinning the HOPG from the backside. This image allowed the lateral diameter of the clusters to be evaluated, which, together with the cluster height measured with UHV-STM, yields the three-dimensional shape of the clusters.

which illustrates the effect of the convolution with the tip shape.

With  $5 \times 10^2$  clusters per  $\mu\text{m}^2$  there was enough gold on the surface to use the TEM also for electron diffraction. The diffraction pattern is shown in Fig. 3 on the left side. The oriented HOPG lattice gives sharp diffraction spots. The gold clusters contribute with diffraction rings.

But before discussing the left side of Fig. 3, we explain the right side of Fig. 3. It shows the diffraction pattern for gold clusters which we produced for comparison with inert-gas evaporation [4] and deposited them on a flat HOPG surface without pits. The deposition was performed at room temperature. Elevated substrate temperatures could not be used in this experiment, as it would have caused significant coalescence due to the high mobility of the clusters on the flat HOPG surface. For these clusters, produced in the gas phase and then deposited as complete units on the HOPG, the cluster size was not as

uniform as for the clusters grown in the pits. The lateral diameter was  $10 \pm 5$  nm. This broad size distribution may be an indication that some diffusion and aggregation of the clusters has occurred after the deposition process. However, this does obviously not change the random orientation of the clusters, because the diffraction rings have the typical intensity for clusters without a preferential orientation (see for example the electron diffraction patterns shown in Ref. [6]). The (111) ring has the highest intensity and with significantly decreased intensity one can observe the (200), (220), (311) and (222) rings.

In contrast, the diffraction rings for the gold clusters condensed in the nanometer-sized pits (Fig. 3 left) show a totally different behavior. The most intense ring belongs to (220), while the (111) ring is much weaker. Additionally, we notice the high index (422) and (440) rings which have already very low intensity for the clusters produced by inert-gas evaporation. This shows that the clusters grown in the pits are oriented with their (111) plane parallel to the HOPG (0001) surface. The high energy electrons in TEM are reflected at the lattice planes almost in grazing incidence. Therefore, only lattice planes perpendicular to the sample surface contribute to the diffraction pattern. The (220), (422) and (440) diffraction rings are the first three belonging to lattice planes perpendicular to the (111) plane. The diffraction rings have only a slight intensity variation in angular direction. This shows that there is no

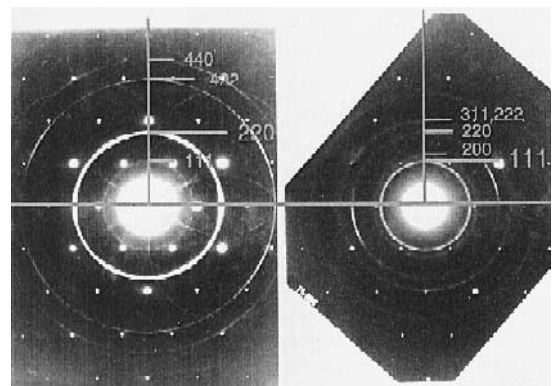


Fig. 3. Electron diffraction pattern of gold clusters on HOPG. Left: clusters grown in nanometer-sized pits, right: clusters produced by gas aggregation and deposited on a flat HOPG surface. The intensity of the gold diffraction rings is marked with the length of the horizontal bars.

significant alignment of the cluster lattice structure in the substrate plane.

The oriented growth of the gold clusters in the nanometer-sized pits can also be compared to the growth of island-films by evaporation of gold atoms on a flat HOPG surface, which is described in Ref. [7]. The effect of temperature and substrate condition (air cleaved or vacuum cleaved HOPG samples) on the resulting topology and crystalline structure of the gold films were investigated. A significant difference was observed for air cleaved and vacuum cleaved samples for an evaporation at room temperature, but this became less noticeable for increased substrate temperatures (in Ref. [7] temperatures up to 450°C were used), because of the desorption of adsorbates which cover the air cleaved samples at room temperature. The gold clusters in the pits were grown at a high substrate temperature of 600°C, so the HOPG surface was almost free of adsorbates before the gold evaporation, although we cleaved the samples in air. At all substrate temperatures described in Ref. [7] the (111) lattice planes of gold were parallel to the (0001) surface of HOPG. An alignment of the  $[01\bar{1}]_{\text{Au}}$  with the  $[10\bar{1}0]_{\text{HOPG}}$  direction was observed for the vacuum cleaved samples, almost perfectly at high temperatures and becoming progressively worse as the substrate temperature was decreased below room temperature. But even at  $-52^{\circ}\text{C}$  the alignment in the substrate plane was stronger than for the gold clusters of our experiment. An observation of  $(111)_{\text{Au}} \parallel (0001)_{\text{HOPG}}$  orientation without directional alignment in the substrate plane is described in Ref. [7] for the air cleaved samples at room temperature and with a small gold coverage. In this case small gold particles  $< 10$  nm have grown, probably due to the condensation with adsorbates acting as nucleation centers.

### 3. Conclusion

Gold clusters of about 10 nm size on a HOPG substrate showed significant differences in their crystalline orientation depending on the way they were produced. Clusters formed by inert-gas evaporation and deposited as complete units on the HOPG surface at room temperature had no preferential orientation on the substrate. Clusters grown by condensa-

tion of evaporated metal in preformed nanometer-sized pits on the HOPG surface at a temperature of 600°C were oriented with the (111) plane parallel to the (0001) HOPG surface.

Without the fixation in the pits the substrate temperature used for the growth of the gold clusters would result in large gold particles even if small clusters were deposited, because of coalescence due to the high mobility of the clusters on HOPG. The crystalline orientation of the clusters and the stability even at elevated temperatures may be an additional experimental advantage of the presented sample system.

A directional alignment in the surface plane which is described for larger gold islands on HOPG, however, was not observed for the clusters. One can assume that the orientation of the (111) plane parallel to the substrate is a general feature which occurs also for small particles, whilst the directional alignment in the substrate plane only occurs if a long range periodicity is acting on a larger contact area.

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