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Scanning tunneling microscopy study of platinum deposited on graphite by metalorganic chemical vapor deposition

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The growth of thin Pt(111) films on highly oriented pyrolytic graphite (HOPG) by metalorganic chemical vapor deposition has been followed by scanning tunneling microscopy. Depositions were carried out on substrates held at 205°C and contacted with intersecting streams of H_2 and of He saturated with $(\eta^5\text{-}C_5H_4CH_3)Pt(CH_3)_3$. The deposition was monitored by the appearance of methane in the product stream. Deposition initiated almost immediately, in contrast with earlier studies showing a significant induction period for deposition on glass. The deposits obtained after several minutes at 205°C consisted of Pt clusters with diameters ranging from 8 to 80 Å along with some very much larger Pt islands. The deposits were morphologically very rough with rather well defined facet orientation. The step heights of the terraces ranged from 20 to 54 Å. Oval shaped disks free of apparent dislocations were also observed. One of the larger crystallites investigated was 2074 × 1482 $Å^2$ and 200 Å in height. The deposits were non-uniform throughout the deposition. The initial crystal growth under CVD was by island nucleation, followed by a growth mode that produced a random rough surface after the islands coalesced. At early stages the films are preferentially oriented with (111) crystallites parallel to the HOPG basal plane; further growth, however, leads to a poly-crystalline deposit.

1. Introduction

Recent reports of scanning tunneling microscopy (STM) studies of the aggregations of Pt clusters of 50 to 500 Å diameter on highly oriented pyrolytic graphite (HOPG) by Lee et al. and Yeung and Wolf [1] prompt us to communicate our observations of Pt deposited through metalorganic chemical vapor deposition (MOCVD). Investigation of supported metal clusters or thin films is of considerable interest, particularly in the light of their potential application in electronics [2] and catalysis [3]. Desirable physical and chemical properties of materials are to a very large extent determined by the structure and morphology of the deposit and therefore by the condition and method of growth. Since its introduction in the early eighties, STM has become a widely used and valuable technique [4] and proven to be very useful in accessing direct information on nucleation and growth of thin metal films [5]. Although initially most of the work has been focused on investigations of Au and Ag deposits [5d,6] there are also a substantial number of studies on Pt films [7] and clusters [8]. For preparation of the Pt samples various techniques have been employed, such as electrodeposition, sputtering, vacuum deposition, laser irradiation of carbonyl clusters, thermal evaporation and impregnation by a precursor salt solution. We were particularly interested in the initial growth and the morphological features resulting from chemical vapor deposition (CVD).

Previously, we reported on the deposition of Pt films of exceptional purity onto various substrates such as SiO_2, Si, and Teflon, by MOCVD using $(\eta^5\text{-}C_5H_4R)Pt(CH_3)_3$ (R = H, or CH_3) as a precursor [9] according to the equation:

$$(\eta^5\text{-}C_5H_4R)Pt(CH_3)_3 + 4\,H_2 \xrightarrow{\Delta/\text{He flow}} Pt + 3\,CH_4 + RC_5H_9.$$

A characteristic feature of this process is an induction period, during which no macroscopic evidence for deposition is obtained. After initiation, film growth accelerates and then levels off in a diffusion controlled region, typical of an autocatalytic process. Indeed, once a Pt film has been initiated, deposition continues even in the absence of any heating. Presumably during the induction period, small clusters may grow by diffusion or accretion until a critical size is reached, after which autocatalysis takes place. We were interested to study these processes by STM. Highly oriented pyrolytic graphite (HOPG) by MOCVD was chosen as a substrate because of its atomically flat planes over many square microns [10]; the Pt films were deposited on the basal (0001) plane of the HOPG.

2. Experimental

Pt films are deposited from (η^5-$C_5H_4CH_3$)Pt$(CH_3)_3$ [11] at ambient pressure in a horizontal, cold wall glass reactor; this has been described elsewhere [9b]. Prior to each experiment the reactor is disassembled, cleaned in aqua regia and rinsed with deionized water and acetone. After drying the reactor is reassembled and purged with helium (100 mL/min) and hydrogen (50 mL/min) for 30 min. The HOPG substrate [12] is cleaved prior to the deposition and is held at 200°C during the purge. The hydrogen and helium were supplied by Liquid Air Corp. and were 99.995% pure. The gases are purified further through 13 × molecular sieve traps immersed in dry ice.

Deposition is begun by directing the helium flow through the organometallic source. The source is held at 25°C. The helium becomes saturated with the organometallic precursor and is then passed downstream vertically onto the heated substrate where it is mixed with hydrogen. The effluent from the reactor is passed through a trap at −78°C to remove unreacted precursor. The hydrocarbon products of the effluent exiting the trap are analyzed on-line with an HP 5880A gas chromatograph, using a Haysep Q column (Alltech) at 180°C and a flame ionization detector. The deposition rate is monitored by the evolution of CH_4 [9b].

X-ray diffraction patterns of the films are obtained with Cu radiation (Kα, $\lambda = 1.5418$ Å) on an automated diffractometer. Samples for the XRD experiment are grown for 1 h at 200°C with a thickness of roughly 5000 Å, as estimated from the calibration of previous experiments [9b].

The STM used in this experiment is based on the design by Demuth et al. and is described elsewhere [13]. The STM is operated in air, and atomic resolution of HOPG is routinely obtainable. All images in this experiment are recorded in the constant current mode (topographic measurement) with bias voltages of −100 to −700 mV and tunneling currents of 1 to 10 nA. The tip is made of a mechanically cut Pt/Rh wire. Various samples with growth times from 5 to 11 min are scanned. The scan area ranges from 35×35 Å^2 to 5500×5500 Å^2. The images presented in this paper are representative data from nearly one hundred images collected. No deposition is visible to the naked eye until after 11 min.

3. Results and discussion

The deposition of Pt is monitored by the appearance of a GC signal for methane. The deposition temperature required on HOPG is unexpectedly high. No methane GC signal is observed after one hour at 180°C, a temperature at which we were able to deposit Pt metal on glass or Si. At 190°C, a methane GC peak appears in gradually increasing intensity, and after 30 min an irregular and non-reflective Pt deposit becomes visible. Smooth, metallic and adhesive films are obtained only above 195°C. Once a thin film is formed saturation growth rate is achieved even at room temperature.

Earlier [9c], we observed an increase in the rate of deposition of Pt on glass with increasing amount of water vapor injected into the carrier gas stream. We postulated that the acidic surface-adsorbed water or hydroxyl groups were responsible for initiation of the Pt deposition. With HOPG, a different mechanism may be operating with (obviously) a lower number of active sites for nucleation. Thus a higher substrate temperature, as compared to Pt MOCVD on other substrates, is needed for initial decomposition of $MeCpPtMe_3$. Since the deposition temperature is close to the decomposition temperature of the precursor, 240°C, gas phase decomposition might contribute to the nucleation process. Under the same gas flow conditions, Pt deposition on a polished sample of commercially available pressed graphite proceeds instantaneously above 140°C [14].

The methane evolution monitored by GC for substrate temperatures of 195, 205, and 230°C, is shown in fig. 1; these data do *not* indicate an induction period, by contrast to earlier observations for other substrates [9]. We observe a signal for methane in the GC 1 min after turning on the precursor stream. The maximum growth rate, i.e. complete precursor consumption, is reached after the film becomes visible to the naked eye. From the methane evolution, the precursor concentration was estimated to be about 1×10^{-6} mol/L. This means that under these conditions roughly 1 mg/h of Pt is delivered to the substrate.

Prior to deposition the freshly cleaved HOPG was characterized by STM. Atomic resolution images show the typical trigonal symmetric pattern. Larger scans (300 × 300 Å^2) show no noticeable point defects. However, steps longer than 500 Å are occasionally observed [14]. For the detailed STM investigations the films were grown on substrates held at 205°C.

The STM image of a 6000 × 6000 Å area of a sample obtained after 8 min of growth is displayed in fig. 2a. The image shows large Pt islands of more than 1000 Å height on top of the graphite plane. Various clusters can be also observed on the same sample. As an example, an image of a 500 × 500 Å^2 area containing clusters, the largest of which is 15 Å in diameter, is presented in fig. 2b. The apparent dips at the shoulder of the clusters are an artifact because of a hysteresis in the piezo element. The shifting of clusters by the rastering tip of the STM is not observed under our conditions, as verified by repeated scans showing no change in the cluster positions; shifting of clusters has however been reported by others [8c,15].

In general, samples removed after 5–10 min growth reveal the coexistence of clusters ranging from 8 to 80 Å in diameter as well as large domains covered by a film of more than 1000 Å in thickness; we believe the latter is an indication of autocatalysis [9c], i.e., rapid growth rate takes place only at the sites occupied by Pt islands large enough to provide this catalysis. The non-uniform deposition by MOCVD in the early stage contrasts with the much more uniform distribution of

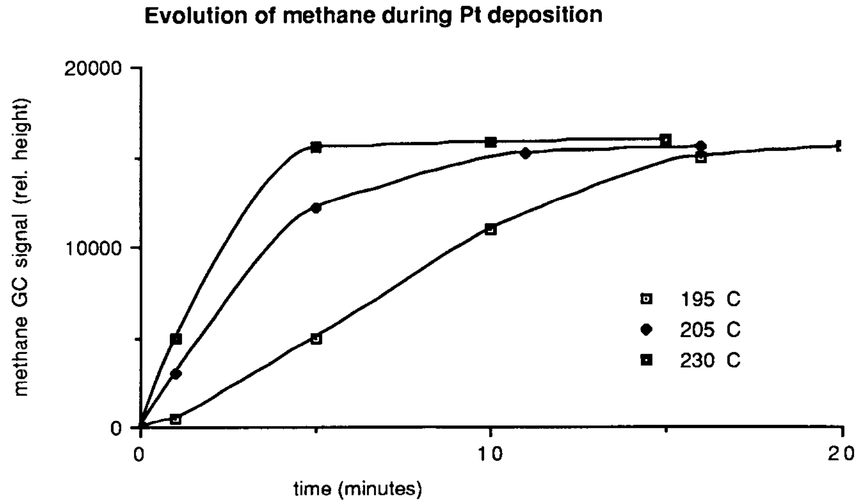

Fig. 1. Methane GC signal for monitoring Pt deposition rate on HOPG.

Pt clusters grown by MBE on HOPG even at low coverage or for Pt films [14]. The appearance of islands only is characteristic of a weak interaction between substrate and deposit (Volmer–Weber growth mode), as opposed to a layer plus island or layer only (Stranski–Krastanov or Frank–van der Merwe modes, respectively) [16].

Larger scale morphology, exhibiting a high degree of roughness, is shown in subsequent images. The STM image of a 604 × 624 Å^2 area for a sample obtained after a growth time of 9 min is shown in fig. 3a. The detailed structure of the edge of a Pt domain which consists of several terraces with a high density of faceting along each terrace is displayed. The middle terraces have a vertical step size of about 54 Å. The topogram corresponding to fig. 3a is displayed in fig. 3b; this displays vertical facets of rather well defined angles of 60° or 120° with respect to each other. Facets with lower Miller indices are thermodynamically more favorable [17]. Assuming that the X-ray data for thick films presented below are also valid for this sample, we tentatively assign a (111) orientation to the horizontal plane. The vertical facets are therefore of {110} type [18].

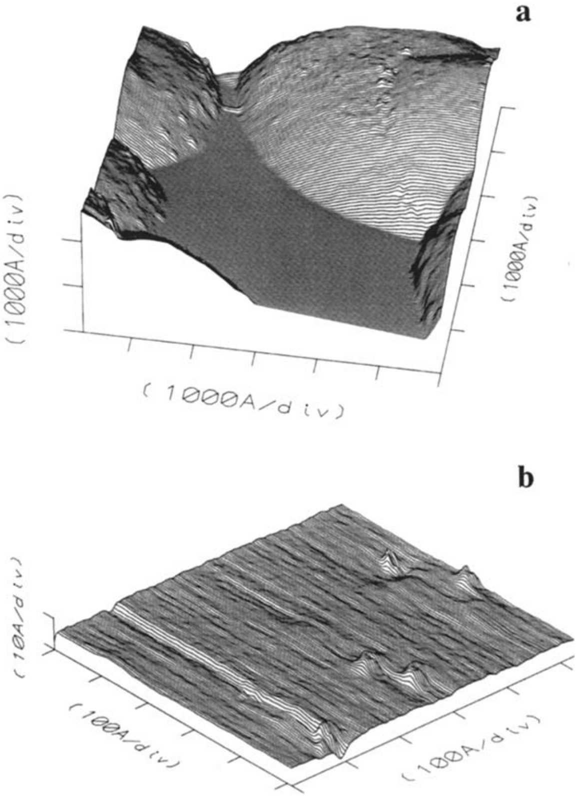

Fig. 2. (a) Smoothed STM image of Pt deposited for 8 min. The scan size is 6000×6000 Å^2; $I_t = 0.4$ nA; $V_{bias} = -100$ mV. (b) Smoothed STM image of Pt deposited for 8 min. The scan size is 500×500 Å^2; $I_t = 15$ nA; $V_{bias} = -166$ mV.

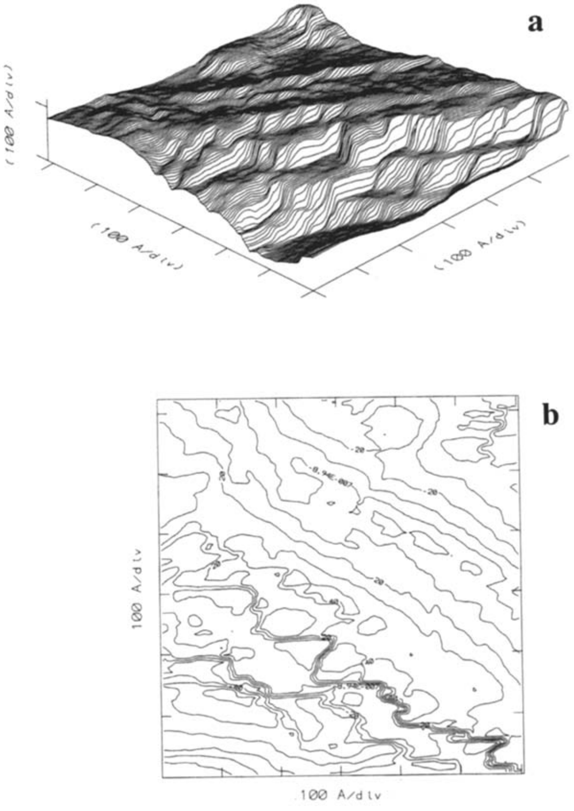

Fig. 3. (a) Smoothed STM image of Pt deposited for 9 min. The scan size is 604×624 Å^2; $I_t = 1.0$ nA; $V_{bias} = -130$ mV. (b) Contour plot of (a). 10 Å per contour line.

The STM image of a sample obtained after a growth time of 11 min is presented in fig. 4. The scan area is 2416 × 2496 Å^2. The image displays two oval disks free of dislocations, as viewed from above. The size of the larger disk is 2074 × 1482 Å^2 and 200 Å in height, while the smaller disk has a dimension of 1375 × 1073 Å^2 and 140 Å in height. In both cases the ratio of longer axis/shorter axis/height is found to be 1.35/

1.00/0.13. The flat surface of the two oval crystallites is presumably the (111) plane. Looking at the image more carefully, one can see that the disks are composed of several layers of similar oval shape growing on top of one another. On the very top of both crystallites one can see another layer forming with step edges of 57 Å on the larger one and 34 Å on the smaller one. The edges of these disks are not smooth but consist of uniform terraces and facets as revealed by close up STM images. Cubo-octahedral Pt crystallites have also been observed on carbon by Komiyama et al. [19].

Further survey scans at different sample locations show the complete coverage of the substrate by the Pt film. While distinct larger size features like the terraces and oval disks are less frequent, a typical image of a 5000 × 5000 Å^2 area of Pt covered substrate and its corresponding close up of a 600 × 600 Å^2 area are displayed in figs. 5a and 5b. The latter exhibits very extensive faceting as already observed above, although specific crystallite orientations are not obvious.

Films were grown for characterization by X-ray diffraction. After one hour of deposition on HOPG only the peak for Pt(111) could be seen (in addition to the peaks due to the substrate). The preferential orientation of Pt(111) planes to basal graphite planes of HOPG in the first formed deposit has been described earlier and explained by the assumption of a weak Pt/graphite interaction [20].

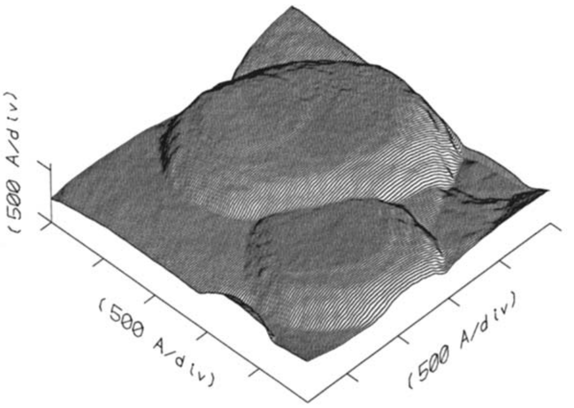

Fig. 4. Smoothed STM image of Pt deposited for 11 min. The scan size is 2416×2496 Å^2; I_t = 1.0 nA; V_{bias} = −700 mV.

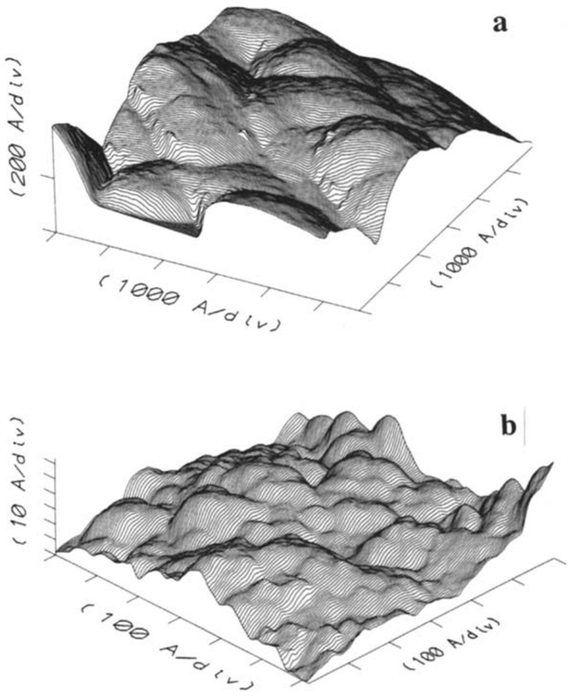

Fig. 5. (a) Smoothed STM image of Pt deposited for 11 min. The scan size is 5000×5000 Å^2 (height exaggerated); I_t = 1.0 nA; V_{bias} = −620 mV. (b) Smoothed close-up STM image of (a). The scan size is 600×600 Å^2 (height exaggerated); I_t = 1.0 nA; V_{bias} = −150 mV.

Similar but more intense Pt reflections could be seen after one hour's growth on single crystal MoS$_2$; this pattern is presented in fig. 6a. In addition to the signals characteristic of MoS$_2$, a very sharp peak for Pt(111) and a minor peak for Pt(222) are observed arising from a single orientation of the Pt crystallites. This is complemented by fig. 6b showing an X-ray diffraction pattern of a sample grown under similar conditions on pressed, non-oriented graphite [14]. The Pt deposit is polycrystalline and exhibits main peaks for Pt(111) and Pt(200) as well as minor peaks for Pt(220), Pt(311) and Pt(222). The same is observed for thicker films on HOPG.

The work described in this paper is a first step to gain an understanding on microscopic level of Pt film growth by MOCVD. Future work will be aimed at the cluster size dependence of MOCVD growth and of catalytic properties of ensembles of various cluster sizes.

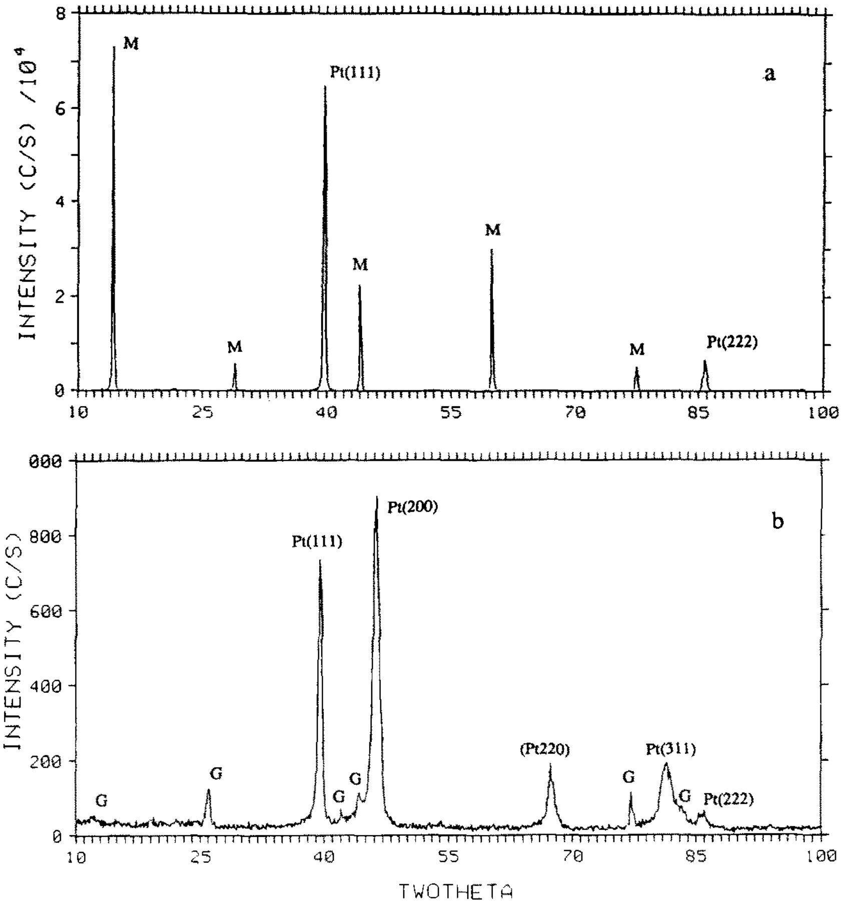

Fig. 6. (a) X-ray diffraction pattern of a Pt film on single crystal (001) MoS_2, deposited for 1 h at 200°C; M denotes peaks for MoS_2. (b) X-ray diffraction pattern of a Pt film on pressed, non-oriented graphite deposited for 1 h at 200°C; G denotes peaks for graphite.

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