

**CARBON ON PLATINUM : INVESTIGATIONS BY FIELD EMISSION MICROSCOPY**

R. VANSELOW and M. MUNDSCHAU

*Department of Chemistry and Laboratory for Surface Studies,  
University of Wisconsin-Milwaukee, Milwaukee, WI 53201, U.S.A.*

**ABSTRACT**

Investigations by FEM, UHV-SEM, and high resolution scanning AES indicate the formation of two types of graphite islands on Pt. One forms at low temperatures (~ 870 K to ~ 1150 K) in the high Miller index areas at the exit point of dislocations, the other grows face specifically above 1150 K in the area of {110}. The growth rate in the vicinal area of {110} is determined by the misfit parallel to the respective step edges. The alignment of graphite {0001} on Pt{110} is graphite  $\langle 11\bar{2}0 \rangle \parallel \text{Pt} \langle 110 \rangle$ , which is in agreement with the calculated orientation of smallest epitaxial misfit.

**1. INTRODUCTION**

Carbonaceous overlayers on transition metal crystals play an important role in heterogeneous catalysis. The overlayer carbon can exist in two states:

- i) the catalytically active "carbide carbon" and
- ii) the "graphitic carbon", which acts as a catalyst poison /1-3/.

Since the apex area of field emitters is well suited to model larger, rounded catalyst crystals, the field emission microscope (FEM) was used to study the properties of carbon on platinum.

**2. EXPERIMENTAL PROCEDURE**

In the present investigations, primarily the FEM was utilized. Its set-up as well as the experimental procedures have been described in detail in recent papers /4,5/. Additional studies were carried out with a high resolution scanning Auger microprobe (Physical Electronics, Model 595) with scanning electron microscope (SEM) capabilities. During all experiments, the residual gas pressure was in the  $10^{-10}$  to  $10^{-11}$  Torr range. The emitters were prepared from 99.999% pure platinum wires (Sigmond Cohn Corporation [SCC] and Materials Research Corporation [MRC]), by electrolytic etching in an aqueous solution of KCN.

**3. EXPERIMENTAL RESULTS**

When electropolished and UHV annealed platinum emitters, which initially showed an FEM-clean surface, are annealed to about 870 K, strongly emitting islands form randomly in the high Miller index areas. The island density is  $3 \times 10^8 \text{ cm}^{-2}$ . Upon further heating, the islands grow and the island density decreases to about  $2 \times 10^7 \text{ cm}^{-2}$ . When the temperature is raised in short annealing steps (annealing time 30 s), the islands dissolve at about 1150 K, and face specifically adsorbed, strongly emitting islands form in the vicinal area of {110}. At an early stage, these face

specific islands grow preferentially along the  $\langle 112 \rangle$  and the  $\langle 100 \rangle$  zone. The faster growth along the  $\langle 112 \rangle$  zone gives these islands a dumbbell-like appearance. With increasing temperature, growth occurs in the other vicinal areas (including the  $\langle 100 \rangle$  zone) and on the unstepped  $\{110\}$  plane itself. The  $\{110\}$  layers may become relatively large if the growth conditions are favorable. They may cover the high Miller areas around  $\{012\}$  and reach into  $\{111\}$  and  $\{100\}$ . Some of the large islands show well developed edges and corners. In the high Miller index areas, the islands cause a work function decrease of 1.6 eV /6/. Over the  $\{110\}$  plane, the work function is increased only slightly if there is no adsorption of other impurities /6/. If impurities other than carbon are face specifically preadsorbed on  $\{110\}$ , the work function increase can be pronounced /7/. Upon heating, the large layers recede first from  $\{111\}$  and then from  $\{100\}$ , and form elongated islands along the  $\langle 100 \rangle$  zone. At about 1200 K the layer is stable only on  $\{110\}$ . It dissolves completely above 1400 K.

Analyses of emitters by UHV-SEM also show the random formation of islands upon annealing at about 870 K. Again, an island density of  $3 \times 10^8 \text{ cm}^{-2}$  is observed. Analyses by AES show an increase of the carbon peak (272 eV) when the islands appear. Some islands were found in etch pits. An AES carbon line scan (272 eV) showed the carbon deposit to be limited to the etch pit areas. Independent etch pit studies on platinum wires used in the present investigations revealed a dislocation density of  $1 \times 10^8 \text{ cm}^{-2}$  /8/.

#### 4. DISCUSSION AND CONCLUSIONS

The FEM investigations show the formation of two types of islands:

- i) islands formed randomly in the high Miller index areas (random islands) and
- ii) islands formed face specifically in the area of  $\{110\}$  (face specific islands).

Analysis by AES shows that the islands are composed of carbon. The emission increase (work function decrease) indicates the existence of graphitic carbon. Carbide carbon would cause a work function increase, and could not be observed.

Since the density of the random islands agrees with the dislocation density, one has to assume that upon heating, carbon dissolved in the platinum bulk diffuses along dislocation pipes. Upon rapid quenching it nucleates on the surface at the exit points of dislocations. The discovery of carbon islands in etch pits, supports this assumption.

When at elevated temperatures carbon can be distributed along the surface by surface diffusion, nucleation and initial growth of face specific graphite layers can be observed in the vicinal area of  $\{110\}$ . A calculation of the misfit for graphite  $\{0001\}$  on platinum  $\{110\}$  shows the best epitaxial fit for graphite  $\langle 11\bar{2}0 \rangle \parallel$  platinum  $\langle 110 \rangle$  and the corresponding perpendicular direction graphite  $\langle 10\bar{1}0 \rangle \parallel$  platinum  $\langle 100 \rangle$ . (It is assumed that the best epitaxial fit is obtained when the combined misfit for two crystallographic directions, which are oriented perpendicular to each other, reaches the smallest possible value). Misfit values were also calculated for graphite adsorbed in the stepped vicinal area of  $\{110\}$ . Using the above mentioned best epitaxial fit, the misfit along the  $\langle 100 \rangle$ , the  $\langle 112 \rangle$ , and the  $\langle 110 \rangle$  zone was calculated for directions parallel ( $\parallel$ ) to the step edges and perpendicular ( $\perp$ ) to the step edges. The following values were obtained:  $\langle 100 \rangle$  zone, ( $\parallel$ ) 8.6%, ( $\perp$ ) -11.3%;  $\langle 112 \rangle$  zone, ( $\parallel$ ) 2.3%, ( $\perp$ ) -37.3%;  $\langle 110 \rangle$  zone, ( $\parallel$ ) -11.3%, ( $\perp$ ) 8.6%. Since the experimentally observed growth rate is fastest along the  $\langle 112 \rangle$  zone, slower along the  $\langle 100 \rangle$  zone and slowest along the  $\langle 110 \rangle$  zone, it appears that the growth rate in the vicinal area is determined by the epitaxial fit parallel to the step edges. The sequence of these misfit values, 2.3% ( $\langle 112 \rangle$  zone) < 8.6% ( $\langle 100 \rangle$  zone) < -11.3% ( $\langle 110 \rangle$  zone), properly reflects the observed growth rates. Higher supersaturations are required to obtain growth in the vicinal area along the  $\langle 110 \rangle$  zone and on the  $\{110\}$  plane itself.

The edges which have been observed on larger graphite layers can be used for an experimental determination of the graphite layer orientation. Using a broken-bond model and applying Wulff's Law /9/, one finds that the  $\langle 11\bar{2}0 \rangle$  edge ("zigzag edge") should be the dominating edge and that the  $\langle 10\bar{1}0 \rangle$  edge ("chair" or "armchair" edge) should occur only on growth or dissolution forms or when its edge free energy is sufficiently lowered by adsorption or interaction with the substrate. Assuming,

therefore, that the experimentally observed edges are of the type  $\langle 11\bar{2}0 \rangle$ , one finds an experimental alignment of the graphite layer corresponding to  $\langle 11\bar{2}0 \rangle \parallel$  platinum  $\langle 110 \rangle$  or  $\langle 10\bar{1}0 \rangle \parallel$  platinum  $\langle 100 \rangle$ . This alignment is in perfect agreement with the calculated orientation of best epitaxial fit.

The sequence of graphite layer stability ( $\{110\} > \{100\} > \{111\}$ ) has been explained by the decreasing platinum surface dipole moment density /5/. Further experiments and model calculations are required to determine whether or not the interaction between graphite and platinum is limited to this dipole interaction. In surface extended energy-loss fine-structure (SEELFS) experiments on the systems graphite/nickel  $\{111\}$  and graphite/nickel  $\{110\}$ , for example, it was found that graphitic carbon on  $\{111\}$  behaves similarly to graphite single crystals, while a graphite layer on  $\{110\}$  strongly interacts with the nickel substrate /10/. In the case of platinum, an interaction of the latter type - though possibly weaker - may contribute to the layer stability on  $\{110\}$  and may explain the small work function increase over  $\{110\}$  upon graphite adsorption.

The above described face specific formation of graphite layers on platinum  $\{110\}$  has been observed also when hydrocarbons are cracked by heating in the appropriate temperature range. For example, Kojima et al. /11/ found a formation of  $\{110\}$  layers after heating platinum field emitters with adsorbed acetylene to 1110 K.

## 5. SUMMARY

Initial nucleation of carbon occurs on dislocations in the curved high Miller index areas. Above 1150 K these randomly distributed islands dissolve and face specific layers are formed on  $\{110\}$ . These layers can extend into neighboring crystallographic areas where they are, however, less stable. The sequence of stability of graphite layers on platinum is:  $\{110\} >$  all other  $\{hk0\}$  on the  $\langle 100 \rangle$  zone  $> \{100\}$  followed closely by  $\{111\}$ .

Layer nucleation and initial growth in the vicinal area of  $\{110\}$  occurs along the  $\langle 11\bar{2} \rangle$  and the  $\langle 100 \rangle$  zones and not on the unstepped  $\{110\}$  planes itself. The growth rate in the vicinal area is determined by the epitaxial misfit parallel to the step edges. An alignment of the graphite layer with the underlying  $\{110\}$  is observed. It corresponds to graphite  $\langle 10\bar{1}0 \rangle \parallel$  platinum  $\langle 100 \rangle$ .

Upon adsorption of graphite, the work function of  $\{110\}$  is increased only slightly /6/. The work function increase is much more pronounced if impurities other than carbon are face specifically preadsorbed on  $\{110\}$ .

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