The Electronic Work Functions of Pure and

Composite Metal Surfaces

Department of Physics
State College of Washington
Pullman, Washington

Principal Investigator:

Paul A. Anderson

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The following problems have been investigated during the course of this work.

1. <u>The Work Function of Lithium</u>

Because they approximate their free electron models so closely, lithium and sodium are of exceptional importance in studies of the theory of the work function. For the purpose of supplementing theoretical calculations on these metals, a thorough experimental investigation of the work function of lithium has been carried out and the results, in combination with the calculations of Wigner and Bardeen, used to estimate the contribution of the surface double layer term to this work function.

As in previous studies of this series, the work function was determined by measurement of the contact difference of potential of lithium with respect to a barium reference surface of known work function. The measured surfaces of both lithium and barium were prepared by condensation of their vapors on glass targets after each of the metals had been subjected to fractional and multiple distillation in the measuring tube itself. The time interval between deposition and measurement of the films was of the order of 30 seconds. The observed contact difference of potential is 0.03 ± 0.02 ev, lithium electro-positive to barium. This result assigns the value 2.49 ± 0.02 ev to the work function of lithium. The effect of gaseous contaminants is to lower the work function.

The volume and surface double layer terms which determine the work function of lithium are of the order of 2.2 and 0.3 ev, respectively, a result which supports the conclusion that the surface double layer makes a relatively small contribution to the work functions of the alkali metals. Published: Phys. Rev. <u>75</u>, 1205-7 (1949).

2. <u>The Work Function of Copper</u>

The work functions and aging characteristics of fourteen copper surfaces have been determined by measurement of their contact differences of potential with respect to barium reference surfaces of known work function. Measurement was by the retarding potential method in tubes sealed from the pumps and gettered with

vaporized barium. The copper surfaces were prepared by subjecting Hilger's "spectroscopic standard" copper to forty vacuum fusions followed by fractional distillation, redistillation of the fractions, and condensation of the vapor on glass. The barium films were prepared by a similar, standardized technique which yields surfaces reproducible and constant to 0.01 ev or better. The time interval between the deposition and initial measurement of the metal films was of the order of ten seconds, obtained conveniently with a tube in which the target is returned to the measuring position automatically after deposition of a metal film upon it.

The copper surfaces, formed from successive fractions of the distillate, showed marked variability of the initial work function and marked drift toward lower work function in films 1-4, progressive improvement in films 5-8 and, finally, good reproducibility and negligible drift in films 9-14 inclusive. Copper evidently retains dissolved gases, in free or combined form, with extraordinary tenacity and these contaminants, evaporated with the copper and reabsorbed by the condensing film, appear to be responsible for the variations observed in films 1-8. The work function value given by films 9-14 is 4.46 ± 0.03 ev, and this value is to be taken as representative of the present work. Published: Phys. Rev. 76, 388-390 (1949).

3. The Work Function of Germanium   With C. E. Dixon

Because of the low vapor pressure of germanium at its melting point and high reactivity of molten germanium with tungsten and crucible materials, Mr. Dixon's extensive work on this problem became largely a study of germanium vaporization techniques. It failed to produce vapor-condensed surfaces of germanium which could be accepted as sufficiently clean to yield reliable measurements. Not published.

4. A Direct Comparison of the Kelvin and Electron Beam Methods of Contact Potential Measurement

Comparison of contact potential values determined for a given pair of surfaces by (1) the Kelvin method, which is insensitive to patch fields, and (2) the electron beam method which is, according to patch theory, sensitive to these fields, offers a means of testing the validity of the theory and of determining the extent to which patch effects influence electron beam measurements. A technique for carrying out such comparative measurements in a single sealed-off tube is described. Barium and silver are selected for the study because of the known reproducibility and long-period constancy of their work functions. The measured surfaces are prepared by fractional distillation following intensive outgassing and the technique allows repetitive checking through renewal of these surfaces. Special attention is given to the conditions required for satisfactory Kelvin measuremxnts in all-glass, sealed-off systems.

The contact differences of potential found for silver films deposited on a tantalum substrate and barium films laid down on the silver were 1.79 ± 0.03 v by the electron beam method and 1.78 ± 0.01 v by the Kelvin method. This result is discussed from the standpoint of theoretical expressions for the Kelvin and e-beam values, the latter generalized to the case of an arbitrary number of patch types and arbitrary coverage factors. It is concluded (1) that crystal growth mechanisms are capable of reducing patch effects to insignificance under favorable conditions, but that (2) the most likely explanation of the present results is failure of the normal energy assumption and hence of the patch theory based on it to hold for the retarding field, slow electron case. It is suggested that an electron optical treatment of the patch field region may supply a more satisfactory theory. Published: Phys. Rev. 88, 655-658 (1952).

5. The Work Function of Cadmium

An extensive series of measurements on vaporized cadmium films by the electron beam method, using tubes similar to those employed for zinc (P. A. Anderson, Phys. Rev. 57, 122-7 (1940) yields the value $4.07 \pm .05$ e.v. for the work function of cadmium. A second series of measurements by the high-vacuum Kelvin method (Section 4 above) gives the value $4.08 \pm .02$ e.v. These measurements constitute a reasonably exhaustive study of this metal. A paper reporting the results is in preparation.

6. The Work Functions of Polycrystalline Gold and of Au(100)

Utilizing a technique for preparing (100) surfaces of the cubic-lattice metals at the site of measurement, and without exposure of the surfaces to other than the residual gases of a sealed-off, gettered tube, an attempt is being made to determine the work function of Au(100), as well as the work function of Au films deposited on glass. The technique parallels that used successfully for silver (P. A. Anderson, Phys. Rev. 59, 1034-41 (1941) but is complicated by the high temperatures required for establishing the Au(100) structure in vapor deposition on rocksalt cleavages. This work will be continued under the OSR contract which replaces our ONR contract.

7. The Effect of Oxygen on the Work Function of Barium   With Angus L. Hunt

The extreme stability of the work function of barium during aging of its vapor-condensed surfaces is anomalous in view of the facts (1) that gaseous contaminants generally alter the work function of a clean metal surface and (2) that barium is an especially effective getter. Mr. Hunt finds that when a barium surface cleans up known, relatively massive, doses of pure oxygen its work function does in fact drop sharply but that a very slow drift toward the work function characteristic of clean barium occurs on standing. Diffusion

of barium over the surface film of oxide appears to be the most likely expla-
nation for the results. This work will be continued.

8. Determination of Potential Distributions and Electron Trajectories Near Patchy Surfaces   With Angus L. Hunt

The surfaces of polycrystalline electron emitters and absorbers are in
general "patchy", that is they contain areas of different work function which
generate local contact potential fields. These fields must affect to some degree
all measurements which involve the emission or absorption of electrons. The
work cited in (4) above, as well as a considerable body of less direct evidence,
suggests that patch theory as now formulated is invalid for slow electron ab-
sorption in retarding fields. The possibility of developing a more general
theory by treating the motion of electrons near patchy surfaces as a problem
in electron optics is being studied. An automatic apparatus for tracing electron
trajectories near such surfaces has been designed to meet the requirements set
by a mathematical analysis of the problem. This work will be continued.

9. The Average Work Function of Polycrystalline Tungsten   With Allen R. Manthei

A technique has been developed for measuring the Kelvin contact potential
difference between a reference surface of vapor-condensed barium and a tungsten
ribbon cleaned by flashing. Recontamination of the tungsten is minimized by
reducing the time interval between flashing and measurement to the order of
1-2 seconds. This work is continuing.