one hundred, the figure must be cut off on the right by a vertical line of abscissa two. Then the ordinates of the points where the successive curves cut this limiting line are, for a given emission current, proportional to the potentials on the anode, each curve giving the distribution of potential between the electrodes for the assigned potential difference and assigned emission current.

Figure 4 shows a set of curves differing from those of Fig. 3 only in that an initial velocity corresponding to

$$W_a = (9ej_l a/4\pi m)^{\frac{2}{3}}(-m/2e)$$

is assumed. The broken curve representing $(r/a)^{\frac{4}{3}}$ has been included for the sake of comparison. Now we have cases in which the field near the cathode retards the ions, causing a dip in the potential curve, and leading, in the extreme case, to the formation of a virtual cathode. While each curve represents a possible potential distribution, the theory developed here does not, of course, specify the experimental conditions under which a specified curve may be realized or the sequence in which different curves are reached when one of the parameters, such as the potential on the anode, is altered.

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The Work Function of Copper

Paul A. Anderson
State College of Washington, Pullman, Washington*

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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. The range of variation in films 1–8 coincides almost exactly with the range of divergent values reported in the literature. 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.

THIS report describes further results in a series of studies of the external work functions of the pure metals. The more significant features of the experimental method, described in detail in previous reports,[1] may be summarized briefly as follows: (1) The surfaces to be measured are prepared by condensation of the metal vapor on glass after an exhaustive outgassing which includes repetitive vacuum fusion, fractional distillation, and, when necessary, redistillation of the selected fractions. (2) Each work function determination is based on the measurement of an extended series of different surfaces, a procedure which either establishes the reproducibility of the measurements or reveals inadequacies in the outgassing technique. (3) The first measurement on each surface is obtained immediately after its deposition and within a time interval which is short compared to the time required to form an equilibrium layer of contaminating gas on the surface. This procedure supplies a definite means for estimating the degree of contamination of the surface at the time of measurement.[2] (4) The work function of each surface is determined by measuring its difference of potential with respect to a barium reference surface prepared by a technique which has been found[1] to give surfaces consistently reproducible and constant to 0.01 ev or better.

A large number of unpublished measurements on copper, taken in this laboratory in 1939–41 with tubes of several different types, gave work function values which varied in random fashion over a range of about 0.5 ev without showing any trend toward better reproducibility. These results were obtained after outgassing treatments which were comparable in all respects to those which have given[1] excellent results on silver, zinc, magnesium, and lithium. In the present work, outgassing of the copper has been carried to an extreme and our earlier tube designs so modified as to simplify the manipulations required for obtaining short deposition-

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[1] P. A. Anderson, Phys. Rev. **59**, 1034 (1941); **57**, 122 (1940) and earlier reports cited therein.

[2] Reference 1, 1940 paper.

measurement intervals. These procedures have given work functions reproducible to a few centivolts in the initial readings and drifts with aging which are so slow that the initial readings can probably be taken as characteristic of clean copper.

TUBE DESIGN AND EXPERIMENTAL PROCEDURES

The experimental procedure, insofar as it involves modifications of our previous techniques,[1] may be described in connection with the design of the measuring tube, Fig. 1. The target on which the films of copper and barium are laid down is a glass drum pivoted on glass bearings and operated as a pendulum. The "measuring position" at which the freshly deposited metal film is centered over the electron gun is the equilibrium position to which the pendulum returns automatically whenever it is released. When a film of either metal is to be deposited, the drum is rotated to the appropriate position by traction of a small Alnico magnet on the glass-enclosed armature. Friction in the bearings damps the pendulum oscillations sufficiently to bring the target to rest a second or two after release; the deposition-measurement interval is thus reduced to the time required for bringing the galvanometer to the selected reference reading. The drum serves the important purpose, also, of isolating the vaporizing compartments from each other and from the electron gun, i.e., of preventing contamination of the copper charge or gun by the barium. The glass spindles of the drum were sealed on with the aid of a glassblowing lathe to insure constant target-gun geometry at all positions of the target.

The barium vaporizing assembly, which provides fractional distillation of the metal and redistillation of the fractions used for preparing the measured surfaces, was similar to that employed in previous investigations of this series. The first copper vaporizer was designed to handle a relatively large charge (order of 1.0–1.5 g) of the metal without excessively heavy current leads and with reasonably high efficiency in terms of the ratio of distillate intercepted by the second vaporizer to the total quantity of copper vaporized. The usual horizontal tungsten foil boat is not satisfactory for this purpose; the fused copper flows along the foil and shorts most of it out.

The outgassing schedule, involving prolonged baking of the tube at 450°C before introduction of the metal charges, another extended bake at 350°C after charging, and repetitive high frequency treatment of all metal parts, was similar to that used for silver.[3] The treatment of the barium followed the procedure described in our recent report on lithium.[4] The copper used in this work was Hilger's spectroscopic material, Lot No. 10300, which was supplied with an exceptionally complete analysis showing 0.004 percent oxygen and 0.0007 percent iron as the only impurities present in amounts exceeding 0.0001 percent. During the outgassing of the tube and before seal-off, the copper charge was melted down five times. After seal-off, alternate fusions and solidifications of the copper interspersed with similar treatments of the barium were continued until approximately half of the charges had been vaporized. Since copper vaporizes rather slowly at temperatures slightly above the melting point, thirty-five fusions were included in this stage of the outgassing. The second vaporizers were flashed to remove the discarded fractions of copper and barium before proceeding with the measurements. The current through the first copper vaporizer was then increased to a value which was high enough to give a suitable deposit on the second vaporizer in about ten minutes, that is enough copper to form an opaque film on the target when the redistillation was carried out. As each new film of copper was deposited on the target it was measured as quickly as possible, usually within ten seconds of its deposition, and then at intervals of one minute to establish the rate of drift of the work function with aging. This procedure was

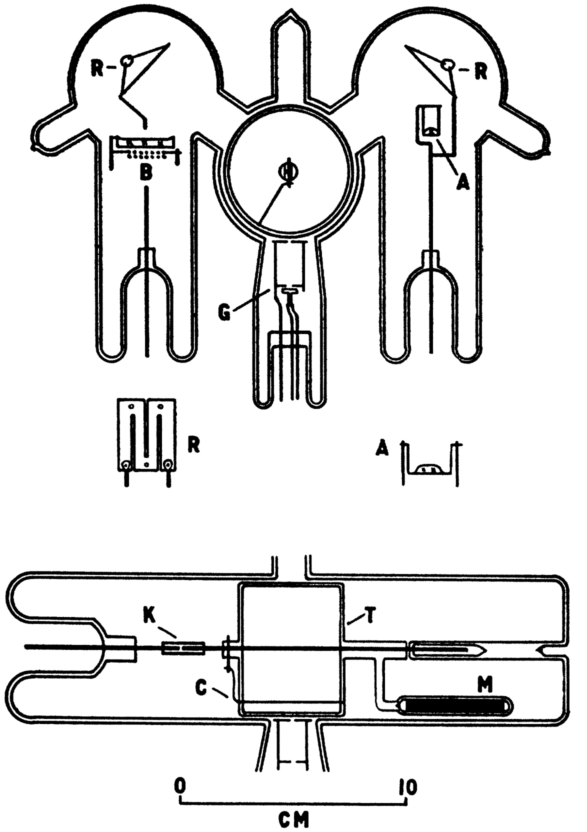

FIG. 1. Tube for measurement of contact difference of potential between vaporized films of Cu and Ba. Side view of complete tube above and of target section, rotated 90°, below. First Cu vaporizer *A* is 1-mil Ta foil 6-mm wide. Second vaporizers *R* of 1-mil Ta foil. Target *T* is Pyrex drum with 60-mil tungsten spindle rotating freely in nickel bearing *K*. Contact to metal film is by 20-mil Pt wire *C* embedded in face of drum. *M* is glass-enclosed soft iron armature. For detail of electron gun *G* and first Ba vaporizer *B*, see reference 1 of text. All leads 60-mil tungsten.

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[3] Reference 1, 1941 paper.

[4] Paul A. Anderson, Phys. Rev. **75**, 1205 (1949).

repeated until the copper charge on the first vaporizer was exhausted. A succession of barium films was then deposited on the copper and measured in like fashion. The electrical circuit used in these measurements has been described previously.[4]

THE CONTACT DIFFERENCE OF POTENTIAL BETWEEN COPPER AND BARIUM

The results to be described are based on measurements on fourteen copper surfaces and eight barium surfaces, prepared as described above. The retarding potential required to establish the reference electron current to the target in the measurement taken immediately after the deposition of a new film is referred to hereafter as the "initial reading." The barium films gave, as usual, initial readings which were consistently reproducible to 0.01 volt or better and constant to 0.01 volt for periods of hours or even days after deposition. The serial numbering of the copper surfaces, running from 1 through 14, conforms to the order in which these surfaces were prepared from successive fractions of the distillate. Copper films 1–4 inclusive gave initial readings which varied at random by amounts corresponding to an extreme variation of 0.24 ev in the work function, a reproducibility markedly better than that obtained in our earlier unpublished measurements but still far from satisfactory. In films 5–8 a regular trend in the initial readings, corresponding to a progressive increase in work function totaling 0.18 ev appeared. This trend then disappeared; films 9–14 gave initial readings which again varied at random but over a range of only ±0.03 ev. The contact difference of potential Cu—Ba derived from the mean of the initial readings on films 9–14 is 1.94±0.03 volts, copper negative to barium.

THE WORK FUNCTION OF COPPER

Neglecting deviations which arise from the Maxwell tails of the Fermi distributions and which are well within the limits of experimental error at room temperature, the difference between the work functions of two metals is equal to the contact difference of potential between them, multiplied by the elementary charge. Addition of our value for the contact difference of potential Cu—Ba to 2.52 ev, the work function of barium,[5] yields the value 4.46±0.03 ev for the work function of copper. This value is to be taken as representative of the present work. Previously reported values[6] for the work function of copper range from 4.1 to 4.5 ev. The thermionic measurements of Goetz,[7] probably the most careful and thorough of the earlier investigations, gave 4.38 ev. It is interesting that this range of values, obtained in seven independent studies by a variety of methods and techniques, coincides almost exactly with the range of values obtained in our measurements on copper films 1–14, namely 4.04 to 4.49 ev. Our observations on the variation of the work function with the aging of freshly deposited copper films, described below, show in every case a trend toward lower work function and suggest that the work function of completely clean copper films deposited on glass at room temperature is probably close to 4.50 ev.

EFFECTS OF GASEOUS CONTAMINANTS ON THE WORK FUNCTION OF COPPER

We are concerned here not only with the initial readings on newly formed copper surfaces but with the behavior of these films on aging. The results of some two hundred measurements on the fourteen copper surfaces may be summarized as follows: (1) The first films to be deposited, characterized by poor reproducibility in the initial readings, showed a relatively rapid drift toward lower work function on aging. Film No. 1, the extreme example of drift, gave a work function of 4.32 ev ten seconds after its deposition, 4.27 at one minute, 4.23 at two minutes, 4.12 at eight minutes, and a slower drift thereafter. (2) Improvement in the reproducibility of the initial reading was accompanied by a striking decrease in both the rate and magnitude of the drift. Film No. 10, typical of the 9–14 group, gave an initial work function of 4.47 and successive readings of 4.47, 4.47, 4.47, 4.46, and 4.46 at one minute intervals without further drop within 12 minutes. (3) In no case was a drift toward higher work function observed. These observations seem to bear out the tentative conclusions reached in our earlier unpublished work, namely, that traces of gas retained by a copper charge through a series of fusions and solidifications are evaporated with the copper and are then reabsorbed by the condensed film. In the present measurements, the quantity of gas left in the copper charge on the first vaporizer appears to have been reduced to negligible proportions only after most of the copper had been evaporated. The fact that the residual gas, presumably oxygen, lowers the work function suggests further that solution in the condensed copper film rather than permanent adsorption on the surface is involved. It is well known that oxygen adsorbed on a clean tungsten surface raises the work function and a similar behavior would be expected of copper if the oxygen remained on the surface as an adsorbed film.

I am indebted to Mr. Frank Peters, departmental glassblower, for the skill and care which he has given to the construction of the tubes used in this work.

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[5] N. C. Jamison and R. J. Cashman, Phys. Rev. **50**, 624 (1936).

[6] A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill Book Company, Inc., New York, 1932), p. 75.

[7] A. Goetz, Zeits. f. Physik **43**, 531 (1927).