PHYSICAL REVIEW VOLUME 88, NUMBER 3 NOVEMBER 1, 1952

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

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(Received June 25, 1952)

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 measurements 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.

THE dependence of the observed work function of a metal specimen on the condition of its surface is determined by (1) foreign surface contaminants which change the surface double layer to a value which is not characteristic of the metal itself, (2) the arrangement of the atoms of the metal in the outermost layers of the specimen, and (3) the method of measurement, if peculiarities in the response of the measuring arrangement to factors (1) or (2) are involved. It is well known that minute surface contaminations may render work function measurements valueless, and this fact has made the development of techniques for the preparation of clean surfaces the central objective in photoelectric and contact potential investigations. Factor (2), the primary structure factor, can be studied profitably only after definite evidence has been secured that surface contaminants are absent or inoperative. Such evidence is hard to get and after several decades of experimental work is available in reasonably convincing form for only a few metals. The study of monocrystalline surfaces of known indices, the only surfaces for which the work function has the full status of a material constant, is just beginning.

Factor (3), the main point of interest in the present work, has to be considered whenever surfaces containing "patches," that is, micro- or macroscopic areas of different work function, are involved. The question then arises as to how the observed work function is related to the average work function of the surface. The average work function is defined, in the symbols of Herring and Nichols,[1] as $\bar{\phi}=\sum f_i\phi_i$, where ϕ_i is the work function of patches of the ith type and f_i is the fraction of the surface occupied by patches of that type. This question has received little explicit attention in contact potential and photoelectric studies but is considered at length in Herring and Nichols' valuable review of thermionic emission phenomena.[1] Examination of this most recent treatment shows, however, that patch theory, in so far as its application to contact potential methods involving the collection of slow electrons in retarding fields is concerned, is useful mainly as an aid to formulating, rather than answering, the question of the relationship of observed to average work functions. In its present form, patch theory is based on the assumption ("normal energy approximation") that the motion of electrons close to a patchy surface is unaffected by the tangential components of the patch fields. This assumption appears to be reasonable for the case of strong accelerating fields but to be invalid for the slow electron, retarding field case.

A practicable line of attack on the problem of observed and average work functions, and means of determining the extent to which patch fields influence retarding-field contact potential measurements, would appear to be that of comparing such measurements with observations taken by a method which involves no interaction between electrons and patch fields. The Kelvin method of contact potential measurement has the characteristics needed for the yardstick method. Subject only to the easily verifiable condition that patch dimensions are small with respect to interplate spacing, conventional field theory shows that the observed contact potential difference is precisely equal to the difference between the average work functions of the surfaces.[1] For the comparison to be valid, it is evident that the contamination and primary structure factors must be eliminated, and this condition can be satisfied beyond question only if the two methods are applied to the same surfaces in a single tube. The

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* Assisted by the ONR.

[1] C. Herring and M. H. Nichols, Revs. Modern Phys. 21, 185 (1949).

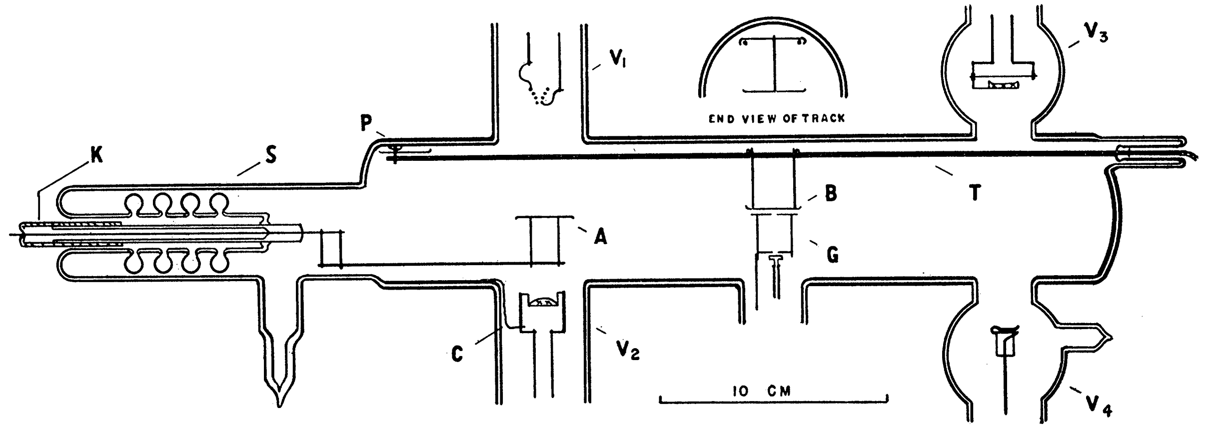

FIG. 1. Scale diagram of the tube. Rocking electrode A, a 10-mil Ta disk riveted to 60-mil Ta posts, is operated by the waxed-on metal tube K through all-glass sylphon S. Sliding electrode B, similarly constructed, is moved on track T (two 80-mil W wires) by tipping tube. Ag is vaporized by 25-mil W wire cone V_1 and 0.025×6 mm Ta foil trough V_2; Ba by Ta foil trough V_4 and 0.025×10 mm Ta foil radiator V_3. C is Pt contact partially embedded in wall. P is Ta foil shield to maintain insulation of T.

objective of the present work was a comparison of this kind between measurements taken by the Kelvin and electron beam methods of contact potential determination. Silver and barium were selected for the study because previous work in this laboratory has shown that each of these metals, when prepared by evaporation in an outgassed, sealed-off tube, consistently yields work function values which are highly reproducible and constant over long periods of time.

METHODS

The theory of the Kelvin method of contact potential measurement is well known. The experimental conditions necessary for satisfactory Kelvin measurements in confined spaces require some comment and are discussed below. The electron beam method, developed primarily for the purpose of minimizing the time interval between the deposition and measurement of a metal surface, has been described previously.[2] The measured surfaces of silver and barium are prepared by the distillation technique which has formed the basis of all of our contact potential studies.[2] This technique involves, in brief, condensation of the metal vapor on a glass or metal substrate after an exhaustive outgassing which includes repetitive fusion, fractional distillation and, when necessary, redistillation of the middle fractions in the measuring tube itself. Reproducibility of the work function is established, or inadequate outgassing revealed, by measurement of a series of different surfaces formed in successive vaporizations. For the purposes of the present problem, redistillation of the middle fractions was unnecessary and was omitted.

CONDITIONS FOR SATISFACTORY KELVIN MEASUREMENTS

In the conventional theoretical treatment of the Kelvin method, complete isolation of the metal pair is assumed implicitly. In practice, the pair is part of an array which must include an electrostatic shield and may include other metal or dielectric components. A set of contact potential differences rather than a single potential difference is involved, and no single applied potential can bring the field at the plates to zero. It is customary to minimize the effects of extraneous fields by making the spacing between the measured surfaces and the shield large with respect to the interplate spacing. The sharpness of the balance point, and precision of measurement, is then determined by the dimensions, spacings, and contact potential differences of the components of the array. Unpublished work in this laboratory has shown that with the customary foreign metal shielding sharp and reproducible balance points are obtained consistently only for plate-to-shield spacings which are too large to be practicable in glass systems which have to be intensively outgassed.[3] An alternative procedure which has been developed as particularly suitable for use with the distillation method of surface preparation and which is capable of eliminating extraneous fields entirely, is as follows. (1) The pair of surfaces under measurement is surrounded with a shield which is composed of one or the other of the metals of the pair, and (2) the supports of each plate are coated with the metal of which the plate itself is composed. Since large contact potential differences may exist between surfaces of the same metal if contamination is allowed, it is necessary that the shield and auxiliary coatings be prepared with the same care as are the measured surfaces themselves. This condition is met in the present work by coating the walls and accessory components of the measuring section of the tube with the vapor of high purity, outgassed silver simultaneously with the deposition of the silver surface which is to be measured. The barium electrode and its

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[2] Paul A. Anderson, Phys. Rev. **76**, 388 (1949); **75**, 1205 (1949), and earlier reports cited therein.

[3] Similar conclusions have been reached independently by Dr. R. Bourion at Bristol (Doctoral thesis; University of Bristol, 1949, unpublished).

supports are treated similarly in an isolated section of the tube. The sharpness of the Kelvin balance obtainable with this technique appears to be limited only by the sensitivity of the detecting circuit.

TUBE DESIGN AND EXPERIMENTAL PROCEDURE

The tube, Fig. 1, is so designed that one of the two plates which form the substrates for deposition of the measured surfaces can be coated completely with silver while the other can be coated completely with either silver or barium. Two vaporizers are provided for each of the metals and are so disposed that practically complete coverage of the plates, front and back, and a continuous silver film on the walls of the measuring section are secured. This arrangement provides the following contact potential measurements: (1) Ag-Ag by the Kelvin method. This measurement checks the condition that the balance point for plates of the same metal must be sharp at an applied potential of zero if uniformity of average work function has been established by the deposition and if extraneous fields are in fact negligible. (2) Ba-Ag by the Kelvin method for an extensive series of pairs; the surfaces may be renewed simultaneously or independently for determining reproducibility and constancy and minimizing the possibility of accidental error. (3) Ba-Ag by the electron beam method for the same silver and barium surfaces measured in (2).

The outgassing procedure, involving baking of the tube, inductive heating of metal components, and repetitive fusion of the silver and barium charges before and after seal-off, was similar to that described in detail in previous reports.[2] The circuit and procedures for the electron beam measurements have been described.[2] The balance point detector for the Kelvin measurements was an FP-54 electrometer tube in an uncompensated circuit of conventional type with bucking voltage and galvanometer in the plate circuit. The rocking electrode *A* was connected to the shield and to ground through the low resistance potentiometer circuit which supplied the balancing voltage. The sliding electrode *B* was connected to the control grid of the FP-54 and to a 10^{10} ohm leak to ground. The extension tube which operated the glass sylphon passed through a slot in the wall of a large shielding cabinet and into an external frame in which the rest position of *A* and the amplitude of its motion were adjusted with set-screws and spring loading. The plate *A* could be displaced through a centimeter or more without danger of breakage.

The measuring schedule, started after the tube was sealed from the pumps, was as follows: (1) With plate *B* near the middle of the tube where it received no vapor, repetitive fusion of the silver and barium charges was continued until fusion produced no evolution of gas as indicated by a change in the anode current of the gun.[2] During this treatment, plate *A* and the Kelvin section of the tube received a heavy coat of silver while the barium deposit was localized at the other end of the tube. (2) Plate *B* was moved close to but not overlapping plate *A* and coated with silver during the simultaneous operation of both silver vaporizers. Plate *A* simultaneously received a fresh deposit of silver. (3) Plate *B* was moved into register with *A* and the Kelvin balance point for Ag-Ag determined by finding the applied potential which eliminated the current pulse produced when *A* was moved away from *B*. (4) Plate *B* was moved over the electron gun and the current-voltage characteristic of the silver surface determined. (5) Steps 2–4 were repeated to establish reproducibility. (6) Plate *B* was moved between the barium vaporizers and coated. Steps 3–5 were then carried through, with the simultaneous and separate renewal of surfaces mentioned above, to obtain the Ba-Ag contact potentials.

RESULTS

The electron beam measurements, taken by our standardized procedure,[2] gave the value 1.79±0.03 volts for the contact potential difference Ag-Ba. Potential settings for the individual surfaces of silver and barium were constant to ±0.01 volt during aging periods extending from two minutes to an hour or more, in agreement with our earlier observations.[4] The observed contact potential was 0.16 volts lower than our earlier value and makes the work function of the silver films on tantalum equal to 4.31±0.03 ev, as computed for a barium work function of 2.52 ev. Our 1941 measurements were made on mirror-like silver surfaces formed by deposition on glass. The silver films studied in the present work showed the coarsely crystalline (matte) structure characteristic of deposition on outgassed tantalum, and the difference in observed values is probably attributable to this difference in structure. It is interesting to note that Mitchell and Mitchell,[5] using the electron beam method of measurement and well-aged tungsten as a reference, have recently obtained 4.33 ev for the work function of silver films deposited on the tungsten. The difference between our present and earlier values is, of course, not significant for the present comparative measurements. The use of tantalum, however, introduces the possibility of preferential orientation of the deposited metal by the relatively large fibrous crystallites of the substrate and, perhaps, of a more complex surface structure than is obtained in deposition on glass. In our current work, designed to extend the method described here to other metals, glass substrates are being favored over the more convenient tantalum plates.

In the Kelvin measurements the contact potential difference Ag-Ag was zero to ±0.01 v in every case. The first pair of Ag-Ba surfaces to be measured gave the value 1.77±0.01 v, and thereafter all pairs of Ag-Ba

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[4] P. A. Anderson, Phys. Rev. **59**, 1034 (1941).

[5] E. W. J. Mitchell and J. W. Mitchell, Proc. Roy. Soc. (London) **A210**, 70 (1951).

films gave the value 1.78±0.01 v. The reproducibility and constancy of this value were such that potentiometer settings of 1.77 and 1.79 v bracketed the balance point in all of the thirty-five measurements taken after renewal of one or both of the surfaces and during aging. From the standpoint of reproducibility and constancy, this series of measurements was the most satisfactory obtained in our contact potential work to date. The stability was such as to suggest the possibility of carrying measurement to the millivolt level if the need for such precision should arise and if other factors can be controlled sufficiently to make a precision of this order significant. It should be emphasized, however, that the Kelvin technique as used in the present work does not provide the short time interval between deposition and measurement of a film which is obtainable with the electron beam method and which is necessary for establishing the fact that contaminants are absent or inoperative. It is possible that determination of a contact potential difference with the greatest practicable reliability should involve an initial study of the contamination factor by a short-interval method and subsequent measurement by the Kelvin method.

DISCUSSION

The measurements described above show that, for the particular conditions obtaining in these experiments, no difference between Kelvin and electron beam values larger than the uncertainty of measurement was detectable. The contact difference of potential between barium (B) and silver (A) given by the Kelvin technique is

$$eV_{BA}=\bar{\phi}_A-\bar{\phi}_B, \tag{1}$$

where each $\bar{\phi}$ is an average work function as defined above. It will be shown in a subsequent paper that if each of two patchy surfaces contains an arbitrary number n of patch types, of which j have work functions greater than $\bar{\phi}$, and if the normal energy assumption is accepted, then the contact difference of potential given by the electron beam method is

$$eV_{BA}'=\phi_A-\phi_B+(f_1\delta\phi_1+f_2\delta\phi_2\cdots+f_j\delta\phi_j)_A-(f_1\delta\phi_1\cdots+f_j\delta\phi_j)_B. \tag{2}$$

Here each of the $\delta\phi$ terms is the work function of the designated patch type less the average work function of the surface concerned. All of the f values (fractions of the surface area occupied by the patch types) are arbitrary in this development.

In terms of Eqs. (1) and (2), our experimental results might be interpreted as indicating either (a) that the bracketed terms of Eq. 2 are individually large enough to be significant but are nearly equal in magnitude, or (b) that these terms are individually so small that their sum is negligible. It is conceivable that condition (a) might be satisfied fortuitously but this explanation is otherwise improbable. In general, (b) deserves careful scrutiny whenever the measured surfaces are formed by vapor condensation under conditions which favor an approach to thermodynamic equilibrium. When the deposition rate is low and the substrate temperature is high enough to allow free migration of the impinging atoms, crystal growth theory[6] predicts that crystal faces of low energy will predominate on the crystallites and that the energy spread between the dominant orientations will be small. The atomic arrangement which determines the surface energy must also determine the double-layer contribution to the work function. Large f values will, then, be associated only with small $\delta\phi$ values and each of the bracketed terms of Eq. (2) will be small. In principle, this trend toward minimization of the bracketed terms will always be operative in vapor deposition but it will, of course, be determinative only under the most favorable conditions. Evidence that barium migrates slowly even at room temperature is accumulating and the reproducibility of its work function may be due, in part at least, to this mechanism. It is unlikely that the silver films prepared in the present work satisfied the near-equilibrium conditions but this question is to be investigated.

The most likely conclusion to be drawn from the results is that Eq. (2) is invalid through failure of the normal energy assumption on which its derivation, like that of patch theory analyses in general, is based. The possibility of substituting for present patch theory a theory based on an electron-optical treatment of the patch field region suggests itself as worthy of investigation. In such a treatment, the tangential components of the patch fields will have little effect on the motion of electrons emitted into a strong accelerating field but will become important when the absorption of slow electrons is involved. Each of the bracketed terms of Eq. (2), as interpreted physically, is the increment in potential which must be applied to the collector to compensate for electron reflection at the high ϕ patches. In the electron-optical treatment, an important fraction of these "lost" electrons will be refracted toward the low ϕ patches and there collected. The application of conventional electron-optical techniques to the study of electron trajectories in patch fields appears to be feasible and is being investigated.

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[6] H. E. Buckley, *Crystal Growth* (John Wiley and Sons, Inc., New York, 1951); P. A. Anderson, Phys. Rev. **40**, 596 (1932), and references cited therein.