STM Study on Nanostructures of Au and Al Deposits on HOPG and Amorphous Carbon[†]

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Initial growth of gold and aluminum nanoclusters on highly oriented pyrolytic graphite (HOPG) or amorphous carbon are investigated using scanning tunneling microscopy. A 2-dimensional hexagonal lattice is formed on HOPG. Such 2-dimensional nanoclusters are oriented to the direction rotated by 30° from graphite lattice, and the atomic distance of the nanoclusters is estimated to be 0.424 nm. The nanoclusters are linked with each other along the directions mentioned above when deposited atoms migrate on the HOPG surface at room temperature.

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I. Introduction

Metal nanoclusters are studied for catalysis application⁽¹⁾, spontaneous alloying⁽²⁾, electronic devices, conducting lines⁽³⁾, and so on, because of their dramatic changes of properties different from the bulk metals. Recently, Hu and Blanckenhagen⁽⁴⁾ have reported a construction of Al nanolines with a width of several ten nm and a length of 400 nm on Si(111) surface, by using an STM deposition method: the line to line separation is 20 nm. In order to apply such nanostructure materials to nanodevices, the size and shape of nanostructures should be controlled, being isolated perfectly without any connections of deposited atoms among them.

Metal nanoclusters on a highly oriented pyrolytic graphite (HOPG) have been studied using scanning tunneling microscopy and spectroscopy (STM/STS). Gantz *et al.*⁽⁵⁾ have reported the 2-dimensional rectangular Ag and Au atoms arrays with 4 nm-diameter on HOPG. On the other hand, Humbert⁽⁶⁾ has observed the 2-dimensional hexagonal Pd lattice on HOPG with the lattice direction rotated by 30° from the graphite lattice. They have also shown the pseudo hexagonal or triangular shapes of 3-dimensional Pd nanoclusters with comparably large sizes of 10–40 nm.

Above mentioned results indicate that the growth process of metal nanoclusters is important for the formation of sharp and separated nanostructures of metal clusters or metal lines on substrates⁽⁷⁾. In this study, we examine the initial nucleation stage of metal nanostructures and their linking process on HOPG, with atomic

resolutions.

II. Experiment

An ultra high vacuum STM/STS system has been designed specially to be workable at low temperature and in ultra high vacuum⁽⁸⁾. A chamber is evacuated by a rotary- and cryo-pump system, with which it is possible to obtain an environment of 10⁻⁸ Pa. A tunneling unit (shown in Fig. 1) of cylindrical type made of machineable ceramics is settled on a vibration-free system supported by the elastic metal pins through the fibrous ceramics in the chamber. A rough approach between a sample and tunneling tip is attained by an ultra high vacuum inchworm motor with a total travel of 15 mm, from Burleigh Instrument, Inc.

A pulse laser beam was passed through the inner side of the tunneling unit from a window equipped on the chamber and was radiated on a target for a laser ablation of materials, as shown in Fig. 1. The pulse laser is a solid state Nd:GGG with the wavelength of 1.06 μm, pulse energy of 20 mJ and repetition rate of 1–40 s.

Au and Al clusters were deposited in a vacuum of about 10⁻⁷ Pa at room temperature. The laser beam is focused on an Au or Al target with a spot in diameter of about 4 mm². The energy density of the pulse beam on the target is varied by the spot diameter. The target with a short coiled shape is made of a pure gold (99.999%) or a highly pure Al (99.9999%) wire in diameter of 0.2 mm, which is attached near a substrate. The substrate, which is HOPG or amorphous carbon, and the tip are settled without exposure to the pulse laser beam and the deposited metal cluster flow. Laser beams were, initially, shot by 5 times, and succeeding shots were performed for the further coverage of clusters on the substrate, if

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Fig. 1 Tunneling unit in the present scanning tunneling microscopy: The unit is a cylindrical type and a rough approach is attained by an inchworm motor. A pulse laser beam was passed through the inner cylinder for the laser ablation.

necessary.

For an observation by STM, images were taken in a condition of the constant current mode and the tunneling bias of 50 mV, using a tunneling tip of Pt-Ir. Samples were observed while the vacuum pump was inoperative to avoid mechanical noise. There are no differences in the resolution of images originated from the vacuum rate.

III. Results and Discussion

Previously, we have shown an STM image of Au nanoclusters on HOPG, a typical example of which is shown in Fig. 2 (scanning area: $8.4 \times 8.4 \text{ nm}^2$)⁽⁹⁾. In the figure, atomic configurations of the graphite lattice are observed at the upper side of the figure, and at the half lower side, small 2- and 3-dimensional Au nanoclusters are seen. In the area, 2-dimensional hexagonal lattices are observable, and an example of which is marked by small dots in the figure. The Au atom arrays are oriented to the directions rotated by 30° from graphite lattice. The atomic distances between Au atoms are estimated to be 0.424 nm in this work. These results are consistent with those of Humbert *et al.* for Pd nanoclusters on HOPG⁽⁵⁾.

From these results, the atomic configuration of 2-dimensional Au nanoclusters is ascribed to epitaxial growth on HOPG, as illustrated in Fig. 3. In this figure, the small gray circles indicate the graphite atoms to be observable by STM and the large gray ones indicate the Au atoms sited on HOPG lattices. A hexagonal structure of Au nanoclusters, as is shown in Fig. 2, is indicated by solid lines connected among the 6 Au-atoms in the figure. Epitaxial alignments of Au atoms grow to the directions along these lines. Such an alignment suggests that nanoclusters are enlarged into a large 3-dimensional

Fig. 2 STM image of 2- and 3-dimensional nanoclusters of Au on HOPG: Inset are the atomic configurations of HOPG surface with the same sized scanning area ($8.4 \times 8.4 \text{ nm}^2$).

Fig. 3 Illustration for atomic configurations of 2-dimensional Au nanoclusters on HOPG. $\bullet$: Au atoms, $\circ$: graphite atoms observable by STM.

cluster in the pseudo-hexagonal shape at high coverage of Au, as shown for Pd by Humbert *et al.*⁽⁶⁾ and Kojima & Kurahashi⁽¹⁰⁾. Indeed, a hexagonal shape large cluster is also observed in this work.

In Fig. 4, where the whole scanning area is the same with that in Fig. 2, many nanoclusters with a diameter of about several nm and a height of several atomic layers are seen. The lower left hand side in this figure is a region of graphite lattice. In this work, Au atoms are elongated to the sites of Au atoms indicated in Fig. 3, and several nanoclusters are linked with each other through the 2-dimensional nanoclusters, as shown in Fig. 4. These results mean that the Au atoms migrate on the HOPG surface at room temperature. The directions of Au nanoclusters in the figure are consistent with any directions of 6 atom sides of the hexagon indicated in Fig. 3.

The initial nucleation of 2-dimensional nanoclusters of Al on HOPG is the same to that of Au atoms, as shown in Fig. 5. The hexagonal structures of 2-dimensional Al nanoclusters and atomic arrays are oriented to the directions rotated by 30° from graphite lattice. The 2-

Fig. 4 3-dimensional Au nanoclusters on HOPG linked with each other through the 2-dimensional nanoclusters at room temperature. The scanning area is $8.4 \times 8.4 \text{ nm}^2$.

Fig. 5 3-dimensional Al nanoclusters on HOPG linked with each other through the 2-dimensional nanoclusters at room temperature. The scanning area is $8.4 \times 8.4 \text{ nm}^2$.

dimensional Al nanoclusters in Fig. 5 are spread more widely over the HOPG surface in comparison with the 2-dimensional Au nanoclusters in Fig. 2.

Atomic configurations at around an isolated Al nanocluster on HOPG are shown in Fig. 6. In this figure, 2-dimensional atomic configurations with hexagonal arrays are seen around the hemispherical 3-dimensional Al nanocluster. Since the scanning area of STM is not exactly the same between x- and y-directions, the angles of the hexagon are not 120° exactly. The 2-dimensional spreading of Al atoms at around the cluster is 3 times wider than those in the distant area.

Metal nanoclusters are epitaxially spread over the crystalline surface at room temperature by migrating of deposited atoms. In order to understand the effect of atom migration on the cluster growth mode, Au nanoclusters were deposited on amorphous carbon. An

Fig. 6 2-dimensional atomic configurations of Al around an isolated 3-dimensional nanoclusters of Al on HOPG. Hexagonal arrays of Al atoms are seen around the 3-dimensional nanocluster. The scanning area is $8.4 \times 8.4 \text{ nm}^2$.

Fig. 7 3-dimensional Al nanoclusters on amorphous carbon. On the amorphous carbon, 2-dimensional nanoclusters are almost unobservable. The scanning area is $8.4 \times 8.4 \text{ nm}^2$.

example of STM image is shown in Fig. 7, where the whole scanning area is the same to that of Fig. 2. Many small 3-dimensional Au, nanoclusters are found in the figure. The 3-dimensional nanoclusters in Fig. 7 are larger than the 3-dimensional nanoclusters in Fig. 2, though their deposition conditions are the same. In STM observations, it is difficult to detect the atomic configurations situated at the bottoms of the rough surface originated from the large 3-dimensional clusters as shown in Fig. 7. Even in this limitation, the 2-dimensional nanoclusters or nanoclusters linked through the 2-dimensional nanostructures of Au atoms can not be

found on amorphous carbon in Fig. 7. We also detected the decrease in the 3-dimensional cluster size on HOPG after exposing at room temperature for several days, but not on amorphous carbon. Therefore, it is reasonable to conclude that the 2-dimensional Al and Au nanoclusters on HOPG are constructed by migration of deposited atoms over the surface from 3-dimensional clusters.

IV. Conclusions

Au and Al nanoclusters are deposited on HOPG or amorphous carbon surfaces by a laser ablation. On HOPG surface, 2-dimensional epitaxial structures of deposited Au and Al atoms are constructed at around 3-dimensional clusters with a characteristic configuration and orientation. Nanoclusters are linked with each other through the 2-dimensional nanoclusters. On the other hand, nanoclusters on amorphous carbon are isolated with each other without the 2-dimensional nanoclusters, and the 3-dimensional cluster size does not change after exposing at room temperature for several days. These results indicate that the 2-dimensional Al and Au nanoclusters are constructed on HOPG by migration of deposited atoms over the surface from 3-dimensional

clusters.

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