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# A New Technique for Preparing Monocrystalline Metal Surfaces for Work Function Study. The Work Function of Ag(100)

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A new method of experimental attack upon the problem of the structural dependence of the work functions of the metals is described. The method utilizes the results of recent electron diffraction studies which show that many cubic lattice metals when thermally vaporized and condensed on heated cleavages of rocksalt form films which are in effect single crystals with a (100) plane parallel to NaCl (100). With silver as a typical metal of this class, there has been developed a technique of preparing an Ag(rocksalt) film in the measuring tube itself and of then determining its contact difference of potential against (1) polycrystalline silver films deposited on glass at room temperature, and (2) a reference metal of known work function, barium. The silver was fractionally distilled and only the middle fractions deposited on the glass and rocksalt targets, the barium fractionally and multiply distilled and its discarded fractions used to getter the tubes in which the measurements were made. The contact p.d. between Ag(rocksalt) and Ag(glass) has been found to range from 0.12 v in a preliminary measurement to 0.32±0.03 v in final measurements made after the technique of preparing the Ag(rocksalt) films had been perfected. The contact p.d. for Ag(glass)—Ba is found to be 1.95 v, in close agreement with our earlier results at liquid-air temperature. Work function values computed from these measurements and the work function of Ba, 2.52 ev, are 4.47 ev for Ag(glass) and 4.79 ev for Ag(rocksalt). Since two independent electron diffraction investigations, both especially complete for silver, indicate that Ag(rocksalt) films formed under the conditions of the present experiments invariably approximate closely to the ideal (100) structure, and since the contact potential method measures the average work function of a surface without weighting vestigial regions of imperfect symmetry, our Ag(rocksalt) work function value is identified tentatively with the work function of Ag(100). Our Ag(100) value is in good agreement with Farnsworth and Winch's recent photoelectric measurements on a massive single crystal but Winch's earlier value of 4.74 ev for the work function of a heat-treated silver wire is probably characteristic of the crystal faces of preferred orientation developed by thermal etching rather than of randomly oriented polycrystalline silver. The method developed in the present work for measuring Ag(100) appears to be directly applicable to the (100) orientations of Ni, Cu, Au, Pd and Al.

A MAJOR problem in the experimental and theoretical study of work functions concerns the influence of the crystalline structure of a metal surface upon its work function. There is now abundant evidence for the existence of such a structure dependence but few quantitative data are available for surfaces of definitely known structure. Progress has been hampered by the extraordinary technical difficulties involved not only in preparing monocrystalline surfaces which are free from serious structural defects but in satisfying simultaneously the requirement, demanded of all work function measurements, that these surfaces shall be free from adsorbed gases and vapors. With the exception of studies on tungsten,[1] by methods applicable only to the ultra-high melting point metals, previous work[2] has been done with massive single crystal ingots and it has been necessary to prepare the required crystal faces by grinding, followed by chemical or electrolytic etching. Surface contaminations then have to be removed as completely as is possible in an outgassing in which the maximum permissible outgassing temperature is limited by the onset of thermal etching, with attendant development of unwanted crystal facets. The method is necessarily laborious and there is some question as to the quality of the faces which can be prepared by its use. Rose,[2] in measuring the contact p.d. between the (100) and (111) orientations of a copper crystal prepared by this method, observed extraneous reflections on the finished faces and concluded that his final values were characteristic of crystal faces contaminated with gas and with unwanted crystal facets.

A relatively simple method of preparing gas-free single crystal surfaces in the measuring tube itself, without atmospheric exposure, mechanical working or chemical etching, is suggested by

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[1] R. P. Johnson and W. Shockley, Phys. Rev. **49**, 436 (1936); C. E. Mendenhall and C. F. DeVoe, Phys. Rev. **51**, 346 (1937); S. T. Martin, Phys. Rev. **56**, 947 (1939); M. H. Nichols, Phys. Rev. **57**, 297 (1940).

[2] H. E. Farnsworth and B. A. Rose, Proc. Nat. Acad. **19**, 777 (1933); B. A. Rose, Phys. Rev. **44**, 585 (1933); H. E. Farnsworth and R. P. Winch, Phys. Rev. **58**, 812 (1940).

Brück's observation[3] that many isometric metals, e.g., Cu, Au, Ag, Ni and Pd, when thermally vaporized and condensed on heated rocksalt cleavages, form films which exhibit electron diffraction patterns characteristic of the (100) faces of single crystals of these metals. With the purpose of testing this possibility, experiments on the contact difference of potential between silver films condensed on glass and on rocksalt were started by the author early in 1936. The first experiments were vitiated by the use of natural rocksalt which, even after prolonged heating near the sublimation point, could not be outgassed sufficiently to allow the maintenance of an adequate vacuum in a sealed-off tube. This difficulty was removed by the use of artificial rocksalt crystals,[4] which are free from impounded water and hygroscopic impurities and give exceptionally good cleavages. Other difficulties have been encountered in the tendency of silver films, deposited on rocksalt at too slow a rate, to show an erratic electrical conductivity and in the problem of making electrical contact to these films, much more fragile than films of similar thickness laid down on glass. Throughout the preliminary measurements, made with a variety of different tube designs and techniques, the silver films on rocksalt, to be designated Ag(rocksalt), were consistently electronegative to silver films on glass, Ag(glass), but reproducibility within satisfactorily narrow limits has been obtained only in the most recent measurements. Unlike the results reported in previous papers of this series and based on the measurement of twenty or thirty duplicate surfaces, the present "final" results are based on measurements of only two Ag(rocksalt) films, prepared and measured in different tubes. The present report is to be regarded primarily as a description of a new method of attack rather than as an exhaustive study of the work function of Ag(100).

## METHOD OF MEASUREMENT

Except for modifications dictated by the special requirements of the problem and described in detail below, the method of preparing and measuring the metal surfaces was similar to that developed in the study of the contact differences of potential between different metals deposited on a single substrate. This method, for the details of which the reader is referred to the earlier papers of this series,[5] may be summarized briefly as follows. (1) Specimens of the two metals under investigation, of high chemical purity but containing absorbed and adsorbed gases, are outgassed by repeated fusion while the measuring tube is undergoing a thorough baking and high frequency treatment on the pumps. One member of the metal pair is always barium; the other is the "unknown." Barium, which gives vaporized films of highly reproducible and constant work function, is used both to getter the tube and to prepare the standard reference surface of known work function to which all our contact potential measurements are referred. (2) The tube is sealed from the pumps and each metal specimen fractionally distilled. A middle fraction of one of the metals is finally condensed on a movable target. (3) Immediately after the deposition of a fresh metal film upon it, the target is moved before an electron gun which supplies a constant energy (about 10 ev), constant intensity electron beam, and the retarding potential required to establish a given reference current is determined. This reference current is so selected as to be near the middle of the straight-line portion of the current-potential characteristic. (4) Step three is repeated for a succession of films of the first metal and the reproducibility of the potential setting for this metal thus determined. (5) Steps three and four are repeated for the second metal of the pair. The contact difference of potential between the two metals, or between films of a given metal deposited on different substrates, is then equal to the difference between the potential settings, i.e., to the shift of the current-potential characteristic with change of surface.

## TUBE DESIGN

Figure 1 is a sketch of the most satisfactory of the tubes used in the present measurements. The barium vaporizer, connected at *B* but not shown, was identical in design to a vaporizer previously

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[3] L. Brück, Ann. d. Physik **26**, 233 (1936).

[4] These crystals, grown from fused NaCl, were furnished to me through the kindness of Dr. H. C. Kremers of the Harshaw Chemical Company, Cleveland, Ohio.

[5] P. A. Anderson, Phys. Rev. **47**, 958 (1935); **49**, 320 (1936); **54**, 753 (1938); **57**, 122 (1940).

described[6] and now being incorporated as a standard part in all of our tubes. It provides for both fractional distillation of the barium and for revaporization of any selected fraction, and contains a rotatable glass shutter which eliminates any possibility of contaminating the silver with barium during the preliminary vaporizations of the metals. The efficiency of this shielding has been checked repeatedly by operating the barium vaporizers with shield closed during the measurement of metal surfaces of high work function. Although such a surface is extremely sensitive to a slight barium contamination, no change in work function has been observed in any one of these tests. The silver vaporizer was a simple conical spiral of 20-mil tungsten wire. The important question of the efficacy of the vaporization method for producing gas-free silver surfaces is given special consideration in another section of this paper. The mounting of the rocksalt target *R* was such as to leave its surface entirely free of contacts or clamping lugs during the deposition of silver upon it, a precaution which is probably essential if structural disturbances in the silver film are to be avoided. As shown in the sketch, the rocksalt cleavage was carried on an inclined glass platform fitted with short glass stops. This design had the further advantage of permitting a fresh cleavage to be introduced into the tube quickly, immediately after it was prepared. To avoid errors originating in tube geometry, the clearance between the electron gun and each of the two targets was equalized carefully during the construction of the tube. In this adjustment a glass "dummy" took the place of the rocksalt cleavage and the cleavage was then made to match the dimensions of the dummy. The rocking contact *C* was designed after simple brush-type contacts had been found unsatisfactory. The lightest practicable brushes, e.g., a whisker of 3-mil tungsten wire, were found to scratch the Ag(rocksalt) films so seriously as to destroy electrical contact between film and brush. During the centering of the target before the gun, *C* was raised clear of the target path by traction on the armature *N*. The contact was then lowered carefully on to the edge of the target and a positive contact pressure maintained by the weight of the armature.

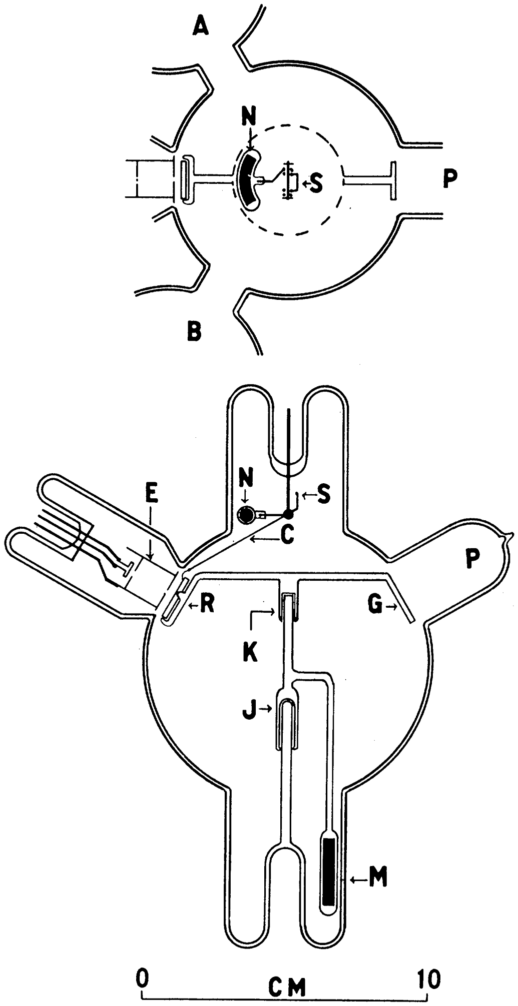

FIG. 1. The tube. The target assembly *RGKJ* is all-glass, driven on bearing *J* by magnetic traction on the glass-enclosed armature *M*. The rocksalt target, lying loosely on the glass platform *R*, and the glass target *G* are both 2×18×20 mm. *K* is a wedge-in-slot separable junction to facilitate mounting. The rocking contact assembly *NCS* comprises the 20-mil (0.5-mm) tungsten wire *C* tipped with a 2-mm loop of 12-mil Pt wire, a four-turn bearing of 30-mil Ta wire, with stop *S*, close wound on the 60-mil W lead-wire, and the glass-enclosed armature *N*. The electron gun *E* is of 4-mil Ta foil; emitter, 1-mil W foil 1.5 mm wide. For the silver and barium vaporizing chambers *A* and *B*, see text.

## MATERIALS

The silver was Hilger's "spectroscopically pure" material, supplied with an analysis showing the total impurity content to be 0.001 percent or less. (Hilger Laboratory No. 9696.) Since the contact potential method measures the average work function of a surface and the silver was

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[6] Reference 5, 1940 paper.

fractionally distilled in the measuring tube, errors due to solid impurities on the final silver surfaces must have been entirely negligible. The barium was taken from the same stock used in previous measurements and previously described.[5]

## PROCEDURE

The pumping and outgassing procedure was similar, in the main, to that followed in the earlier studies of this series. An initial baking at 500–550°C was carried out before the rocksalt target and barium charge were introduced into the tube. The vacuum was then relieved by dried air or dried helium (no advantage in the use of the latter could be observed) and the rocksalt and barium quickly introduced through suitably placed side tubes, not shown in the sketch. The final cleavage on the rocksalt specimen was made immediately before it was placed in the tube. The side tubes were then sealed off quickly and the tube immediately repumped. After baking for at least 72 hours at 350°C, with repeated high frequency heating of the electron gun to temperatures at which the tantalum began to vaporize, the silver and barium charges were melted down and the tube then sealed from the pumps. Before starting the measurements, or depositing any metal on either of the targets, the silver and barium were melted down repeatedly. During these preliminary fusions and vaporizations about 50 percent of the silver, and 80 percent of the barium, charge was discarded. Both the Ag(rocksalt) and Ag(glass) films were prepared and measured against each other before barium was deposited upon either target and before any barium vapor was allowed to enter the measuring chamber. To minimize the possibility of silver vapor condensing on the rocksalt before this target was heated, the Ag(rocksalt) film was deposited first. In the case of the tube sketched in Fig. 1, the rocksalt target was brought to the temperature selected for deposition, 200°C, by placing the whole tube in a small oven fitted with Calrod stove unit and mica windows. In earlier tubes the rocksalt cleavages were heated by radiation from tungsten wire grids mounted within the tube. This method shortens the time lapse between deposition and measurement of a film to the time required to swing the target to the measuring position and take a galvanometer reading, i.e., to about 10 seconds. It was an essential preliminary to the simpler technique and was discontinued only after it was found that neither the Ag(rocksalt) or Ag(glass) films showed any significant change of work function over a period extending from ten seconds to several hours after deposition. After securing the potential setting for the Ag(rocksalt) film, a succession of silver films was laid down on the glass target at room temperature and each film measured immediately after it was formed. After establishing the contact difference of potential between Ag(rocksalt) and Ag(glass), barium was deposited upon each of the targets with the purpose of checking our value[7] for the work function of Ag(glass) and determining the effect, if any, of the structure of the silver substrate upon the work function of barium.

## APPRAISAL OF GAS CONTAMINATIONS AT VAPORIZED SILVER SURFACES

As mentioned above, the silver was fractionally distilled in the sealed-off measuring tube and only the middle fractions condensed on the targets. During vaporization of the first discarded fractions the small silver globule was melted and solidified[8] at least sixteen times. Between fusions, and in order to utilize the slow diffusion of gas through the solid metal, the silver was held at a temperature just below that at which vaporization was noticeable. Barium fusions, each accompanied by vaporization, were interspersed between the silver fusions and the entire post-seal-off outgassing regime extended over a period of several weeks to allow thorough clean-up after each barium vaporization. Before this outgassing treatment was completed the silver ceased to emit any detectable quantity of gas upon remelting, an observation which indicates that equilibrium between the gases dissolved in the silver and the residual gas in the tube was

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[7] Reference 5, 1936 paper.

[8] Since much of the gas which remains dissolved in a molten metal is segregated and forced out upon solidification, alternate fusion and solidification is an especially effective means for outgassing a metal. The efficacy of fusion in removing gas is due, of course, not only to a rapid increase in the diffusion rate with temperature but to convective stirring of the molten metal.

established or at least approached very closely.[9] When such an equilibrium is established the silver contains the minimum quantity of absorbed gas possible for a given residual gas pressure. The main constituent of the dissolved gas, and the constituent most likely to form a contamination active in altering the work function, was probably oxygen. Since the oxygen evolved during outgassing reacted, in effect irreversibly, with the barium getter, the equilibrium pressure of oxygen must have been vanishingly small. If, now, silver thus outgassed is vaporized and condensed on a cool surface, the dissolved gas content will be temporarily reduced below the equilibrium value provided that, as is generally true for most gas-metal systems, the restitution coefficients for the gases are greater than the restitution coefficient for silver at a silver surface. Given a silver specimen outgassed to equilibrium, it is clear that a multiple distillation can be more effective than a single vaporization only if the dissolved gas equilibrium is thus disturbed, and such a disturbance must be followed by reestablishment of the equilibrium during the aging of the film. If it alters the work function measurably, i.e., if it is extensive enough to be significant in a work function determination, this process must be detectable in a series of work function measurements started within a time interval which is short compared to the time required for the redeposition of an equilibrium layer of gas, a layer which becomes the source for any rediffusion of gas into the metal. In the present investigation, work function measurements started within 10 seconds of the formation of a fresh silver film showed no drift over aging periods extending to several hours. At the residual pressure obtaining in a barium gettered tube the redeposition of an equilibrium gas layer requires a time period far in excess of 10 seconds[10] and we have, therefore, some reason to conclude that the equilibrium gas film which must have formed eventually was either (1) too dilute to have a measurable influence on the work function, or (2) was composed of gases to which the work function of silver is insensitive. In this connection it should be pointed out that the common assumption that an equilibrium gas layer is always a completed "monomolecular layer" is not born out by kinetic analysis.[10] If the residual gas pressure is sufficiently low and the time of sojourn of an adsorbed gas molecule sufficiently small, the covering factor may be much less than unity for the equilibrium layer. In a barium gettered tube the residual gas available for deposition on a freshly vaporized metal surface is the gas which is in equilibrium with the barium. Not only is the residual gas pressure extremely low; the residuum must be composed of gases which are not strongly adsorbed by metal surfaces.

## The Structure of Silver Films Deposited on Rocksalt

The results of the most recent structural studies[11] on silver-rocksalt films, insofar as they bear directly upon the present problem, may be summarized briefly as follows. (1) When a stream of silver vapor[12] impinges upon a rocksalt cleavage heated to a temperature of 150–200°C, condensation starts with the formation of nuclei which have the orientation of a silver lattice twinned on any one of the four possible octahedral (111) planes with respect to a silver lattice paralleling the lattice of the rocksalt substrate. As Menzer[11] shows in detail, this structure satisfies the condition which requires approximate matching of interatomic spacings in the contiguous NaCl and Ag layers. Since no one of the four possible orientations is favored, nuclei with all these orientations form at random on the (100) rocksalt surface. (2) As the condensation of silver proceeds, the nuclear crystals form, by interpenetration, a lattice which parallels NaCl (100) and which has the full cubic symmetry of Ag(100). (3) If the deposition of silver is stopped at a film thickness of the order of a few hundred A.U. there remain on the surface, in addition to the interpenetration regions of (100) symmetry,

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[9] The dissociation pressure of $Ag_2O$ is 388 mm at 773°K and increases with temperature. The combined oxygen must have been released in the first stages of the outgassing treatment.

[10] Reference 5, 1940 paper.

[11] G. Menzer, Zeits. f. Krist. **99**, 410 (1938); O. Goche and H. Wilman, Proc. Roy. Soc. **51**, 648 (1939).

[12] In the structural studies little attention has been given the well-known fact that the condensation of a metal vapor upon a dielectric is conditioned by the rate at which vapor is supplied to the surface as well as by surface temperature. Although only the target temperatures are specified, the order of vapor stream intensities can be inferred from descriptions of the deposition periods for films of specified thickness.

relatively small areas of lower symmetry in which the interpenetration has not been completed. These "interstitial" areas account for the satellites characteristic of electron diffraction photographs taken on extremely thin Ag(rocksalt) films. If the deposition is carried to film thicknesses greater than about 1000A the satellites disappear and the diffraction pattern becomes characteristic of Ag(100) alone.

It is to be noted especially that in none of the independent structural investigations was precaution taken to deposit the thicker silver films under exactly controlled conditions. The fact that the thick films nevertheless gave undistorted (100) diffraction patterns in all cases warrants the conclusion that the technique is quite reliable. Since the contact potential method of determining work functions measures the average work function of a surface without weighting regions of abnormally high or low work function, vestiges of the original interstitial regions persisting in a thick film might be expected to have little influence upon measurements made by this method.

Most of our preliminary measurements were made before the more definitive structural results appeared. The conditions under which silver films of good electrical conductivity are formed, a consideration which did not enter into the structural work, were determined empirically. In the first tube to be constructed after the more obvious requirements for a satisfactory technique had been determined, the Ag(rocksalt) film was deposited at such a low vapor stream intensity that a 90-minute exposure was required to form a semi-opaque film at a target temperature of 200°C. The electrical conductivity of this film was somewhat erratic; it behaved as if composed of a mosaic of large patches separated by crevasses extending to the rocksalt surface. For a position of the contact which established a conducting path through the film, a contact p.d. of 0.12 v was observed between this film and the Ag(glass) films.[13] In our latest measurements, the results of which are described below, the rate of deposition of the Ag(rocksalt) films has been so increased as to form an opaque film in from 20 to 30 minutes at a target temperature of 200°C, i.e., at a rate comparable to that employed in the later electron diffraction studies. These films showed a normal conductivity and, except for their fragility, could be measured with all the ease and precision of silver films on glass.

## The Contact p.d. Between Ag(Rocksalt) and Ag(Glass)

Measurements on two Ag(rocksalt) films, prepared in two different tubes at the higher deposition rates described above, against two series of Ag(glass) films have given contact potential values lying within the extreme limits of 0.29–0.35 v. As in all the preliminary as well as final measurements, the Ag(rocksalt) films were electronegative with respect to the Ag(glass) surfaces. The reproducibility was of the same order as that found in previous measurements on Ag(glass)—barium.[7] Deviations from the mean value of 0.32 v appeared to be due largely to work function variations between the fourteen individual Ag(glass) films included in the final set of measurements. As described above, barium was deposited on both the Ag(glass) and Ag(rocksalt) surfaces after these surfaces had been measured against each other. The contact difference of potential Ag(glass)—Ba so determined was 1.95 ±0.02 v, in close agreement with our previous value of 1.94 v obtained with both silver and barium at liquid-air temperature.[7] Since the difference between the room and liquid-air temperature values is less than the reproducibility of either set of measurements it cannot, of course, throw light on the temperature dependence of this contact p.d., except to indicate that the temperature coefficient is probably very small. The contact p.d. between barium and Ag(rocksalt) differed from that for Ba-Ag(glass) by values which fell within the limits of reproducibility for Ag(glass)-Ag(rocksalt). This result indicates that the structure of the silver substrate had no profound effect upon the structure, or at least on the work function, of a thick barium film deposited upon it at room temperature. During the preliminary measurements an interesting incidental observation was made on a Ag(glass) film deposited at a target temperature of 200°C. The silver film thus prepared had the characteristic "milky" appearance associated with partial

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[13] P. A. Anderson, Phys. Rev. 56, 850 (1939).

agglomeration and was 0.09 v electronegative with respect to a mirror-like silver film formed by condensation on glass at room temperature.

## THE WORK FUNCTION OF POLYCRYSTALLINE SILVER

Combination of our value for the contact p.d. between Ag(glass) and vaporized barium, 1.95 v, with the work function of vaporized barium, established at 2.52 ev by the careful work of Jamison and Cashman,[14] assigns the value 4.47 ev to the work function of Ag(glass) films deposited and measured at room temperature. Although this value agrees closely with our previous value of 4.46 ev for silver films deposited at liquid-air temperature, a recent paper by Farnsworth and Winch[2] makes necessary a re-examination of the question of the work function which is to be assigned to polycrystalline silver. As has been pointed out previously,[7] the "polycrystalline state" appears to have distinctive meaning in work function measurements only when defined as a microcrystalline aggregate in which the crystallites, especially those crystallites exposed at the surface of the specimen, are oriented entirely at random. That such a definition is imperative is indicated by the fact that any group of crystallites which expose only faces of a single orientation must give the work function characteristic of that orientation alone. When silver is deposited on glass at liquid-air temperature, the condition of random orientation is probably satisfied as closely as is possible in practice. But in discussing our work function value for silver films thus prepared, Farnsworth and Winch compare it directly with Winch's early value of 4.74 ev, obtained for a silver wire outgassed by heating for 1200 hours at temperatures up to 850°C.[15] They assume implicitly that agreement between these two values is to be expected. It should be pointed out, in the first place, that Farnsworth and Winch's suggestion that the discrepancy in question may be due to a diffusion of barium through our silver films is rendered untenable by our measuring technique. As described explicitly in our previous paper,[7] the potential setting for silver was obtained not from measurement of a single silver film laid down on barium but from a succession of silver-on-silver films. Each silver film, measured as laid down, showed no significant deviation from the potential setting for films preceding and succeeding it in the series. This procedure completely excludes any possibility of errors originating either in the diffusion of barium or in the persistence of incompletely covered patches of the substrate. Incidentally to the present work, furthermore, the silver films were deposited directly on glass and measured before any barium was introduced into the measuring chamber. In our earlier paper[7] the discrepancy was attributed tentatively to a difference in surface structure between (1) silver deposited from the vapor at liquid-air temperature, and (2) silver with the structure of Winch's heat-treated wire. Considered in the light of crystal growth theory,[16] now well established and known to determine the development of crystal faces by thermal etching as well as by atom-by-atom growth, Farnsworth and Winch's own recent measurements lend strong support to this conclusion. The prolonged heating of Winch's silver wire must have produced extensive recrystallization with growth of a relatively small number of crystallites of preferred orientation. Furthermore, and as remarked by Winch, extensive thermal etching occurred. The Kossel-Stranski theory, as applied to the face-centered cubic metals, shows that the crystal facets developed by the thermal etching of any metal of this class will consist predominantly of the crystal planes of densest packing. It is probable, therefore, that the surface of Winch's wire consisted predominantly of facets bounded by (111) planes. If, now, we compare Winch's work function value, 4.74 ev, with the value of Farnsworth and Winch for the (111) face of a single crystal of silver, 4.75 ev, we have strong evidence for the conclusion that Winch's value is to be identified with Ag(111) rather than with randomly oriented polycrystalline silver. It should be remarked that Farnsworth and Winch's recent work indicates that both their value for Ag(111) and that of

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

[15] R. P. Winch, Phys. Rev. **37**, 1269 (1931).

[16] W. Kossel, *Leipziger Vorträge* (Hirzel, Leipzig, 1928); I. N. Stranski, Zeits. f. physik. Chemie **B11**, 342 (1930); A. Smekal, *Handbuch der Physik* (Julius Springer, Berlin, 1933), Vol. 24, No. 2, p. 809.

Winch refer to surfaces contaminated by an equilibrium layer of gas.

### THE WORK FUNCTION OF Ag(ROCKSALT); OF Ag(100)

A simple computation, similar to that described above for Ag(glass) films, assigns the value 4.79 ev to the work function of silver films deposited on rocksalt. As described in detail earlier in this report, electron diffraction studies have shown that thick Ag(rocksalt) films give undistorted (100) patterns when they are deposited under conditions similar to, but less favorable than, those realized in the present work. We are justified therefore in tentatively identifying the work function observed for Ag(rocksalt) with the work function of Ag(100). It is conceivable that vestigial regions with symmetry lower than (100) may persist even in a thick Ag(rocksalt) film to a degree insufficient to be detectable in electron diffraction photographs but sufficient to affect a work function measurement. Since it is, of course, impossible to obtain an ideal crystal face by any experimental means whatever, the question of the magnitude of errors originating in deviations from the ideal structure can be answered only by independent measurements on a large number of surfaces known to approximate this structure. The deviations in question must be to some extent accidental and if it is found eventually that satisfactory reproducibility can be obtained for a sufficiently large number of surfaces it may be possible to conclude that the error involved in identifying the observed work function with $\phi_{100}$ is negligible.

In their thorough study of a massive single crystal of silver, Farnsworth and Winch[2] obtain the value 4.81 ev for the work function of a (100) face. From observations on the effect of depositing vaporized silver upon it, they conclude that this face was contaminated with gas and that the value 4.81 ev is therefore characteristic of Ag(100) so contaminated. The deposition of the fresh silver film lowered the work function and, considering only the effects of gas contamination, their measurements could be interpreted as indicating that the true value of $\phi_{100}$ is in fact lower than 4.81 ev. But the surface formed by the deposition of silver vapor, apparently on the cold monocrystal, was found to deviate markedly from the (100) structure and the complications introduced by simultaneous changes in both structure and gas contamination make it difficult to appraise the influence of either factor alone. The agreement between the two values for $\phi_{100}$ is better than the probable experimental error involved in either set of measurements would lead us to expect and is probably, to some extent at least, fortuitous. The main significance of the present work is its indication that the condensation of metal vapors on monocrystalline dielectrics promises to furnish a convenient and reliable method for preparing, in the measuring tube itself, metal surfaces of known and reproducible structure which are free from contaminations and the effects of mechanical working. The method appears to be immediately applicable to Ni, Cu, Pd, Al and Au.