

# Atomic force microscopy study of Pd clusters on graphite and mica

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We report on a growth of single crystals of Pd clusters on highly oriented pyrolytic graphite (HOPG) and mica. On HOPG, edges of the clusters were parallel to the imaged substrate atom rows. On mica, both clusters with edges parallel to and 30° off from the imaged atom rows were observed. The atomic resolution with a separation of 0.28 nm on Pd clusters on mica was obtained with atomic force microscopy (AFM). We propose structural models for the epitaxial nature of Pd on HOPG and mica.

## I. INTRODUCTION

Palladium metal can absorb a huge amount of hydrogen at room temperature, which attracts great interest in the field of both science and technology. The hydrogen state in Pd has been studied in terms of volume change and electronic and magnetic properties.<sup>1-4</sup> Recently, there are few reports<sup>5,6</sup> on the microscopical study of a Pd single crystal by using scanning tunneling microscopy (STM).<sup>7</sup> A sulfur overlayer was found to be reconstructed on Pd surface but Pd atoms were difficult to image.<sup>5,6</sup>

To understand how the hydrogen absorption changes the property of Pd on an atomic scale, we have started to fabricate single crystals of Pd clusters and to measure the structures by using atomic force microscopy (AFM).<sup>8</sup> In this study, we concentrated on Pd clusters fabricated on highly oriented pyrolytic graphite (HOPG) and mica substrates. We report on the epitaxial growth of Pd on HOPG and mica and discuss its growth mechanism.

## II. EXPERIMENT

Samples were fabricated by evaporating Pd onto HOPG or mica substrates in an ultrahigh vacuum (UHV) chamber with a base pressure of  $1 \times 10^{-10}$  Torr. After being cleaved in air, the substrate was set on a holder in the chamber and was heated gradually up to 500 °C. The substrate was kept at this temperature for 5–10 h during which the substrate was flashed up to 800 °C several times. This cleaning procedure resulted in a pressure of  $5 \times 10^{-10}$  Torr even when the substrate was kept at 500 °C. Then we deposited Pd onto the substrate by heating a tungsten wire on which a thin Pd wire was wrapped. During the deposition, the pressure was kept at  $5 \times 10^{-8}$  Torr. A typical deposition rate was about 1.5 nm/min and the deposited Pd thickness was about 10 nm as measured by a quartz crystal thickness monitor. After the deposition, the sample was cooled to room temperature in a natural way by switching off the heating source. Then the sample was taken out for AFM measurements in air.

We used an AFM (SPA300, Seiko Instruments, Inc.) system with a quadrant photodetector in order to measure both

normal and lateral forces<sup>9</sup> with a microfabricated Si<sub>3</sub>N<sub>4</sub> cantilever, whose spring constant was 0.1 N/m (Olympus Opt. Co., Ltd.). The AFM images were taken with constant force of about 10 nN in air at room temperature. Typical humidity was about 60% in our laboratory.

## III. RESULTS AND DISCUSSION

### A. Pd on HOPG

We show results of Pd clusters on HOPG. A typical AFM topographic image is shown in Fig. 1(a). There appear hexagonal and triangular Pd clusters. A typical hexagonal cluster on the upper half in the figure is 30 nm in height and 100 nm in length. There exists a difference in the thickness between thickness monitor and AFM image due to the fact that the deposited Pd did not form continuous film but clusters leaving some of the HOPG surface uncovered.

It is clear that in Fig. 1(a), top surfaces of Pd clusters are flat and their edges are only in three directions, indicating that single crystals of Pd clusters are formed with a strong influence from the HOPG surface. In order to make clear the relation of the edges of the Pd clusters to the atomic structure on the HOPG surface, we took a lateral force image on the substrate just beside a particular Pd cluster. Figure 1(b) shows a low-pass filtered image of the HOPG surface taken at the scanning direction identical to that in Fig. 1(a). The distance between the bright spots in Fig. 1(b) is measured as 0.25 nm, which corresponds to every other carbon atom on the HOPG surface.<sup>10-12</sup> It is clear that the edges of the Pd clusters are parallel to the AFM imaged atom rows of the HOPG surface, indicating an epitaxial growth of Pd(111) on HOPG.

Although no clear atomic resolution on the Pd clusters themselves was obtained at present, we can speculate how Pd atoms locate on the HOPG surface. Provided that Pd atoms locate at the center of the graphite hexagonal unit, the edges of the Pd clusters will become parallel to carbon atom rows in the AFM image. The nearest-neighbor distance between atoms in the bulk of the Pd(111) plane is 0.274 nm, greater than the distance (0.246 nm) between centers of the graphite hexagonal units. Therefore, the initial growth of Pd on the HOPG surface may include some strains in the Pd(111), which favors the form of clusters instead of films. In fact,

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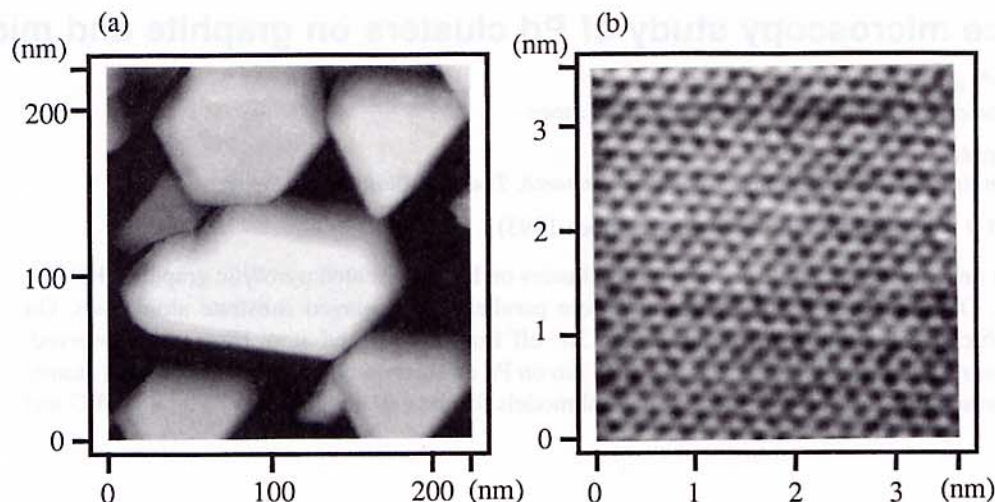


FIG. 1. Topographic AFM image of a Pd on HOPG sample fabricated at 500 °C (a) and lateral force image of the HOPG surface beside a particular Pd cluster (b). The data were taken with a constant force of 10 nN.

Humbert *et al.*<sup>13</sup> showed that Pd atoms exhibited a hexagonal lattice with a nearest-neighbor distance of 0.426 nm, where the Pd lattice was 30° rotated from the graphite lattice in their STM image. Their result indicates that initial Pd atoms occupy centers of the hexagonal units in a way leaving their six nearest-neighbor centers empty. It is conceivable that during the increase of Pd atoms, all centers will be occupied. At the interface of Pd on HOPG, there could be some strains due to the difference between the lattice distances mentioned above. During the growth of the Pd cluster, the lattice distance will relax to that of the bulk crystal plane.

## B. Pd on mica

We also performed experiments on mica because it is used as the flat substrate for the growth of various kinds of materials.<sup>14–16</sup> Mica is of a layered structure and the cleaved surface is of atomic flatness, on which oxygen atoms arrange to form nearly hexagonal arrays, resulting in ring structures of oxygen atoms.<sup>17,18</sup> A typical AFM topographic image of the Pd sample on mica is shown in Fig. 2. Hexagonal Pd clusters are also observed but different from those on HOPG. First, the typical size is 6 nm in height and 20 nm in length, about one-fifth of that on HOPG. Second, there exist two types of clusters with edges of 30° off to each other being of six directions in all as labeled by “A” and “B” in Fig. 2.

We measured one of the Pd clusters (A-type) on an atomic scale with a lateral force imaging mode. A raw data is shown in Fig. 3(a) where an atomic resolution is obtained. We note that the distance between bright spots is 0.28 nm which is close to the lattice distance (0.274 nm) of the Pd(111) crystal. To confirm that this image of Pd was not an artifact, we moved the position to image the mica surface immediately. Figure 3(b) shows the image of the mica surface, indicating a distance of 0.54 nm between bright spots. Therefore, we are quite convinced that the measured atomic image shown in Fig. 3(a) is not an artifact but Pd atom’s image.

Recently, there are reports on sulfur effects on Pd single crystals.<sup>5,6</sup> Sulfur atoms are found to be reconstructed on the

Pd surface, resulting in lattice distances of 0.39 nm,<sup>6</sup> much larger than the present distance of 0.28 nm in Fig. 3(a). Therefore, we can conclude that the atom image shown in Fig. 3(a) is due to Pd atoms on Pd(111), not to the possible sulfur contaminations.

Based on the result of Pd clusters shown in Fig. 2 and the atom image of the mica surface in Fig. 3(b), we propose a model for Pd atom’s location on mica surface. An idealized mica surface is shown in Fig. 4 where ring structures are formed by oxygen atoms (open circles).<sup>17</sup> We note that the distance between the center of the ring structure is 0.54 nm which is equal to the distance between the bright spots in Fig. 3(b). Moreover, the bright spots are not due to the individual oxygen atoms but to their groups.<sup>17</sup> Therefore, shadow circles as shown in Fig. 4 could be used to explain

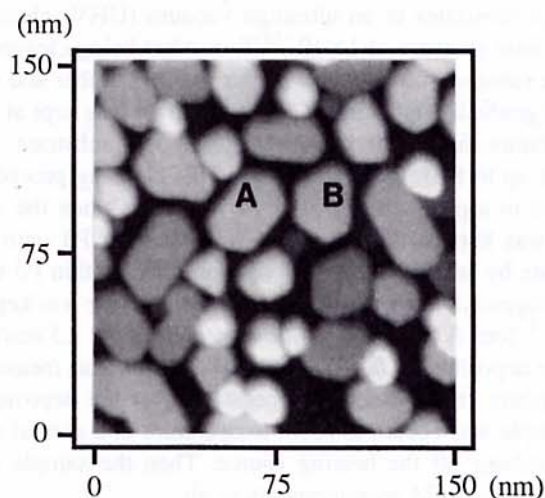


FIG. 2. Topographic AFM image of a Pd on mica sample fabricated at 500 °C. The image was taken with a constant force of 10 nN. There are two types (labeled as A and B) of hexagonal clusters whose edges are 30° off to each other.

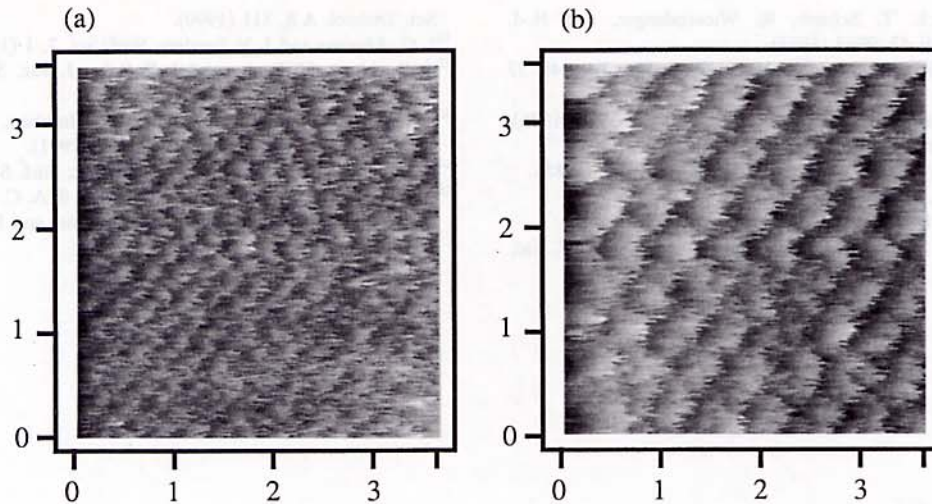


FIG. 3. Lateral force images for Pd on mica (a) and mica surface (b). The images were taken with a constant force of 10 nN. The measured lattice distance is 0.28 nm in (a) and 0.54 nm in (b).

the bright spots in Fig. 3(b) by comparing the AFM image with the oxygen atom's arrays in Fig. 4.

In order to explain the two types of Pd clusters observed in Fig. 2, we consider some possible locations of Pd atoms on mica. Provided that Pd atoms (black circles) initially locate at all of the positions of hexagonal ring structure and at centers of the hexagons, then the edges of the formed Pd clusters will be  $30^\circ$  off from the AFM imaged bright spots. This configuration corresponds to the B type of Pd clusters shown in Fig. 2, but needs the initial Pd atoms located 0.31 nm away from each other on the mica surface, greater than the Pd(111) bulk lattice distance. In another possible location of Pd atoms on mica, Pd atoms occupy two types of sites: (1)

the sites where oxygen atoms are not imaged; (2) the sites that form an equilateral triangle centered where the oxygen atom groups are imaged as bright spots. In this configuration the distance between Pd atoms is 0.27 nm, close to the Pd(111) bulk lattice distance. This configuration corresponds to the A type of Pd clusters shown in Fig. 2, on which an atomic resolution has been obtained as shown in Fig. 3(a) with a lattice distance of 0.28 nm. However, an image, in which both the Pd cluster and mica surface are of atomic resolution, has to be measured for confirming this model shown in Fig. 4.

#### IV. CONCLUSIONS

The edges of single crystals of the Pd clusters are parallel to the imaged carbon lattice on HOPG but parallel to or  $30^\circ$  off from the imaged oxygen group lattice on mica. On a Pd cluster on mica, Pd atoms image with a lattice distance of 0.28 nm was obtained. The reason for the difference of Pd clusters on the two substrates is tentatively attributed to the different distances between centers of their hexagonal units. We can speculate that there are more kinds of sites for Pd atoms to locate on the surface of mica than on that of HOPG.

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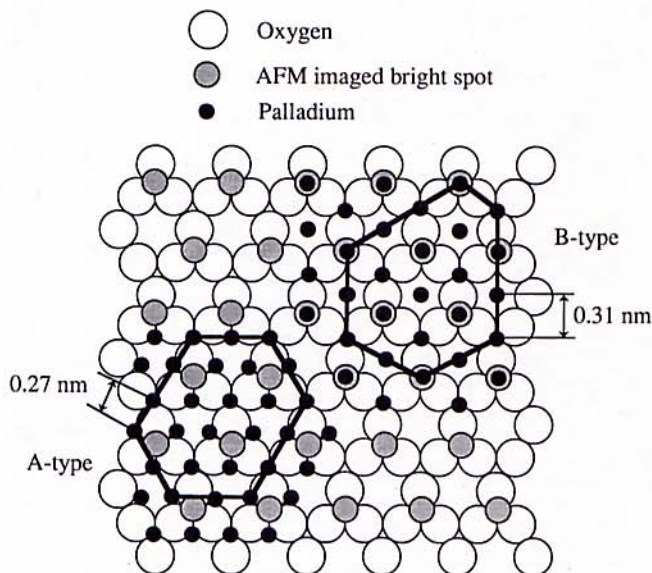


FIG. 4. A model for Pd location on mica. Open circles are depicted for oxygen atoms of mica, shadow circles for AFM imaged bright spots, and black circles for Pd atoms, respectively. Two types (A and B) of Pd clusters are illustrated in the figure.

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