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Photoelectric Work Functions of (100) and (111) Faces of Silver Single Crystals and Their Contact Potential Difference*

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The work functions of the (100) and (111) faces of silver single crystals have been determined photoelectrically by the Fowler method of analysis, and were compared with the contact potential difference measured by the Kelvin null method. The equilibrium value of the work function for the (100) face is 4.81 ± 0.01 ev, and that for the (111) face is 4.75 ± 0.01 ev. These values were obtained after heating for more than 2000 hours at various temperatures up to visible red heat. The gas pressure in the tube during the final stages of outgassing was between 1 and 3×10^{-8} mm Hg with the crystals hot. Values of the measured contact potential difference obtained at frequent intervals during the outgassing agreed with the differences of the photoelectric work functions to within ±0.01 volt. After these equilibrium values were obtained the crystals became contaminated by an unidentified impurity from heated tantalum with the result that the photoelectric data no longer agreed with the Fowler theoretical curve or with the measured contact potential difference. The apparatus permitted deposition of silver from the vapor state onto the crystal faces, after two previous distillations of the silver had been made to eliminate gas effects. Presence of the contamination referred to above complicated the results following deposition, but evidence is presented to show that the deposited silver gave a more gas-free surface than heating alone. The rate of return of gas to the surface following the deposit was determined by a comparison of the experimental results with a theory presented by Emslie. The results are explained by postulating that long heating of the crystals produced a stable gas configuration of a monomolecular layer on their faces, and that deposition of a gas-free layer of silver produced a surface free of most, if not all, of this layer of gas. The work function of the gas-free surface is 0.09 ± 0.03 volt less than that of the underlying structure previous to deposit.

INTRODUCTION

It is now rather generally accepted that the work function of a metal single crystal is a function of the crystal face which forms the surface boundary. During the past several years various experimenters[1] have attacked this problem. Except for the fact that the specimen under investigation must be in the form of a single crystal, the methods employed are the same as those formerly used on polycrystalline specimens. While the photoelectric and thermionic methods should yield absolute values of work function under proper experimental conditions, a measurement of the contact potential difference furnishes values for the differences in work functions so that if the work function of one face is known, one can obtain by this method values for any other faces which can be prepared. Although it has been experimentally established for polycrystalline surfaces that the difference in photoelectric work functions is equal to the contact potential difference,[2] this has not been done previously for two different faces of the same single crystal. It is, therefore, of some importance to test this relationship for single-crystal surfaces.

A comparison could be made between the values obtained subsequent to prolonged heating of the crystals and those subsequent to a freshly evaporated film. Previous observations[3] indicate that a deposited layer forms on the surface of a crystal of the same material in a single lattice with the same orientation as the underlying crystal. Although completely reliable results on the deposited film were not obtained because of contamination, some interesting observations were made.

CRYSTALS

The silver crystals were cut and etched with one large plane surface parallel to a desired set

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* Preliminary report, Phys. Rev. **56**, 1067 (1939).

† Experiments performed at Brown University.

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[1] For example: B. A. Rose, Phys. Rev. **44**, 585 (1933); N. Underwood, *ibid.* **47**, 502 (1935); R. P. Johnson and W. Shockley, *ibid.* **49**, 436 (1936); C. E. Mendenhall and C. F. DeVoe, *ibid.* **51**, 346 (1937); S. T. Martin, *ibid.* **56**, 947 (1939); M. H. Nichols, *ibid.* **57**, 297 (1940).

[2] G. N. Glasoe, Phys. Rev. **38**, 1490 (1931); P. A. Anderson, *ibid.* **54**, 753 (1938).

[3] H. E. Farnsworth, Phys. Rev. **43**, 904 (1933); **49**, 605 (1936).

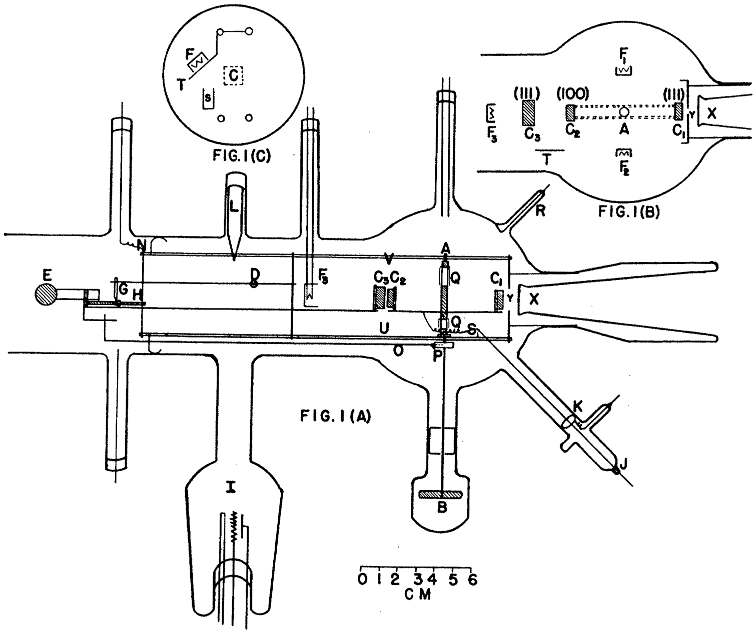

FIG. 1. Schematic diagram of the research tube. (A) is a vertical section along the axis of the tube, (B) is a horizontal section along the same axis, and (C) is a vertical section at right angles to the axis in the plane *UV* of (A). The inside of the bulb was covered with a thin conducting layer of tungsten. Iron armatures *E* and *B* were sealed in Pyrex envelopes.

of crystal planes. The method of cutting and preparing the crystals has been described previously.[4] In the present case it was found that smoother etched surfaces were obtained if the crystals were placed in hot distilled water before dipping in the HNO_3 etching solution. The crystal with the (100) face was approximately $1.0\times 1.1\times 0.4$ cm and the crystals with (111) faces were approximately $0.9\times 0.95\times 0.4$ cm and $1.4\times 1.2\times 0.5$ cm with the prepared faces on the surfaces of largest area.

APPARATUS AND PROCEDURE

The arrangement was such that either of two different crystal faces could be brought opposite the quartz window *X*, Fig. 1(A), for photoelectric readings, by the rotation of an external electromagnet acting on the iron armature *B* attached to the vertical axle *A*. *Q* denotes quartz insulation. The mounting of the crystals was similar to that described by Underwood.[1] The crystals C_1 and C_2, when in front of the filaments F_1 and F_2, could be outgassed by electron bombardment. Molybdenum shields were placed at several positions in the tube to condense evaporated metal, and all bombarding filaments were surrounded by molybdenum shields except on one side.

The contact potential difference (referred to hereafter as CPD) was measured by the Kelvin null method with a Compton type quadrant electrometer. For this measurement a third crystal C_3 with a (111) face was mounted on a sliding mechanism operated by an external electromagnet acting on the iron armature *E*. The sensitivity was such that the CPD could be measured to within ±0.002 volt. When one of the rotor crystals was in position for photoelectric measurements, the other was accurately aligned with the slider crystal for CPD measurements. A special mechanism assured alignment of the crystals when measurements were made, and prevented the slider crystal from coming forward and striking the rotor crystal for any position of the latter. The minimum spacing between a rotor crystal face C_1 or C_2, and the slider crystal face C_3 was controlled by the spacer bar *G*, Fig. 1(A) and was normally about 0.25 mm.

Figure 1(C) shows the evaporator arrangement for depositing a film of silver on the faces of the silver crystals. The tantalum cup *s* which contained previously distilled silver was heated by electron bombardment (filament not shown). The tantalum plate *T*, which received some silver from *s*, could be similarly heated to deposit

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[4] H. E. Farnsworth, Phys. Rev. **40**, 699 (1932).

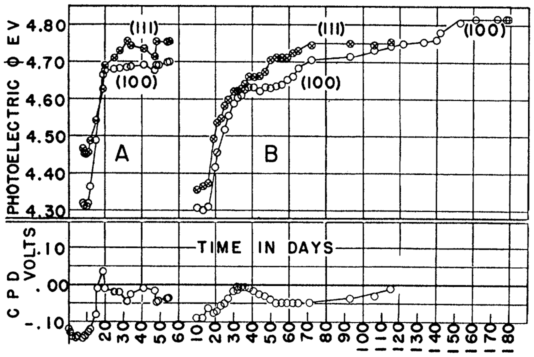

FIG. 2. Work functions, determined by Fowler[6] method, and CPD's as a function of elapsed time in days. Both crystals were heated continuously except for (1) times required during observations, (2) in case of (111) rotor crystal, a period between the 32nd and 47th days of experiment *A*, (3) in case of (100) rotor crystal, a period between the 41st and 47th day. Total heating time for (100) crystal during experiment *B* is 2639 hours. Total heating time for (111) crystal during experiment *B* is 1634 hours. While the (111) crystal remained at room temperature from the 32nd to the 47th day in experiment *A*, ϕ_{111} decreased only 0.04 ev. Similarly, while the (100) crystal remained at room temperature from the 41st to the 47th day the decrease in ϕ_{100} was 0.015 ev. This fatigue effect was even less in the later stages of outgassing. The sign of the CPD is taken as positive when the (100) face has the higher work function.

silver on the crystals.[5] During deposition on *T* the positions of the crystals were such that no silver from *s* could reach the crystal faces. Both *s* and *T* were preheated in an auxiliary vacuum tube. In the later stages of the experiment and before making final deposits on the crystals, the plate *T* was heated 1040 hours at temperatures up to 1400°C and the cup *s* 1340 hours at temperatures up to about 900°C at which temperature silver evaporated copiously from the cup. The first few deposits on *T* were driven off before exposing the crystal faces.

Prior to assembly of the tube, all parts were cleaned chemically and were outgassed by induction heating in an auxiliary vacuum. The assembly was carried out in a dust-free, dry room, and all parts were touched only by clean tools. Masks were worn to prevent contamination of the parts by the breath.

The Pyrex tube was connected with 1¼″ Pyrex tubing to a vacuum system consisting of two oil diffusion pumps in series backed by a Cenco Hyvac. Two large traps in series separated the tube from the diffusion pumps, and a third trap separated the diffusion and backing pumps. The traps were cooled by solid carbon dioxide in acetone. This same vacuum system has been used previously in this laboratory to evacuate the tube used for low speed electron diffraction. No evidence of contamination from pump oil vapors was obtained in diffraction studies with low speed electrons of less than 50 ev energy. No grease or wax joints were on the research tube side of the traps. The research tube was left attached to the pumps throughout the experiment since it was deemed inadvisable to use any getter, such as barium, whose vapor might condense on the crystal faces and completely alter their work functions.

The residual gas pressure in the tube was measured with an ionization gauge *I*, Fig. 1(A). During all measurements, except the very early ones, this was from 1 to 3×10^{-8} mm Hg, and most of the time it was near the lower limit. In the early stages, the outgassing was conducted at a rate such that the pressure remained below 5×10^{-7} mm Hg after the second baking of the tube. In the final stages the pressure was independent of the temperature of the crystals.

A General Electric quartz capillary high pressure mercury arc served as a light source for photoelectric readings. A Bausch and Lomb quartz single monochromator, with the source and lenses, was mounted on a rotating table so that it could be turned to throw the image of the exit slit on the crystal face or on the receiver of a vacuum thermopile for measurement of the light intensity. Monochromator slit widths of 0.2 mm or less were used for all readings. Since the sensitivity of the thermopile was found to change slowly, with time, a calibration with standard lamp was made during each set of readings. An amplifier with a General Electric FP-54 Pliotron tube measured the photocurrents. The Fowler method[6] was used to determine the work functions.

Although tests of the monochromator showed the presence of some scattered light, this was found to affect only the observations very close to the long wave limit. In using the Fowler

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[5] Some early results obtained by us (Phys. Rev. **53**, 935 (1938)) show that it is not sufficient to simply melt the silver in a vacuum, and then distill it onto the surface to be tested.

[6] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

method a deviation of the observations near the long wave limit due to scattered light is easily detected, and allowance can be made for it.

RESULTS AND DISCUSSION

Silver crystals outgassed by heating

Figure 2 shows the experimental values of work functions (hereafter referred to as ϕ) and CPD's as a function of elapsed time in days. Actual heating times are given in the caption. Experiment *A* was terminated after 55 days because a short circuit developed in the tube. Then, before obtaining curve *B*, the tube was dismantled for alterations; all three crystals were resurfaced and etched, after which the tube was reassembled and evacuated as soon as possible. It is to be noted that, except at the very beginning of three of the curves, the values of ϕ increase with outgassing and decrease very slightly when exposed to very low gas pressures for long periods of time. Most of the photoelectric readings were taken immediately after the crystals had cooled to room temperature, although ϕ changed only very slowly with time after heating so that during several hours there was no observable change.

In experiment *A* the (100) crystal never reached its equilibrium ϕ, but in *B* it reached this value of 4.81±0.01 ev after 2283 hours of heating at various temperatures up to visible red heat. An additional heating for 356 hours did not change this value further. After the crystal had subsequently remained at room temperature for 2130 hours (not shown in Fig. 2) while measurements of another type were being made, ϕ_{100} decreased to 4.65 ev. Following this, 218 hours of heating brought ϕ_{100} back to the equilibrium value of 4.81 ev which was not altered by some further heating.

An equilibrium value of 4.75±0.01 ev was obtained for ϕ for the (111) face in both experiments. In experiment *B* this value was attained after 1227 hours of heating, and was not altered by 407 hours of additional heating. This crystal had been outgassed in a previous experiment so it attained its equilibrium value in a much shorter time than did the (100) crystal which was somewhat larger and had not been outgassed previously.

It is to be noted that the observations on CPD, shown in the lower part of Fig. 2, check with few exceptions with the corresponding differences in photoelectric ϕ's within ±0.01 volt. This and the fact that the experimental results are in agreement with the Fowler curve as shown below indicate that throughout the outgassing process ϕ is uniform over the surface.

Observations were made on *I* (the photocurrent per unit light intensity) as a function of elapsed time immediately after the crystals had been heated, and before they had reached room temperature. The results obtained were similar to those shown by Mendenhall and DeVoe[1] in their Fig. 2 except that our change with time was not as great. Their explanation of this change was based on the assumption that the heating of the crystal produced a gas-free surface, and that the change with time after heating was due to gas returning to the surface. There is undoubtedly some temperature dependence which has not been taken into account. Our results are consistent with the assumption that the change is entirely due to the changing temperature of the crystal as it cools to room temperature.

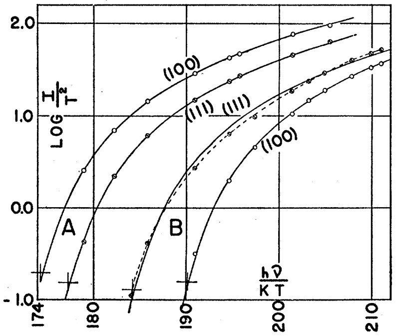

FIG. 3. Typical Fowler plots. *A*—Experimental points obtained before outgassing was completed. *B*—Results for (100) crystal after reaching equilibrium, and for (111) crystal after being contaminated. Solid curves are Fowler theoretical, and all points are experimental.

In Fig. 3 the pair of curves marked *A* show typical Fowler plots from which the values of ϕ were determined for Fig. 2. The solid curves are theoretical, and the points are experimental.

From the sample pair of curves marked *A* in Fig. 3, ϕ of the (111) face was found to be 4.490 ev, and that for the (100) face 4.413 ev giving a difference of -0.077 ev. Under these same conditions the CPD of the (111) with respect to the (100) was measured to be -0.076 volt. These particular values check better than is to be expected from the errors in matching the experimental points to the Fowler curves.

Effects of contamination

At the point where the (111) curve ends in experiment *B*, Fig. 2, it is believed that the (111) crystal became slightly contaminated while heating the tantalum plate *T*, Fig. 1, near it. The crystal was in such a position that no contamination could go directly from *T* onto the face of the crystal, but it could go onto the edge of the crystal and migrate around onto the face[7] with subsequent heating. Calculations, based on the results of D. Langmuir and L. Malter[8] on the rate of evaporation of tantalum, showed that the contamination could not be caused by evaporated tantalum at the temperature to which the plate had then been heated (about 1000°C at the hottest place).[9] This contamination on the (111) face caused a decrease in ϕ, and a deviation of the experimental results from the Fowler theoretical curve. An example is shown for this (111) face in *B*, Fig. 3. As before, the solid curve is the Fowler theoretical curve, and a dotted curve has been drawn through the experimental points. The accompanying curve in this figure for the (100) face was obtained at the same time and shows a good fit of the experimental points to the theoretical curve, indicating that the (100) face had not been affected. Incidentally this is a plot of results obtained after the (100) face had reached its equilibrium ϕ of 4.81 ev. The difference of the ϕ's came out to be 0.147 ev while the measured CPD was 0.073 volt. While there is some choice in locating an average fit of the points to the theoretical curve for the (111) face, the above difference is greater than is permitted by this choice. Pairs of curves of the type shown in *B*, Fig. 2 were reproduced a great many times while the (111) face was contaminated and, since the results from the (100) face always fitted the theoretical curve while the results from the (111) face failed to fit in the manner shown, this result is not due to experimental error.[10] In fact, smaller deviations from the theoretical curve than those shown were found to be real in the early stages of contamination. The deviations were of the order which have been ignored by some observers in fitting results to a Fowler curve.

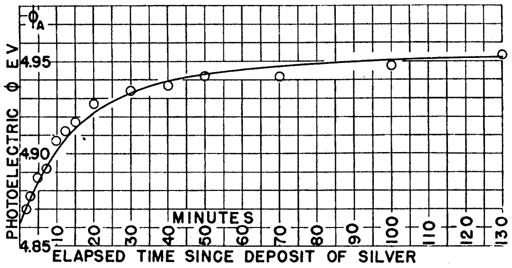

FIG. 4. A comparison of Emslie's theoretical curve with our experimental points for the change of ϕ with time after deposit of silver on the complex structure. The face underlying this complex structure was a (100).

Calculations by Emslie[11] show that an assumption of patches with different values of ϕ from that of the silver will modify the Fowler theoretical curve in the manner shown by the experimental points for the (111) face, but because of two arbitrary constants the formulation is unsatisfactory as a means of determining the relative areas and ϕ's of the patches.

After the part of experiment *B* previously

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[7] There is abundant evidence for such migration, e.g., J. D. Cockcroft, Proc. Roy. Soc. **119**, 308 (1928).

[8] D. B. Langmuir and L. Malter, Phys. Rev. **55**, 748 (1939).

[9] Spectroscopic tests made at the National Bureau of Standards did not reveal the nature of the contamination. Photographs of the electron diffraction pattern from the crystal surfaces were also kindly made for us by L. H. Germer. Although the pattern showed some faint extra rings, we have been unable to identify the substance producing them. The visual appearance of the crystal surfaces when removed from the tube was as good or better than it was when they were first prepared.

[10] Measurements were made of the reflectivity of the two crystal faces in the ultraviolet to determine any differences which might affect the photoelectric results. The arrangement was such that light from the monochromator, after reflection from the crystal faces in the experimental tube, emerged through the quartz window and was then reflected by an aluminum mirror onto the molybdenum surface of a photo-cell. This photo-cell was chosen because of its smooth sensitivity curve in the ultraviolet. The photocell was calibrated before and after the reflectivity measurements. The results showed that any difference in the reflectivities of the two crystal faces was less than experimental error, and too small to account for differences in the measured photoelectric characteristics. Also, the reflectivity changed very little with wave-length over the range used in the experiment, so that no correction for such a change was necessary.

[11] Private communication.

described, the (100) crystal face was exposed to the tantalum plate T while at 1050°C at the hottest place. An exposure of 110 minutes caused a deviation of the results from the theoretical curve similar to that for the (111) face but less pronounced. A few more such exposures made this still more evident.

It was hoped, at the outset of the experiment, that the same equilibrium ϕ could be obtained for the two (111) faces in the tube so that they would show no CPD. Because the (111) slider crystal was larger than the (111) rotor, and had not been outgassed previously, a much longer heating time would have been required to reach its equilibrium ϕ, but before this time had elapsed the (111) rotor became contaminated. However, the fact that the same equilibrium value of ϕ_{111} was obtained in two different experiments (between which the (111) crystal was resurfaced) indicates that the failure to reach the above objective is not significant.

Deposition of silver on the crystal faces

Deposition of silver on the (100) crystal face caused ϕ to decrease abruptly from the value ϕ_A, Fig. 4. This was followed immediately (while the crystal was at room temperature) by an increase in ϕ. A typical deposition was made by heating the silver-coated tantalum plate for 100 seconds at a power input of 7.9 watts which maintained a temperature of about 930°C at the center and 750°C at the edges. Calculations indicate that about 1500 ± 1000 atomic layers of silver were deposited on the crystal surface.

The experimental values represented by circles, Fig. 4, were obtained in the following manner. Readings on five different wave-lengths were taken rapidly in rotation as a function of time after the deposit was completed.[12] A series of plots of $\log I/T^2$ against elapsed time was then made for these wave-lengths. These curves gave the values of $\log I/T^2$ at any given instant of time, and Fowler plots were then drawn to obtain the values of ϕ. Beyond the figure, ϕ continued to increase slowly for about 24 hours, reaching ϕ_A at the end of that time. The total increase in ϕ following six different deposits is given by 0.09 ± 0.03 ev. The vertical shifts, obtained in matching the experimental plots to the Fowler theoretical curve, were the same (-0.62 ± 0.02) for all of the ϕ determinations shown in Fig. 4. This shows that ϕ was changing without a change in the so-called "photoelectric efficiency."

These results are explained on the assumption that a monomolecular layer of gas exists on the surface before the deposit, and that the deposited silver produces a nearly gas-free surface which has a lower ϕ than a surface with a monomolecular layer. The change of ϕ with time after the deposit may be accounted for by condensation of gas from the residual gas in the tube. Figure 4 shows one theoretical curve calculated by A. G. Emslie.[13] A constant residual gas pressure was assumed. It will be noted that a smooth curve drawn through the experimental points would rise more rapidly at first and less rapidly thereafter than does the theoretical curve. This difference would be expected if the gas pressure in the tube were increased slightly during the deposition process and then decreased again with time after deposit, instead of remaining constant as postulated in obtaining the curve. The pressure increase during deposit was so small that it was hardly detectable on the ionization gauge, and could not have been more than about 2×10^{-9} mm Hg, but this appears to be enough to account for the above difference.

On removal from the research tube, the crystal faces were studied by high speed electron diffraction,[9] and the diffraction pattern from the (100) face was found to be very complex. It resembles to some extent but is much more complicated than the abnormal pattern obtained by Goche and Wilman[14] from a silver film condensed on a heated rocksalt cleavage-face in vacuum. They attribute their pattern to the presence of more than one set of crystal planes which are parallel to the rocksalt surface. It is believed that the contamination which collected on the crystal face after obtaining the results shown in Fig. 2, and prior to the first deposit of silver, caused the deposited silver to grow in

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[12] The first observation was obtained 80 to 90 seconds after the deposit was completed. The time intervals between the next several successive readings were also 80 to 90 seconds, as timed with a stopwatch.

[13] Private communication.

[14] O. Goche and H. Wilman, Proc. Phys. Soc. 51, 648 (1939).

this complex structure. This structure, once started, probably continued even though the contamination soon became completely covered. Tests made in the latter part of the experiment seemed to indicate that contamination was no longer coming from the tantalum plate T. As an added precaution T was kept coated with a heavy layer of silver, and the time of deposit was limited to 100 seconds after which T was again coated with silver prior to the next deposit. The high ϕ shown in Fig. 4 is attributed to this complex structure, and is not considered to be characteristic of the (100) face. Since the (111) and (100) planes are the most densely populated ones in the face-centered lattice, the high ϕ may be due to the predominance of a less densely populated plane such as the (110).

Deposits were also made on the (111) rotor face with results similar to those shown in Fig. 4 for the (100) face. However, a detailed comparison cannot be made since the filament F_2 used for heating the (111) crystal burned out shortly after the end of the summary curve shown in Fig. 2(B), thus preventing the same procedure as used with the (100) crystal. A single deposit of silver on the (111) face caused its photoelectric readings to fit the Fowler theoretical curve over a range of 400A, showing that the patch work on the surface had been covered and that a uniform surface then existed. The absolute value of ϕ after making several deposits, thick enough to be opaque, was several tenths of a volt less than the high value shown in Fig. 4. This emphasizes that ϕ for a deposited metal film is greatly influenced by the underlying structure, so that a determination of ϕ for such a film, even when thick enough to be opaque, has no significance without a knowledge of the influence of the backing. Cashman[15] has arrived at a similar conclusion.

The initial deposit of silver on the (100) face produced a larger decrease in ϕ than any observed subsequently, and the rise in ϕ after the deposit was considerably less than the decrease due to the deposit. In no other case was the rise after deposit less than the decrease due to the deposit. (The thickness of the silver layer deposited on the crystal face in all cases was nearly the same.) This result and the following ones in this paragraph are not entirely clear in their interpretation, but it is believed that the presence of the contamination and the beginning of the complex structure growth are responsible. Several deposits subsequent to the first caused a small decrease in ϕ followed by a rise which was greater than the decrease. A small amount of heating of the crystal at this stage produced a remarkable rise in ϕ. For example, after a total of four deposits of silver had been placed on the (100) face, the crystal was heated for 10 minutes at about 500°C or less. This resulted in an increase of 0.06 ev in ϕ. Further heating caused ϕ to rise less and less rapidly until finally long continued heating produced no further change in ϕ. Deposits and heating were used in alternation until an equilibrium was reached such as that shown in Fig. 4 where the ϕ after deposit came back to, but not beyond, its value before deposit, and heating after the deposit produced no change in ϕ. It is believed that the complex structure grew when a deposit was placed on the crystal, and also when the crystal was heated until finally this structure reached a stable value. After this, silver grew during its deposit with the orientation of the underlying surface, and heating after the deposit caused no further growth. When this state was reached the only result of the deposit was to produce a more gas-free surface. The last step in the whole experiment was to place a deposit of silver on the (100) crystal so that when it was removed and studied by electron diffraction it had a fresh deposit of silver which had not been heated subsequently.

Some of the results used by Emslie in his paper were taken before this stable value of the complex structure was reached and some after, showing that his same explanation of the accumulation of gas on the surface after the deposit can be used throughout.

Comparison of results

The equilibrium values of the ϕ's obtained here, i.e., $\phi_{100}=4.81\pm0.01$ ev and $\phi_{111}=4.75\pm0.01$ ev, may be compared with 4.74 ± 0.03 ev obtained by one of us[16] for a thin filament of

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[15] R. J. Cashman, Phys. Rev. **54**, 971 (1938).

[16] R. P. Winch, Phys. Rev. **37**, 1269 (1931); R. H. Fowler, *ibid.* **38**, 45 (1931). In Winch's experiment a mercury diffusion pump was used and the vacuum system included two traps, cooled with liquid air, between the research tube and the pumps.

polycrystalline silver which had been heated for 1200 hours. This heating included short intervals at temperatures as high as 850°C where evaporation is rapid. These repeated flashings of polycrystalline silver at 850°C caused no change in ϕ so it is reasonable to assume that higher temperature heating of the crystals would only ruin the faces without freeing the crystals further of their surface gas.

From a measurement of the CPD between barium and silver, and ϕ of barium obtained by Cashman,[15] Anderson[2,17,18] obtained 4.46 ± 0.05 ev for ϕ of polycrystalline silver deposited on a barium-on-glass surface from the vapor state, after first making observations on the barium. It seems probable to us that this value is too low, because of the presence of the barium. Although the whole tube was immersed in liquid air, local heating may have caused some of the barium to diffuse through the silver film as it formed. The fact that he obtained ten times as much variation from one film to another for silver as for barium may be due to varying amounts of barium on the surface of the silver films as well as to the structural differences which he mentions.

Anderson[18] obtained 0.12 ± 0.01 volt CPD between polycrystalline silver deposited on glass and the (100) face of a silver crystal formed by depositing silver on a rocksalt cleavage plane, with the (100) face having the higher ϕ. This experiment is not subject to the above criticism. If we add this value to Winch's value of 4.74 ± 0.03 ev for polycrystalline silver, we obtain 4.86 ev, in agreement with our equilibrium value of 4.81 ± 0.01 ev for the (100) face.

CONCLUSIONS

We believe that $\phi_{100}=4.81$ ev and $\phi_{111}=4.75$ ev are the best values that can be obtained for silver crystals by heating alone since the crystals would etch rapidly if heated to appreciably higher temperatures than those employed here. The measured CPD between the crystal faces agrees with the difference of their ϕ's as long as the photoelectric data for both crystals agree with the Fowler theory. It is to be noted that ϕ_{111} is less than ϕ_{100} for silver as was also found to be the case for copper,[19] although the difference of 0.06 ev for silver is considerably less than the corresponding difference of 0.46 ev for copper.

The evidence from this experiment indicates that, as gas leaves the surface of a silver crystal, ϕ increases until a monomolecular layer of gas remains, and that removal of the last monomolecular layer of gas causes a decrease in ϕ. The above values of ϕ are thought to be characteristic of these faces when they are covered by a monomolecular layer of gas which cannot be removed by heating alone. This postulate and our evidence from the deposition of a gas-free layer of silver on a complex structure covering the crystal face indicate that ϕ is decreased by 0.09 ± 0.03 ev when the last monomolecular layer of gas is removed. There is uncertainty as to the influence of the underlying surface on this numerical value and hence the values for ϕ_{111} and ϕ_{100} quoted above have not been corrected for the presence of the monomolecular gas layer.

The results show that a slight amount of unknown contamination, which causes a nonuniform surface, may be detected photoelectrically by the deviation of the experimental results from the Fowler theoretical curve and by the failure of CPD to agree with the difference in the values of ϕ. Such slight amounts of contamination may be missed when CPD measurements alone are being made.

For the lower melting point metals, a more gas-free surface may be obtained by deposition of samples properly distilled in vacuum than by heating alone. However, ϕ for a film even though opaque may depend to a large extent on the backing. This makes it necessary to determine this dependence before any absolute values of ϕ for deposited films may be determined.

We have had the assistance of Mr. W. E. Johnson with the numerous calculations required.

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[17] P. A. Anderson, Phys. Rev. **49**, 320 (1936).

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

[19] H. E. Farnsworth and B. A. Rose, Proc. Nat. Acad. **19**, 777 (1933).