Acta Cryst. (1991). A47, 17-21

Scanning Tunneling Microscopy of the Annealing of a Thin Platinum Film on Highly Oriented Pyrolytic Graphite

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(*Received* 24 *July* 1990; *accepted* 7 *August* 1990)

Abstract

Scanning tunneling microscopy (STM) was used to study morphological changes of a Pt thin film deposited on highly oriented pyrolytic graphite (HOPG) during an annealing process. In air, it was possible to image the morphology of the thin film with a vertical resolution of 0·5 Å and a lateral resolution of 20 Å. Surface structural change was observed after the annealing processes. When the annealing temperature was below 573 K, surface morphology changed only slightly. Between 573 and 873 K, the originally uniformly distributed rolling hills of Pt coagulated into larger clumps. Above 873 K, Pt crystal facets started to form on the surface. At 1123 K, a large portion of the surface turned into well defined Pt crystal facets. Above 1123 K, the Pt film started to crack and formed scattered crystals on the HOPG surface. A complementary X-ray diffraction measurement showed that the crystallized Pt film was preferentially oriented with the (111) plane parallel to the substrate graphite (0001) basal plane, indicating epitaxy of the Pt overlayer with the graphite substrate underneath.

Introduction

Scanning tunneling microscopy is a prominent tool for studying the morphology of conducting surfaces with high spatial resolution (Binnig, Rohrer, Gerber & Weibel, 1982*a*, *b*). It has been proven that STM can be useful in studying epitaxic growth of an Au(111) thin film on mica (Chidsey, Loiacono, Sleator & Nakahara, 1988). Surface features such as monoatomic steps, dislocations and grain boundaries were studied against various deposition conditions. There is even a report of observation of atomic corrugation on an Au(111) thin film (Hallmark, Chiang, Ravolt, Swalen & Wilson, 1987).

The present study was motivated by the desire to reveal the presence of so-called surface sites, which according to Somorjai (1981) are such surface structures as terraces, steps and kinks *etc.*, on metal catalysts. We have made an attempt to study these surface structures with STM. The present report is about an unprecedentedly detailed observation of surface structural changes of a Pt thin film deposited on HOPG during an annealing process.

Experimental

Platinum films to 300 Å were deposited on newly cleaved HOPG (ZYX, from Union Carbide) by electron beam evaporation. Deposition background pressure was $1{\cdot}3\times10^{-7}$ Pa, deposition rate was 1 Å s^{-1} with source-substrate distance of 15 in, and the substrate was at room temperature at the beginning of the deposition.

Annealing processes were performed in a quartz furnace in hydrogen atmosphere. The hydrogen (99·999% from Air Products) was prepurified by passing through a series of columns filled with activated carbon, 13 AX molecular sieve, and 5 Å molecular sieve in sequence. The columns were immersed in liquid nitrogen to remove any oxygen, carbon dioxide and water residues (Goethwl & Yang, 1986). To prevent oxidation of graphite by residual oxygen on the Pt surface, the temperature was always increased slowly at the beginning of each annealing process.

STM images were collected by using a commercial unit, LK1000 from L. K. Technologies. This unit utilizes a tubular piezoelectric element as scanner, a proportional-integral (PI) type of servo module for *z*-position control, and a 286-AT IBM compatible computer for data acquisition and image display. Our version of the instrument has a maximum scan area of 3000×3000 Å. Images taken in this study contain 256×256 points in each frame. Mechanically formed platinum/iridium (90/10) tips were used.

Samples were scanned immediately after being taken out of the deposition chamber and/or annealing furnace. However, we found that even if the samples were exposed to air for two days, images of good quality could still be obtained. This indicates that, for the resolutions we used in this study, surface oxide and other contaminations have a relatively weak effect on STM imaging. All the images were obtained with samples positively biased at 35 mV and a tunneling current of 0·1 to 0·5 nA. Higher current was found to increase high-frequency noise level. Scan speed was adjusted between 1000 and 3000 Å s^{-1}.

X-ray diffraction was performed on a powder diffractometer using Cu $K\alpha$ radiation.

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0108-7673/91/010017-05$03.00

Results

Fig. 1 shows an image of a Pt film with thickness of 300 Å before any annealing treatment. The surface is fully covered by uniformly distributed rolling hills with vertical variation of 20 to 35 Å. These hills appear ellipsoidal in shape. Similar shapes, though less pronounced, were observed by Komiyama, Morita & Mikoshiba (1988) on colloidal gold particles. They attribute this to movement of the gold particles during the scanning. They also indicated the possibility of particle coagulation and coupled x and y piezo movements. In the present study, the top layer is a continuous film of 300 Å thickness. Therefore, the movement of the top layer is unlikely. By examining a large collection of HOPG images with atomic resolution, we determined that there is a counter-clockwise rotation of y axes by 10 to 15° in the xy plane in our instrument. This would make a sphere appear as an ellipsoid with a long-to-short-axis ratio of 1·1 to 1·2. From Fig. 1, we see that the long-to-short-axis ratio of the ellipsoid is about 2, therefore the ellipsoid shape in the figure is not solely due to instrumental distortion. We compared several samples obtained from different deposition batches and found that the topography of the samples varied from one batch to another. Therefore, the ellipsoidal image shown in Fig. 1 is due to the actual topographic structure of the deposited film, which depends on deposition conditions (Chidsey *et al.*, 1988).

We found that the Pt film was stable and its image was not affected by exposing the sample to air for a period of two days. However, a prolonged exposure of the sample did deteriorate the surface. The change can be seen from STM images. Fig. 2 presents a topograph of a Pt film, with a thickness of 50 Å, which was exposed to air for more than two weeks. The white spots in the image, which were not observed on this sample immediately after Pt deposition, are considered to be due to serious surface contamination which is probably a thick plantinum oxide layer. In addition, we noticed the regular spherical shape of rolling hills in the figure. The images in Figs. 1 and 2 were collected the same day and with the same tip. This fact supports our earlier statement that the ellipsoidal shape in Fig. 1 is not mainly due to instrumental distortion.

Samples were annealed at different temperatures for a fixed period of 3 h. At 373–573 K, no significant change in surface morphology was observed. At 573 K to 873 K, morphological changes were visible. Fig. 3 shows the topography of the same sample as in Fig. 1 after being annealed at 873 K for 3 h. Coagulation is obvious on the surface. However, no crystal facet is observed.

Increasing the annealing temperature caused a dramatic change in surface morphology. Figs. 4(a) and

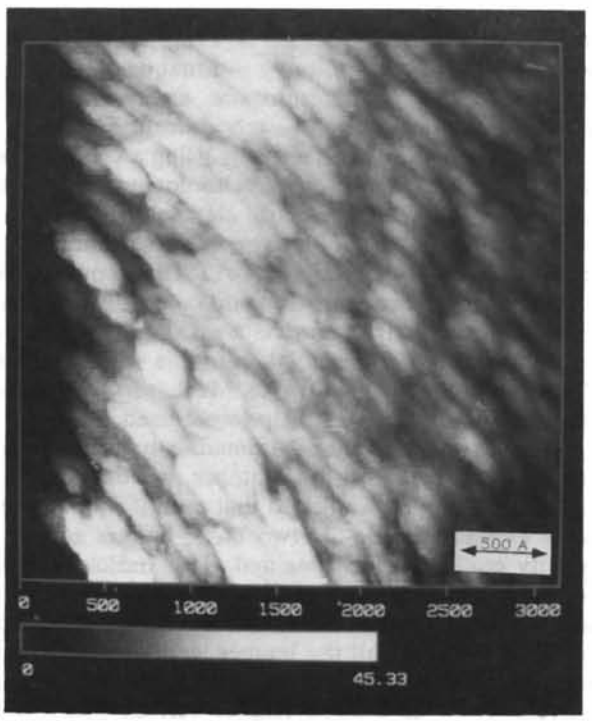

Fig. 1. STM image of a 300 Å Pt thin film on HOPG. The image was taken immediately after deposition. The Z axis, in ångströms, is shown by the gray-scale insert at the bottom of the figure.

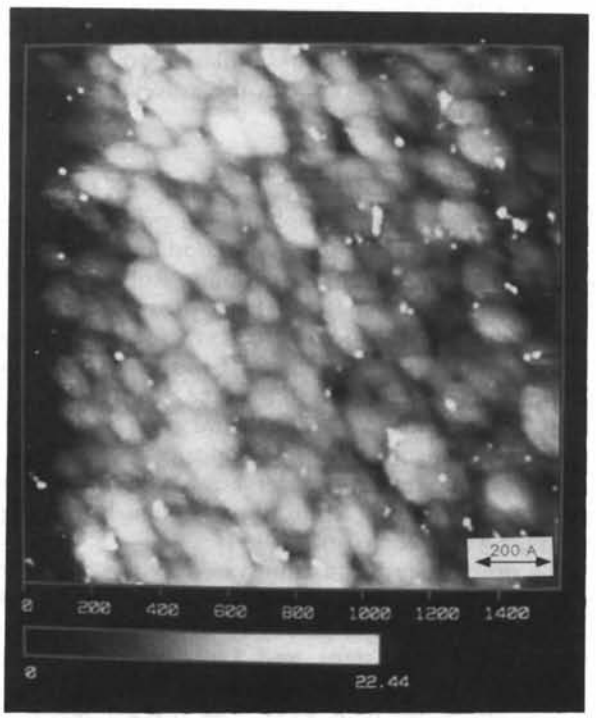

Fig. 2. STM image of a 50 Å Pt thin film on HOPG after being exposed to air for two weeks. The Z axis, in ångströms, is shown by the gray-scale insert at the bottom of the figure.

4(b) are images of a Pt topograph after the sample shown in Fig. 3 was further annealed at 1123 K for another 3 h. In this figure, facets, edges and corners are clearly seen. To demonstrate the ability of STM in revealing detailed surface structures, Fig. 4(b) shows an image that was obtained by zoomed scanning part of the surface shown in Fig. 4(a). The rough surface texture is likely to be due to an overlayer that covers the Pt surface. From random sampling at different locations on the surface, we found that about 50% of the surface was covered with these crystal structures. The rest of the surface was covered with large coagulated rolling hills with diameters over 1500 Å and large crystal-like structures which were too large for our STM instrument to image the whole structure. About 10% of the surface was exposed graphite substrate due to cracking of the originally continuous Pt film.

When the annealing temperature was above 1123 K, crystals with diameters larger than 3000 Å were formed. Fig. 5 was obtained when the sample in Fig. 4 was further annealed at 1273 K for another 3 h. This image is only a portion of a large Pt crystal. Obviously, sintering occurred at this high temperature. Owing to limitation of our STM instrument, we could not scan an area beyond 3000×3000 Å. While it is impossible to tell the shape of the whole crystal, features like facets with 120 and 60° corners are still seen on the surface.

When the Pt film sintered and formed relatively large grains after being treated in H_2 at 1273 K, a large portion of the graphite surface was exposed

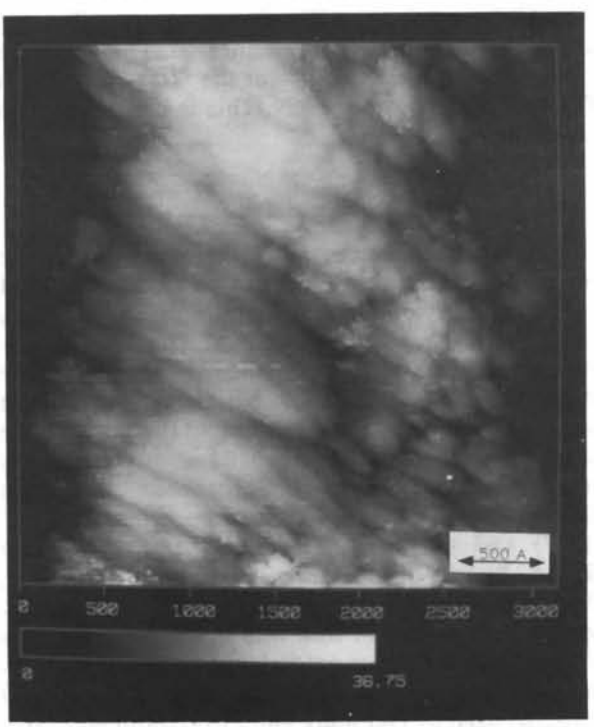

Fig. 3. STM image of a 300 Å Pt thin film on HOPG after being annealed in H_2 at 873 K for 3 h. The Z axis, in ångströms, is shown by the gray-scale insert at the bottom of the figure.

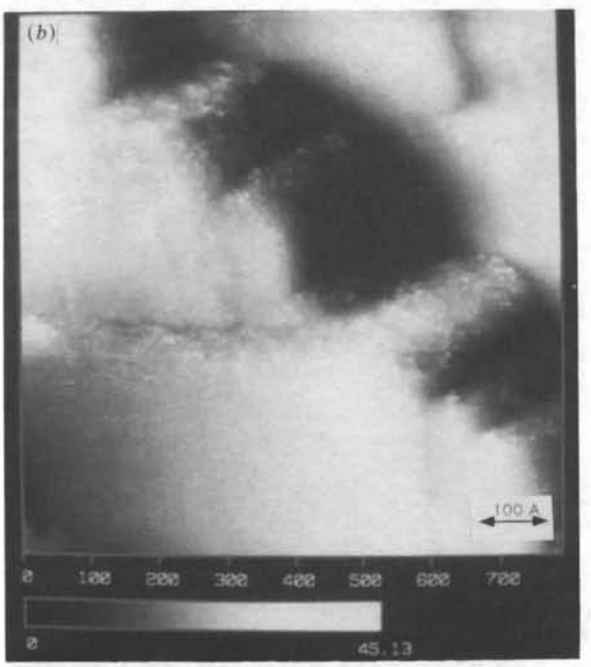

Fig. 4. (a) STM image of a 300 Å Pt thin film of the sample in Fig. 3 after being annealed in H_2 at 1123 K for another 3 h. (b) image of an upper upper-right portion of the area shown in (a). The Z axis, in ångströms, is shown by the gray-scale insert at the bottom of the figure.

On the exposed graphite surface, we observed steps with edges mostly running along the ⟨1120⟩ direction. The step height varied between one to three atomic layers. These steps were produced by the Pt-catalyzed hydrogenation of graphite (Goethwl & Yang, 1986; Santiesteban, Fuentes & Yacaman, 1983). Once again, due to our small scan range of the STM instrument, we could not see the complete channels, which are formed by the movement of Pt grains on the surface during the reaction and have widths of thousands of ångströms according to Goethwl & Yang (1986).

One of the interesting phenomena that we noticed while scanning the Pt surface was the presence of a noise pattern appearing in a line scan signal. This signal is z voltage in a 1D scan. It was obtained by monitoring the z voltage on an oscilloscope without passing through a low-pass filter which was used to smooth the signal going to an A/D converter for computer data acquisition. When the tip was scanning over the Pt surface, the line signal had a high-frequency noise component. At a tunneling current above 0·5 nA, the magnitude of the noise increased as tunneling current was increased, while the envelope of the line signal remained the same. This high-frequency noise appeared on a grey-scale image as very fine bright spots. In contrast with this, when the tip scanned over the graphite surface there was no high-frequency noise appearing in the line scan signal even at a tunneling current above 3 nA. This high-frequency noise in the line scan signal helped us to distinguish the Pt surface from the graphite surface. As for the origin of this noise, we attribute it to an alternation of tunneling to oxide overlayer on the Pt surface and directly to the Pt surface atoms underneath the overlayer. This overlayer was likely to be present because our STM measurement was carried out in air.

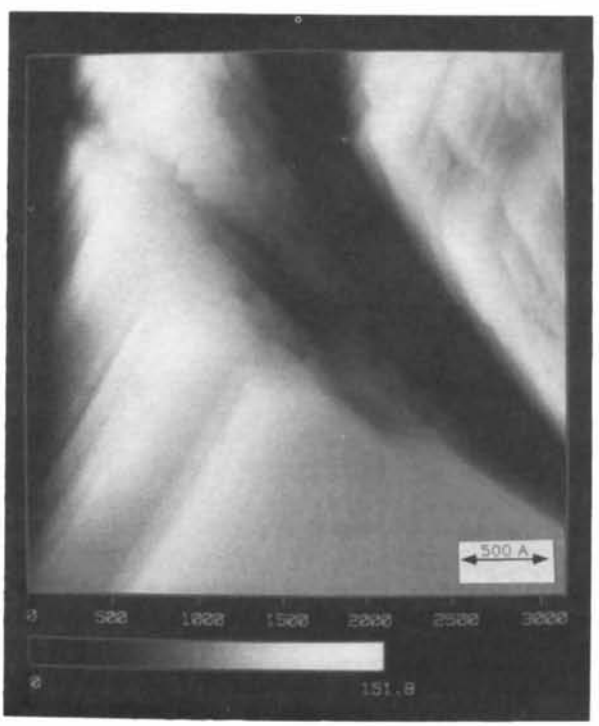

Fig. 5. STM image of a 300 Å Pt thin film of the sample in Fig. 4 after being annealed in H_2 at 1273 K for another 3 h. The Z axis, in ångströms, is shown by the gray-scale insert at the bottom of the figure.

In order to reveal the orientation of the thin crystal film formed by annealing, X-ray diffraction was performed on samples at various annealing stages. X-ray reflections due to graphite (0002) and {0004} were observed at $2\theta = 26{\cdot}58$ and 45·67° on all samples. On a sample without annealing, no measurable reflection due to the Pt crystal lattice was observed. This indicates that the Pt thin film, deposited by electron beam evaporation, is either polycrystalline with very small crystal grains or in an amorphous phase. When the sample was annealed at 873 K, a fairly broad reflection band due to Pt{111} at $2\theta = 39{\cdot}85°$ of moderate intensity was observed and no reflections due to other lattice orientations were seen. When the sample was annealed at 1073 K, very intense and narrow reflection bands of Pt[111] were observed. The bands due to $K\alpha_1$ and $K\alpha_2$ were clearly resolved at $2\theta = 39{\cdot}81$ and 39·91°, indicating the high quality of the Pt crystal. Again, no reflections due to other Pt lattice orientations were obtained. We measured the integrated areas of the reflections bands due to Pt{111} for comparing the degree of crystallization of the thin film after being annealed. The areas are 0·48 and 1·29 counts deg^{-1} for the films annealed at 873 and 1073 K respectively. This is consistent with our STM result.

Discussion

This study has demonstrated that even in air the morphology of Pt thin films can be studied by STM with a regularly obtainable lateral resolution of 20 Å and a vertical resolution of 0·5 Å. The resolution is almost the same as that obtained on a gold surface in air (Chidsey *et al.*, 1988). No atomic corrugation was ever observed on our Pt surfaces though with the same tips we did observe atomic corrugation on a graphite surface. Atomic corrugation has been observed on an Au(111) surface by Hallmark *et al.* (1987) and on Pt(100) by Elrod and co-workers (Elrod, Bryant, de Lozanne, Park, Smith & Quate, 1986). One reason for our inability to observe atomic corrugation on the Pt thin film is the presence of a contamination and/or oxide layer on the Pt surface. We used a much lower tunneling current (0·1–0·5 nA) than that used by Hallmark and Elrod (both are above 5 nA). With such a low tunneling current, we obtained images of the topography of the overlayer. Any attempt to penetrate the overlayer by increasing the

tunneling current caused instability of the tip as evidenced by the appearance of a high-frequency noise in the scan signal.

Our X-ray diffraction results indicate that the orientation of the annealed Pt film is predominantly ⟨111⟩. This is consistent with the fact that the f.c.c. Pt {111} plane has the same symmetry as the underlying graphite (0001) basal plane, therefore appearing to be the favourite plane for epitaxic growth. This result is in disagreement with some of the previous studies of carbon on a Pt surface (Mundschau & Vanselow, 1985; Vanselow & Mundschau, 1986) and Pt on a graphite surface (Santiesteban *et al.*, 1983). In field emission microscopy (FEM) studies, Mundschau & Vanselow (1985; Vanselow & Mundschau, 1986) found that carbon islands preferentially form on the {110} area of Pt. Santiesteban *et al.* deposited Pt particles on a graphite surface and found that about 60% of the Pt particles have (110) faces in contact with the basal plane of graphite. The different orientation of our Pt film on graphite could be due to the difference in preparation methods. In the present study, the Pt coverage started at 100% while in the other studies the starting coverage was much lower. This difference in Pt coverage could play a major role in determining the orientation of the epitaxic layer (Pashley, 1965). In the present study, the metal films were deposited on newly cleaved graphite in a high vacuum system while in Santiesteban's work, no continuous film was formed on graphite and the metal particles were formed by impregnation of $H_2PtCl_6.6H_2O$ followed by reduction in H_2. Understandably, the cleanness of the metal-graphite interface was very different between our sample and Santiesteban's.

We have noticed that ambient atmosphere could have significant effects on the annealing process. A different atmosphere could result in a different crystallization temperature and even a different orientation of the metal film. Further study will follow to investigate the influence of ambient gas on the annealing process. In addition, the azimuthal relation of the Pt film with the substrate will be revealed in future studies.

The last point that we want to raise is a possible usefulness of the crystallized Pt thin film formed in the present study. On a surface such as that shown in Fig. 4 there are varieties of structural features like terraces, edges and corners *etc.* The presence of these features makes the Pt film a candidate for a model catalyst which has properties between single-crystal catalysts due to its richness in surface features. Yet the thin film is clean and, most importantly, can be characterized by using STM and possibly STS (scanning tunneling spectroscopy) to a near atomic scale. A study of the catalytic properties of the thin film is certainly worthwhile.

We thank Dr K. Chang for carrying out the X-ray diffraction measurement.

References

BINNIG, G., ROHRER, H., GERBER, CH, & WEIBEL, E. (1982*a*). *Appl. Phys. Lett.* **40**, 178-180.
BINNIG, G., ROHRER, H., GERBER, CH. & WEIBEL, E. (1982*b*). *Phys. Rev. Lett.* **49**, 57-61.
CHIDSEY, C. E. D., LOIACONO, D. N., SLEATOR, T. & NAKAHARA, S. (1988). *Surf. Sci.* **200**, 45-66
ELROD, S. A., BRYANT, A., DE LOZANNE, A. L., PARK, S., SMITH, D. & QUATE, C. F. (1986). *J. Res. Dev.* **30**(4), 387-394.
GOETHWL, P. J. & YANG, R. T. (1986). *J. Catal.* **101**, 342-351.
HALLMARK, V. M., CHIANG, S., RAVOLT, J. F., SWALEN, J. D. & WILSON, R. J. (1989). *Phys. Rev. Lett.* **59**(25), 2879-2882.
KOMIYAMA, M., MORITA, S. & MIKOSHIBA, N. (1988). *J. Microsc.* **152**(1), 197-203.
MUNDSCHAU, M. & VANSELOW, R. (1985). *Surf. Sci.* **169**, 23-36.
PASHLEY, D. W. (1965). *Adv. Phys.* **14**, 327-416.
SANTIESTEBAN, J., FUENTES, S. & YACAMAN, M. J. (1983). *J. Mol. Catal.* **20**, 213-231.
SOMORJAI, G. A. (1981). *Chemistry in Two Dimensions: Surfaces.* Ithaca, NY: Cornell Univ. Press.
VANSELOW, R. & MUNDSCHAU, M. (1986). *Surf. Sci.* **176**, 701-708.

Acta Cryst. (1991). A**47**, 21-29

A Model Study of the κ-Refinement Procedure for Fitting Valence Electron Densities

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(*Received* 26 *April* 1990; *accepted* 9 *August* 1990)

Abstract

Monopole electron-density deformations for first- and second-row atoms are obtained using Hirshfeld partitioning of near Hartree-Fock-limit electron densities for 28 diatomics. The κ-refinement model [Coppens, Guru Row, Leung, Stevens, Becker & Yang (1979). *Acta Cryst.* A**35**, 63-72] is applied to these monopole deformations and its success in modelling them is gauged by means of deformation

0108-7673/91/010021-09$03.00