The Contact Difference of Potential Between Barium and Silver. The External Work Function of Silver

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A method has been developed for measuring contact differences of potential between metal surfaces in which both surfaces are prepared by thermal vaporization in a gettered vacuum. The design of the tubes permitted them to be immersed in liquid air during the measurements. The fresh surfaces were measured immediately (2–3 seconds) after they were formed and the reproducibility of the contact potential difference determined by measuring in alternation films formed in fractional distillations of the two metals. Barium surfaces were reproducible to ±0.002 volt and constant to ±0.001 volt. The silver surfaces were reproducible to ±0.02 volt and constant to ±0.001 volt. The contact difference of potential at liquid-air temperature between microcrystalline barium and silver is found to be 1.94±0.02 volts. Combination of this result with the value 2.39 volts found for the work function of barium in measurements on tungsten-barium places the work function of microcrystalline silver at 4.33±0.05 equivalent volts, as compared to 4.08 volts for the thermionically determined heat function (Goetz) and 4.74 volts for the work function of thermally etched silver wires measured photoelectrically (Winch). A valid comparison of these three values will be possible only after the variations of the work functions with temperature and with crystal surface structure have been determined.

IN a study of the contact difference of potential between tungsten and barium[1] it has been found that clean barium surfaces prepared by vaporization of the metal in a very high vacuum are extraordinarily reproducible. With a method of measurement sensitive to work function changes of the order of a millivolt a reproducibility better than ±0.005 volt could be obtained consistently in an extended series of films so prepared. The investigation revealed, also, an unexpected constancy in the work function of these barium surfaces. The films were measured immediately after deposition and in a satisfactory vacuum changed so slowly that readings to ±0.001 volt could be taken with confidence. In the communication cited it was proposed to adopt thoroughly outgassed tungsten as a standard reference surface in the measurement of contact differences of potential. The strikingly satisfactory behavior of barium, however, and the relative ease with which clean barium surfaces can be prepared suggest its use as a working standard, and as a primary standard after its work function has been finally established.[2] A further important advantage in such a choice lies in the fact that barium is the most efficient of the gettering metals; the otherwise independent operations of forming the reference surface and gettering the tube may be combined and the design of the tube simplified accordingly.

In work function investigations of the intermediate melting point metals (e.g., silver, copper, gold) by thermionic, photoelectric, and contact potential methods it has been customary to study massive specimens of the metals and to rely on prolonged heating for the outgassing and cleaning of these specimens. Consideration of the vapor pressure curves for these metals and for the metallic salts and oxides which must be assumed to be present on the most carefully handled specimens (the oxides and salts of the alkali and alkaline-earth metals which are most likely to be present are especially effective in vitiating results and have, also, especially low vapor pressures) forces the conclusion that it is impossible to clean a massive specimen completely by such treatment no matter how it is prolonged. Our methods of measurement have been based, therefore, on the premise that it is possible to secure clean surfaces of these metals only by fractional distillation in an adequate vacuum, where an "adequate vacuum" is defined as one for which the rate of deposition of residual gas on the surface is so low as to produce no measurable change in the work function of that surface in the time required for its preparation and measurement. This criterion requires, in turn, a method of measurement capable of fol-

[1] P. A. Anderson, Phys. Rev. **47**, 958 (1935).

[2] A revision of the work function of barium would, of course, carry over to all other work functions determined by measurement of the contact differences of potential of other metals against barium and would leave the value of such measurements unaffected.

lowing any work function changes which may occur immediately after the preparation of a fresh metal film. With these considerations in mind it was the purpose of the present work to study the contact difference of potential between vaporized barium films and films of silver likewise prepared by vaporization of that metal in a gettered vacuum.

Method. The Tube

As regards its electrical features the method of measurement was that described in the previous paper.[1] The scheme of preparation of the surfaces may be described in connection with the design of the tube, Fig. 1. The barium and silver were vaporized from shallow molybdenum foil troughs A and B (B was similar to A and is omitted from the sketch) and films of these metals deposited alternately on the flattened end of the glass re-entry tube R. The troughs were of 1-mil foil about 5×30 mm in size, attached with molybdenum rivets to 1.5-mm molybdenum supporting wires, which were in turn welded to the 1.5-mm tungsten wires of the press. The geometrical arrangement of the vaporizing ovens, connecting tubes, and condensing surface was such that each vapor jet covered the entire condensing surface but was prevented from coming into contact with the electron gun.[3] Contact with the films was established at the edge of R by a light tungsten spring carried on the stiff tungsten wire K. The electron gun E was mounted symmetrically under R. This gun, of the type described by Farnsworth,[4] was constructed of 4-mil molybdenum foil with diaphragm openings 1.5 mm in diameter. The emitter was a strip of 1-mil tungsten foil 2×30 mm bent into a noninductive T as shown. The potentials placed on the gun during the measurements were, emitter: -8 volts; accelerating diaphragm: $+12$ volts; terminal retarding diaphragms: 0 volts, giving an approximately homogeneous beam of about 8 volts energy. The grounded terminal section of the gun was connected by a whisker with a thin film of gold which had been evaporated to the middle section of the wall of the measuring chamber before the press carrying the gun was sealed in.

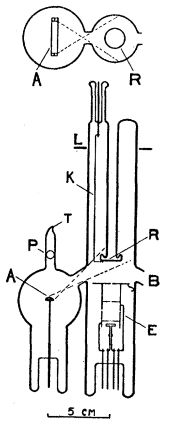

FIG. 1. The tube. Vaporizing ovens A and B form on R metal films which are measured by an electron beam projected from the gun E. Metal introduced into oven at T. Contact to films by lead K. Connection to pumps at P (seal-off). Tube immersed in liquid air to L.

Procedure

Materials

The barium, obtained from Osram and taken from the same block as used in the previous measurements on tungsten-barium, contained traces of strontium and iron as the only detectable impurities. The silver was purified electrolytically from initially highly pure stock. Through the kindness of Dr. S. E. Sheppard of the Eastman Research Laboratories it was examined spectroscopically and found to contain "no detectable impurities." Before its introduction into the tube the silver was melted down upon an electrically heated molybdenum foil strip in an evacuated auxiliary tube to remove dissolved oxygen. To prevent resolution of oxygen the silver pellets were taken from the premelting tube only when the measuring tube was ready for them.

Outgassing

The tube was connected at P with the pumping system described in the previous paper and, before charging with barium and silver, given a preliminary baking at 500°C for 48 hours. At intervals during this baking the electron gun was subjected to high frequency heating at 1000°C or higher and the ovens A and B flashed

[3] Although localized changes in contact potential along the gun cancel out in a calculation of the final electron energy such changes, unless symmetrical, affect the distribution of field and the configuration of the electron beam.

[4] Farnsworth, J. Opt. Soc. Am. and Rev. Sci. Inst. **15**, 290 (1927).

at about 2000°. The tube was then opened at T, the silver and barium quickly introduced, and the tube reclosed and immediately re-evacuated. It was then subjected to seven or eight bakings of eight hours each at about 350°C, between which were interspersed high frequency heatings of the electron gun, flashings of the ovens at temperatures sufficient to melt down the barium and silver, and flashings of the electron emitter at temperatures well above its normal operating temperature. The tube was sealed from the pumping system while still hot and a fresh coat of barium immediately vaporized to the walls of the tube.

Measurements

Before starting a series of measurements the tube was immersed in liquid air to the level L and the emitter run at its operating temperature long enough to establish steady emission. The barium and silver ovens were flashed simultaneously at temperatures sufficient to melt down the metals, the barium oven then flashed alone to deposit a thick film of barium on R, and the electron current-retarding potential characteristic for this film determined. As described in the previous paper[1] a reference deflection and corresponding potential setting near the middle of the straight-line portion of the characteristic was chosen and the test for a satisfactory vacuum made by checking the deflection for constancy, starting the observations immediately after the deposition of a fresh film. About half of the tubes have had to be discarded at this point, though they had passed the ordinary tests for pinhole leaks. The reproducibility of the potential setting for barium was then determined by measuring the potential required to establish the reference deflection for each of a series of fresh barium films. After obtaining the reproducible potential setting for barium a series of silver films was prepared and measured in the same manner and the reproducible setting for silver thus determined. The contact difference of potential established by these two sets of measurements was then checked by repeating in alternation the process of preparing and measuring the films of the two metals. Four to eight checks could be secured before the oven charges in a given tube were exhausted. Occasionally the complete potential-current characteristics for barium and silver surfaces were taken and the $V-\log i$ curves plotted. Such curves are parallel straight lines below their "break points" and the displacement along the potential axis of one curve with respect to the other is equal to the contact difference of potential. The results so obtained have been found to agree in every case with those given by the method described above. The procedure involving $V-\log i$ curves eliminates, in the measurement of any single pair of films, the possibility of errors arising from fluctuations in the total electron output of the gun. On the other hand, considerable time is required for determining the complete characteristics and the advantage of taking potential settings on unquestionably fresh surfaces is lost. If, as in the procedure which has been adopted, not one but a number of pairs of surfaces is measured total electron fluctuation is effectively eliminated as a possible source of error. This conclusion is borne out by the fact that throughout the measurements on barium-tungsten and barium-silver such fluctuations in potential settings as have been observed have been definitely characteristic of surfaces of a given metal rather than common to all the metals, as they would be if they originated in total electron fluctuations.

Results

As in the earlier work on tungsten-barium the barium surfaces were found to be highly constant and reproducible from the start. The variations in potential settings for successive films were of the order of ± 0.002 volt from the mean (a reproducibility of ± 0.001 volt has frequently been obtained) and were in the nature of fluctuations rather than of the progressive changes to be expected if appreciable amounts of solid or gaseous impurities were condensing with the barium. In view of the initial purity of the specimens and the fact that about half of each specimen had been vaporized during the preliminary fusions and getterings this result was not surprising. The silver films exhibited the same order of constancy as was shown by the barium surfaces but their reproducibility was ± 0.02 volt as compared to ± 0.002 volt for barium. The variation in work function of the silver surfaces was found to occur between films prepared in close succession to the same degree

TABLE I. *Contact difference of potential between barium and silver at 90°K.*

(−V) Ba	(−V) Ag	CONTACT POTENTIAL
10.79	8.85	1.94 volts
10.79	8.84	1.95
10.79	8.86	1.93
10.79	8.84	1.95
10.79	8.87	1.92
10.79	8.86	1.93
10.79	8.84	1.95
10.79	8.86	1.93

as between films selected at random from different series of measurements, and is evidently not due to impurities condensing with the silver. It is, possibly, connected with the fact that a film of metal formed by condensation at liquid air temperatures is not in a state of structural equilibrium and that variations arising in this way are aggravated in metals with relatively rigid lattices. The electronic work function of a surface is intimately related to its electrode potential and it is well known that polycrystalline specimens of the harder metals, in contradistinction to such soft metals as sodium and lead, do not give reproducible electrode potentials.[5] A few measurements made on silver films deposited at room temperature, which are to be extended and included in a forthcoming report on the temperature dependence of contact potentials and work functions, bear out this explanation.

Table I is a résumé of measurements of the contact difference of potential between barium and silver, all made with the tubes immersed in liquid air. The measurements listed have been selected to show the maximum observed deviations from the mean and none of the measurements which have been made fall outside the limits indicated. 1.94 volts is chosen as the value for the contact difference of potential Ba-Ag which best represents these measurements. Application of the Sommerfeld relation $V_{Ba,\,Ag}+\phi_{Ba}=\phi_{Ag}$, with ϕ_{Ba} taken as 2.39 ± 0.05 volts,[1] yields the value 4.33 ± 0.05 equivalent volts for the external work function of silver. In a thermionic study of solid and liquid silver in the neighborhood of the melting point Goetz[6] found the value 4.08 volts for the thermionic work function, or "heat function,"[7] of solid silver at 925°C. Winch,[8] using the photoelectric method and wire specimens which were subjected to prolonged heating at 600°C, obtained apparent thresholds at temperatures between 296–873°C which, when subjected to Fowler's extrapolation, yield 4.74 volts as the true threshold for his specimens.[9] The fact that the present measurements give a value which is close to the mean of these results has little significance other than indicating that the method of contact potentials is giving results of the same order as have been obtained in careful thermionic and photoelectric studies. As Bridgman[10] and Becker and Brattain,[7] among others, have pointed out, the comparison of heat functions and work functions will be possible only after the temperature dependence of the work functions have been determined. It should be remarked, furthermore, that differences of a few decivolts between the results of independent measurements of the work function of a given metal by contact potential or photoelectric methods may well be due to differences in the crystal structure of the specimens measured.[11] The use of the term "work function of silver" is justified only when qualified by a description of the surface, and this description is possible in general only for the two limiting cases in which the surface is (a) microcrystalline with the crystallites oriented at random, or (b) a definite face of a single crystal. In the present measurements the surfaces must have approximated to Case (a) while Winch's silver wires after their heat treatment probably consisted of a few monocrystalline sections thermally etched until low energy crystal facets[12] predominated, a process which is known to occur during the "aging" of a tungsten wire.[13]

[5] Lewis and Randall, *Thermodynamics* (McGraw-Hill 1923), Chapter 30. Single crystals of the harder metals have been shown to give highly reproducible electromotive potentials: P. A. Anderson, J. Am. Chem. Soc. **52**, 1000 (1930).

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

[7] Becker and Brattain, Phys. Rev. **45**, 694 (1934).

[8] Winch, Phys. Rev. **37**, 1269 (1931).

[9] The "true threshold" so obtained is, of course, the corrected threshold for the surface measured whatever the state of that surface. It is not necessarily the value characteristic of the clean metal.

[10] P. W. Bridgman, Phys. Rev. **27**, 623 (1926); **31**, 90 (1928); **31**, 861 (1928) and *Thermodynamics of Electrical Phenomena in Metals* (Macmillan, 1934).

[11] Rose, Phys. Rev. **44**, 585 (1933) found a contact difference of potential of 0.38 volt between imperfect (111) and (100) faces of a copper crystal.

[12] P. A. Anderson, Phys. Rev. **40**, 596 (1932) and references cited there. The molecular process of crystal growth in the face-centered cubic lattice of silver must be similar to that in a hexagonal close-packed lattice.

[13] I. Langmuir, Phys. Rev. **22**, 374 (1923).