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Work function of Pt(111)

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The work function of the Pt(111) surface was measured in ultrahigh vacuum with use of the photoelectron-threshold-yield technique, resulting in a value of $\Phi = 6.10 \pm 0.06$ eV.

The single parameter which best characterizes the properties of a metal surface is its work function. It is our only experimental quantity relating the potentials inside and outside of solids, and it determines in part the interaction between dissimilar materials in contact. In spite of this, accurate values for the work function of well-defined single-crystal surfaces are not known for the majority of metals. In particular, this Brief Report will deal with the work function of Pt(111). Despite a fairly extensive literature on the properties of this surface, its work function is not reliably known with good accuracy. A number of measurements exist,[1–7] but these do not agree well with each other.

All of the measurements were performed in an ion-pumped ultrahigh vacuum chamber with nominal base pressure 3×10^{-8} Pa. The chamber is equipped with a sample manipulator, a window-collector arrangement used during experimentation, an Ar-ion-sputter gun, and a commercial four-grid low-energy electron diffraction (LEED) optics. The sample is spot welded to a Ta wire which is mounted in the manipulator and can be rotated to face the incident light or the ion-sputter gun. The sample itself is a single crystal of platinum in the form of a disk oriented with a (111) surface; both sides of the disk were used. Treatment of the surfaces in vacuum consisted of cycles of ion sputtering, annealing, and heating in oxygen at relatively low temperatures. The incident light enters the vacuum system through a uv grade sapphire window. Wavelengths of 180–400 nm with a 2.1-nm linewidth are available. The variation of yield with wavelength was found and the work function extracted from this data using the method first proposed by Fowler[8] (plots of $Y^{1/2}$ were not used here due to a small loss of information they entail[9]).

Data for the Pt(111) surface are given in Fig. 1. Work function data were taken following a variety of surface treatments. The circles represent experiments done after extended (2300 s) annealing only. Squares signify heat treatment in oxygen and a brief anneal before taking data. Between runs 4 and 5 (i.e., the triangle), the surface was sputtered, heated in oxygen, and annealed (600 s). Before the first result in Fig. 1 (marked run 1) was obtained, the surface had already been sputtered and subjected to numerous cycles of heating in oxygen and annealing. These results show that the work function is reproducible and not greatly dependent on the immediately preceding surface treatment. The entire procedure was redone on a different sample surface as a reproducibility check, and the resulting value is in agreement within experimental error. The data in Fig. 1 were taken before the four-grid LEED optics was installed. Subsequent to its installation, the surface was checked for order using LEED and for contamination using retarding field Auger (RFA) spectroscopy. The work function measurement was redone on a characterized surface and the results in Fig. 1 were verified.

Random errors affecting the measurement (e.g., backlash in the monochromator mechanism, the linewidth of the light, noise in the photocurrent measurement, and uncertainty in the intensity calibration) result in an error bar of ±0.06 eV. The surface is thought to be clean since no contamination was observed, but of course there could be contamination below the RFA level of detection; silicon is a particular problem since its strongest line overlaps a platinum line. Silicon contamination has usually been a problem only when high-temperature oxygen treatments have induced surface formation of SiO_2, however, and this practice was avoided (for that reason) in this study. The magnitude of the systematic errors is estimated to be less than 0.05 eV. Scattered light will always lower the measured value, but this was virtually eliminated. The presence of defects on the surface (due, e.g., to a slight misorientation of the surface) will also lower the measured value of the work function. The magnitude of this effect can be estimated using dipole moment per step values given by Besocke *et al.*[10] The

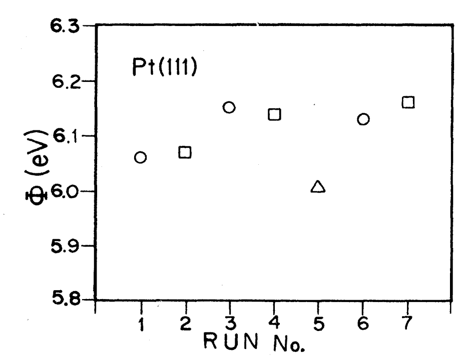

FIG. 1. Work function results for Pt(111) following a variety of surface treatments (see text for meaning of symbols).

final result is that the work function of Pt(111) is $\Phi = 6.10 \pm 0.06$ eV.

Previously published values[1–7] of the Pt(111) work function vary from 5.6 to 6.4 eV. Although the typical error bar claimed is ± 0.1 eV, the numbers cover a range of 0.8 eV. Measurements made using the secondary electron cutoff of valence band spectra[4–7] will in general be considerably less accurate than claimed, a point discussed in detail elsewhere.[9] Field-emission measurements for individual crystal faces are also quite uncertain when the average work function of the tip is not known;[11] this is the case for Refs. 1–3.

Recent linear augmented-plane-wave surface electronic structure calculations for Pt(111) have been performed using a three-layer film (both clean and H covered).[12] The work function for the clean Pt(111) surface resulting from this calculation is about 5.98 eV, in reasonably good agreement with the present result.

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