Photoelectric Work Function of a Copper Single Crystal for the (100), (110), (111), and (112) Faces

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The electron work function was measured by the Fowler method for four faces of a copper single crystal. The crystal was cleaned by repeated cycles of ion bombardment and annealing at 700°C under ultrahigh vacuum conditions. With uncertainties of $\delta \Phi = \pm 0.03$ eV, the work functions were found to be $\Phi_{110} = 4.48$ eV, $\Phi_{112} = 4.53$ eV, $\Phi_{100} = 4.59$ eV, and $\Phi_{111} = 4.94$ eV.

We wish to report here the anisotropic photoelectric threshold of copper as measured on a single crystal cleaned by a technique established in low-energy electron diffraction studies.¹ Copper is one in a series of metals for which theoretical calculations of work functions associated with the principal lattice planes were recently published.² However, reliable experimental data on single crystals are scarce, and the computed anisotropies were not compared with experiment. For copper, a considerable discrepancy was found between the calculated isotropic part of the work function and the experimental results for polycrystalline surfaces. Our experimental data, on the anisotropy, should be helpful in finding the theoretical revisions believed necessary.²

Previously, measurements of the photoelectric threshold of a spherical copper single crystal have failed to produce an anisotropy.³ Anisotropy has been reported in epitaxial films⁴ and in oriented single crystals.⁵ The single crystals showed work functions closer to those of clean polycrystalline surfaces. However, studies have shown that, in addition to the heat treatment given to those crystals, repeated cycles of ion bombardment and annealing are necessary in order to obtain clean surfaces with good low-energy electron diffraction patterns with copper.¹

We have applied this cleaning procedure to a copper crystal with four crystallographically oriented surfaces and measured the photoelectric thresholds. Using a spark cutter, the surfaces were cut parallel within 1° to the lattice planes (100), (110), (111), and (112) on the sides of a cylindrical copper ingot of diameter 12 mm and purity 99.999%.⁶ The specimen was electropolished by a standard method and mounted on a rotational drive in the vacuum chamber, the only contact being made to 99.999%-Cu holders. An oil-free stainless-steel vacuum system with a base pressure well below 10⁻¹⁰ Torr was used.

Outgassing for 250 h at 800°C and at pressures

in the low, 10⁻¹⁰-Torr region was followed by repeated cycles of bombardment with 500-eV Ne ions and annealing at 700°C. All faces were given identical treatment, and work functions were measured in succession without environmental changes. The work functions were checked after each step in the cleaning process and showed the same behavior as found for iron.⁷

Work functions were measured by the Fowler method with the use of mercury or xenon lamps and a Hilger and Watts prism monochromator as a radiation source. The photocurrent was measured on a vibrating-reed electrometer. However, instead of fitting Fowler curves, we have used the equivalent procedure of plotting the square root of the yield versus photon energy.⁴ Except for a slight rounding off near the threshold because of the finite-temperature tail of the the Fermi-Dirac distribution, such plots yield straight lines with well-defined abscissa intercepts at a photon energy taken to be the work function.

After an initial heat-treating period of 7 h at 800°C, we obtained results similar to those of previous work.⁵ However, the work functions would then increase rather strongly with temperature. This feature is indicative of contaminated surfaces.³ Further heating changed the values considerably in a direction toward those of clean surfaces with most of the change taking place during the next 15 h. After outgassing, three to four cleaning cycles were sufficient to obtain reproducible, stable work functions with zero or slightly negative temperature coefficients as found for clean surfaces.³

Throughout the measurements a collecting field of approximately 25 V/cm was applied in a planar geometry. At the end of the run this field was varied to test the patch effect.⁸ Fields lower than 10 V/cm were sufficient to break down the patch fields. Also, the light beam could be moved around on the surface without produc-



FIG. 1. Square root of photoelectric yield as a function of photon energy for four crystallographically oriented surfaces on copper. Estimated uncertainties are $\delta \Phi = \pm 0.03$ eV.

ing work-function variations. We therefore conclude that the surfaces were of good homogeneity.

Figure 1 shows a set of curves from which the final work functions may be found. The results for the thresholds, as indicated in the figure, are based on four such sets of curves.

Polycrystalline surfaces made by evaporation in vacuum are by far the simplest ones to handle experimentally, and in Ref. 2 a value of 4.65 eV for the work function of such a surface was chosen for comparison with theory. That value also happens to agree within experimental error with the simple, but arbitrary,² arithmetic average of our results for the work functions of the three principal surfaces. This average as well as the differences between the work functions of the principal surfaces, $\Phi_{100} - \Phi_{110} = 0.11$ eV and Φ_{111} $-\Phi_{100} = 0.35$ eV, respectively, are significantly higher than those of Refs. 4 and 5.

Only a qualitative comparison can be made between the theory and our experimental results. The observation that the thresholds of the three principal surfaces increases in the order (110), (100), and (111) agree with theory and implies the reverse order of the surface energies. This is consistent with the fact that the (111) surface was easiest to clean, while the (110) surface stabilized its work function more slowly. Also, since the effect of ion bombardment is to increase the energy by damaging the surface, the observed lowering of the work functions upon bombardment follows as a consequence.

The behavior of the most open and perhaps poorest defined of the surfaces studied, the (112) surface, was not followed in detail. However, a stable, reproducible final work function was obtained with the numerical value falling between those of the (110) and (100) surfaces.

Quantitatively the previously noted discrepancy for the average work function has been confirmed. Also, we find experimentally an overall anisotropy, $\Phi_{111} - \Phi_{110}$, about 30% higher than the theoretical prediction.²

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