Surface-Impurity Segregation on Pt and Its Potential Role in the Reconstruction of Pt{100}

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Field emission microscopy studies and very high-resolution Auger electron spectroscopy analyses of platinum field-emitter surfaces show that P, Si, and S impurities strongly segregate to the {100} areas, and that Si stabilizes the nonequilibrium {012} planes. Auger spectra demonstrate the difficulty of detecting Si and S impurities on Pt because of peak-overlap problems at 92 and 152 eV, respectively. Evidence is presented which suggests that these impurities have been largely overlooked in Pt{100} reconstruction studies.

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The cleanliness of reconstructed platinum {100} surfaces has been questioned[1-3] ever since it had been proposed that the reconstruction was a characteristic of the clean surface.[4] Early suspicions proved justified when Auger electron spectroscopy (AES) revealed that reconstructed Pt {100} surfaces studied in the mid to late 1960's were grossly contaminated with carbon.[5] When the C was removed by heating the Pt in oxygen, most of the complex low-energy electron diffraction (LEED) patterns, formerly assigned to the clean, reconstructed surface, disappeared.[5,6] The original patterns reappeared when the surface was deliberately recontaminated with C. However, even after the removal of C, a Pt{100}(5×1) pattern could be observed.[6] It was ascribed to a hexagonal overlayer of Pt surface atoms on top of unreconstructed {100} bulk layers. A series of closely related patterns has since been described.[7]

Throughout the 1970's and into the 1980's Pt{100} reconstruction was considered by most authors to be a phenomenon associated with the clean Pt surface, since AES apparently did not reveal the presence of impurities. This view seemed to be further supported by reports of similar reconstructive rearrangements on {100} planes of aluminum, gold, and iridium.[7,8] In addition, {100} planes of the body-centered metals, chromium and vanadium, were also found to show complex LEED patterns, which again were attributed to the reconstruction of the clean surface.[9,10] However, unlike the reconstruction of {110} planes of fcc metals, which can be understood as simple microfaceting of a nonequilibrium plane,[11,12] the hexagonal model has become beset with problems. First, it has not been possible to perform a completely satisfactory, quantitative LEED intensity calculation to determine surface atom positions.[7] Thus the exact structure of the reconstructed Pt{100} is still in doubt. Second, there is no completely satisfactory explanation as to why the clean {100} surfaces of the other fcc platinum-group metals, palladium and rhodium, do not reconstruct. Furthermore, earlier statements concerning the reconstruction of "clean" V {100} surfaces had to be retracted[13] because an AES peak overlap between oxygen and V had been overlooked. The LEED reconstruction pattern of V is now attributed to an oxide overlayer. A similar problem exists in the case of Cr.[13,14] Therefore, it appears that neither clean Cr nor clean V {100} surfaces reconstruct. Finally, in 1981 it was shown that an AES peak-overlap problem occurs between the 93-eV peak of Pt and the 92-eV peak of Si.[15-17] Moreover, it was pointed out that many of the papers published on Pt{111} indicate Si contamination.[16] It was found in addition, that oxidation of segregated Si produces a refractory Si oxide,[15,16] which has been mistaken as an anomalous Pt oxide. Although Si contamination of the {111} surface was shown to be extensive, there was little discussion on the possible contamination of other Pt planes.

We have used field emission microscopy (FEM) to study impurity segregation on Pt. This technique is very sensitive to the presence of impurities, which can greatly affect electron emission. The FEM also permits the simultaneous observation of a wide range of crystallographic directions. Thus the effect of impurities on different crystal planes can be readily compared.

On FEM-clean Pt [Fig. 1(b)], prepared by prolonged heating at high temperatures, combined with intermittent flashing close to the melting point, and followed by rapid quenching (800 °C s^{-1}), only the {111} and {100} planes are stable. This is in agreement with theoretical calculations and other experimental findings.[18,19] The surface shown in Fig.

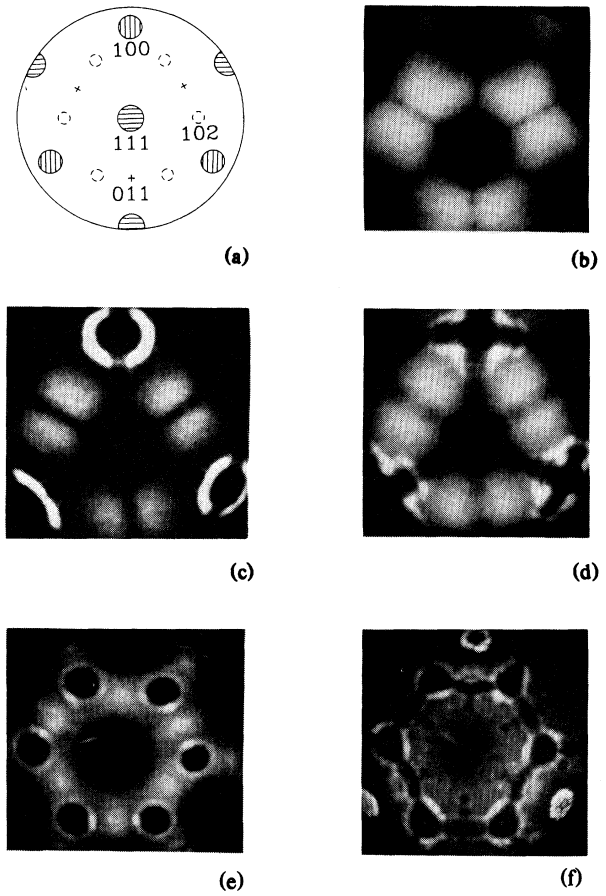

FIG. 1. Field emission micrographs of platinum: (a) Stereographic projection. (b) FEM-clean Pt surface. Only {111} and {100} are stable. (c) SCC Pt after annealing close to the melting point. (d) SCC Pt after annealing (c) to 600 °C. The {100} impurity structure shows Si, S, and traces of C in addition to P. (e) MRC Pt after annealing to 600 °C. The surface is highly Si contaminated when the additional {012} planes appear. (f) MRC Pt after silicon deposition and annealing to 610 °C.

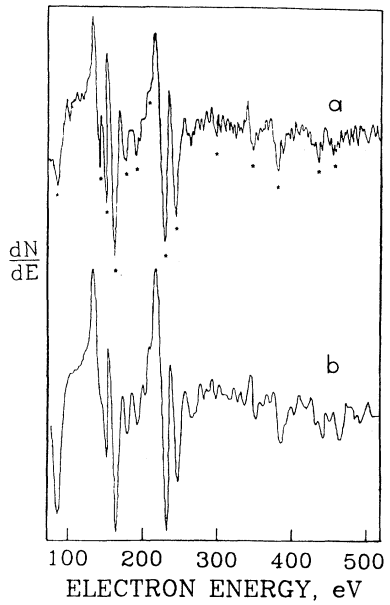

FIG. 2. Auger spectra: (a) SCC Pt after flashing at 1500 °C. The Pt 150- and 158-eV peaks are clearly resolved and the 93-eV peak is of relatively low intensity. Asterisks mark Pt transitions. (b) MRC Pt annealed for 60 s at 600 °C. Unresolved 150–158-eV peaks and intense 92–93-eV peaks are indicative of S and Si contamination, respectively. Similar spectra have been used as evidence for "clean" surfaces in many Pt{100} reconstruction studies.

1(b) can be rapidly recontaminated by bulk impurities if the sample is heated at lower temperatures.

The impurities were identified by analyzing the apex areas of emitters with very-high-resolution scanning AES (Physical Electronics model 595).[20] All work was done in the low 10^{-10} to upper 10^{-11} Torr range. Platinum from the Sigmund Cohn Corporation (SCC) was found to be high in P, whereas Pt from the Materials Research Corporation (MRC) was especially high in Si. Both companies state 99.999% purity.

The {100} area is considerably more affected by segregated impurities than is the {111} area. The {100} ring of Fig. 1(c) appeared only on the P-contaminated SCC Pt. It persists even after heating to about 1500 °C.[18,21] Phosphorus deposited on MRC Pt is especially difficult to remove[20] and also forms a ring on the {100}.[20]

The very stable {100} ring structure of Fig. 1(c) acts as a preferential nucleation site for other surface impurities. Figure 1(d) shows a secondary impurity structure which forms after heating SCC samples to 600 °C for 200 sec. In addition to P this structure contains Si, some S, and traces of C. The latter three impurities can be greatly reduced by heating to 980 °C, leaving the {100} ring structure of Fig. 1(c) intact.

No P was detected at the apex areas of MRC Pt and no stable {100} rings appeared. Instead, {012} planes developed upon heating to 600 °C for 60 s or upon heating between 600 °C and 1500 °C followed by slow cooling (200 °C/s) to room temperature [Fig. 1(e)]. These surfaces were found to be heavily contaminated with Si [Fig. 2(b)]. A formation of {012} planes was not observed on SCC Pt which had a lower Si concentration. The small amounts of silicon present were trapped in the {100} ring structure. However, when the Si surface concentration was increased by vapor deposition, {012} planes

readily formed upon heating. When larger amounts of Si ($\Theta \simeq 5$) were deposited on MRC Pt, very drastic surface changes, due to silicide formation, could be observed after heating to 250 °C and above. At 610 °C, clusters, apparently of platinum silicide, nucleated on the {100} area [Fig. 1(f)]. The observation of an epitaxial growth of a silicide on the {100} area has also been reported in LEED studies.[22]

It should be noted that silicides also have been found to grow on Rh and Pd {100},[23,24] giving rise to complex LEED patterns. Since there is no Auger peak-overlap problem (although silicon oxide presents a problem in the case of Pd[24]), these patterns are now assigned to metal silicides, although they had formerly been assigned to the reconstruction of clean {100} planes. When an effort is made to remove the Si, the complex LEED patterns disappear.[23]

Because of the overlap of the Pt 93-eV peak with the major Si peak at 92 eV,[15,16] careful attention must be paid to relative peak intensities. For our cleanest samples the 93-eV peak is just slightly larger than the 150-eV Pt peak [Fig. 2(a)]. Samples with larger 92–93-eV peaks [Fig. 2(b)] are considered Si contaminated.

Another overlap problem involves S. The main S peak appears at 152 eV, between the 150- and 158-eV peaks of Pt. Unresolved 150- and 158-eV peaks, as seen in Fig. 2(b), are a sign of S contamination.[25] While this lack of resolution may be caused by instrumental limitations, these peaks must be resolved to prove that the surface is S free. As in the case of Si, S causes the appearance of {012} planes.[26]

Our investigations raise questions about the possible presence of contaminants in reconstruction studies involving the Pt {100} surface. In a thorough search of the corresponding literature which deals with the reconstruction of clean Pt {100} surfaces, we could not find a single AES spectrum showing the simultaneous absence of P, Si, and S. (Neither could we find spectra which can support the cleanliness of reconstructed Au and Ir {100} planes.) Unfortunately, most authors do not show the critical Si and P regions which would allow judgement of the surface purity.

In addition, two detailed studies[27,28] on MRC Pt single crystals mention the appearance of {012} planes upon annealing. This indicates probable contamination in samples upon which much recent LEED {100} reconstruction work is based.[7] An examination of the corresponding AES spectrum[27] reveals that the 150–158-eV peaks are unresolved and that the 92-eV Si region is not shown.

In conclusion, the Pt {100} area is most strongly affected by segregated P, Si, and S impurities. Silicon and sulfur, which cause the formation of {012} planes, are particularly difficult to detect by AES because of overlap problems at 92 and 152 eV, respectively, and therefore, have been largely overlooked in Pt{100} reconstruction studies. Increased efforts should be made to assure that these surface reconstructions are not the result of undetected impurities.

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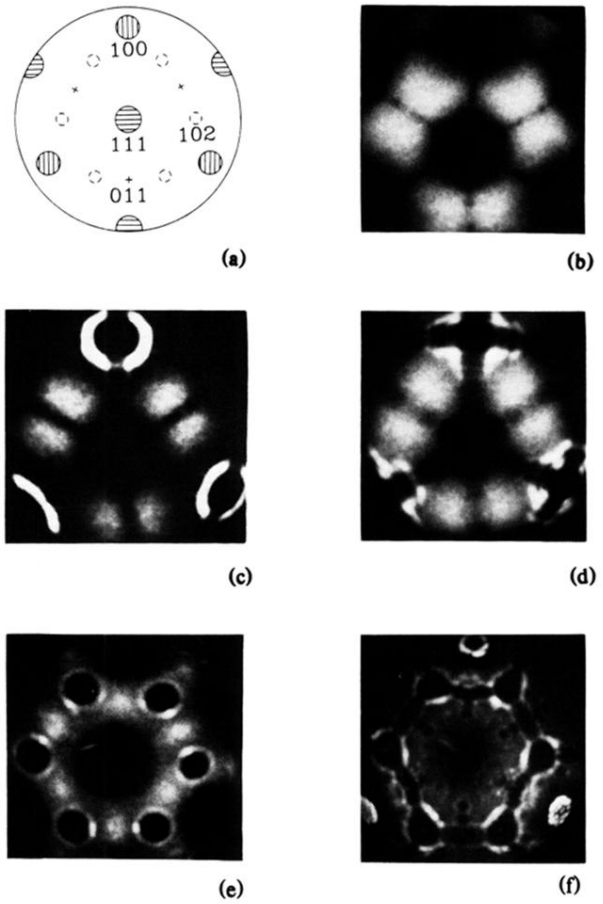

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