the use of such short lengths and the complicated method used to measure temperature. His measurements were of the transverse expansion on crystal rods 2.5 mm in diameter.

In conclusion, the writer wishes to express his sincere appreciation to Professor E. P. T. Tyndall for suggesting this problem and for his encouragement and advice throughout the work.

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Field Emission from Tungsten and Thoriated Tungsten Single Crystals*

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A reproducible time sequence of different pattern types has been found to appear in electron projector images of field emission from tungsten single crystals when the crystals are kept at temperatures above 1100°K. These pattern types, some of which have been observed before and attributed to migrations of surface tungsten atoms, can best be explained (with a single possible exception) as the result of rearrangement of adsorbed gas atoms on certain crystallographic surface areas under the influence of temperature and field. Their classification by means of their relation to surface conditions provides a sensitive test for a clean tungsten surface. The relative variation of emission intensity with crystallographic direction observed in thermionic emission is duplicated in field emission from clean tungsten, but the magnitudes of the variations are greater in field emission. These magnitudes seem to be greater than can be accounted for by the dependence of field emission on the exponential third power of work function which is indicated by some experiments. Such experiments in turn are at variance with theory, which predicts only an exponential three-halves power dependence. Attempts to extend electron projector methods of investigation to the simple composite surface of thorium on tungsten have uncovered no positive tests for surface conditions. Distinctly different types of field emission patterns were obtained from thoriated points formed from thoria-incorporated tungsten wire than from points of pure tungsten upon which thorium was evaporated externally. These differences disappeared, however, when the former patterns transformed into the latter after outgassing of the points for one or two hours at temperatures between 2700°K and 2900°K. In this final pattern, thorium adsorbs chiefly on the regions around but not including the 100 direction, and on a triangular region about and including the 111 direction. Once deposited, the thorium could not be completely removed from the tungsten surface.

INTRODUCTION

WHEN applied to the Fermi-Sommerfeld picture of a metal, the conception of wave mechanical penetration by electrons of a surface potential barrier lowered and thinned by an intense, externally applied, electrostatic field leads to the field emission equation first derived[1] by Fowler and Nordheim:[2,3]

$$J=1.55\times10^{-6}(F^2/w)10^{-2.98\times10^7(w^{\frac{3}{2}}/F)\phi(y)}. \quad (1)$$

In this equation J is the field emission current density in amperes per square centimeter, F the surface potential gradient in volts per centimeter, w the work function[4] in electron volts, $y=3.62\times10^{-4}(F^{\frac{1}{2}}/w)$, and $\phi(y)$ is a function containing the ratio of two elliptic integrals which has been tabulated for values of y from 0 to 1 by Nordheim.[3]

Although the general features of Eq. (1) have been confirmed experimentally,[5–8] difficulties resulting from the extremely high surface fields required have prevented conclusive establish-

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[1] Errors in the original derivations may be avoided by consulting the complete derivation given in A. Sommerfeld and H. A. Bethe, *Handbuch der Physik* (1934), Vol. 24, Part 2, Sec. 3, Art. 19, p. 436.

[2] R. H. Fowler and L. Nordheim, Proc. Roy. Soc. **A119**, 173 (1928).

[3] L. Nordheim, Proc. Roy. Soc. **A121**, 626 (1928).

[4] Defined as the difference in potential energy of an electron in the highest occupied energy level allowed by quantum statistics at 0°K, and that of the electron when removed from the metal and carried to a distance large compared to the lattice constant, so that the image force becomes practically zero, but small compared to the dimensions of the crystal face.

[5] E. W. Müller, Zeits. f. Physik **102**, 734 (1936).

[6] J. E. Henderson and R. K. Dahlstrom, Phys. Rev. **55**, 473 (1939).

[7] F. R. Abbott and J. E. Henderson, Phys. Rev. **56**, 113 (1939).

[8] G. M. Fleming and J. E. Henderson, Phys. Rev. **58**, 887 (1940).

ment of the power to which w is raised in the exponential term.[5,9–12] The variation of field emission with crystallographic direction seems to be larger than can be accounted for by the corresponding work function variation with crystallographic direction, if the work function dependence given in Eq. (1) is assumed.[10,11]

Finally, changes occurring at high temperatures in patterns produced by field emission from single crystals in electron projectors have recently been attributed[9,11] to changes in the position distribution of metallic surface atoms caused by the large electrostatic forces involved. The experiments reported here describe such pattern changes as were found reproducible with tungsten single crystal surfaces. They indicate that, with one possible exception, these changes are due to position changes of impurity atoms adsorbed on the surface rather than to position changes of surface tungsten atoms.

EXPERIMENTAL PROCEDURE

A. Apparatus and Vacuum Technique

The type of tube used is shown in Fig. 1. Following the suggestion of K. K. Darrow,[13] it will be called an "electron projector." With several thousand volts on the collector ring, field emission electrons, proceeding radially through the high field immediately about the point, strike the fluorescent screen (whose potential is maintained slightly below that of the collector ring by secondary emission) and thus produce on the screen a highly magnified emission image of the surface of the point, bright regions corresponding to areas of large emission from the point. The construction of the fluorescent screen and its treatment with a potassium silicate coating have been described in detail by Martin.[14] The high voltage used to produce the field in quantitative measurements was held constant to better than 0.01 percent by an electronic voltage stabilizer of the amplification-bridge type described by Hunt and Hickman.[15]

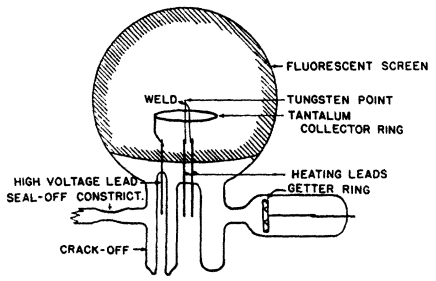

FIG. 1. Spherical electron projector.

To obtain projector patterns at all stable, vacua of 10^{-8} mm Hg or better were essential. Because of the extreme dependence of field emission on vacuum conditions,[7] great care was taken in the preparation of glass and metal parts. An evacuation schedule (on a mercury diffusion pump backed by a mercury jet pump and a mechanical pump) similar to that described by Nottingham[16] was used, with alternations between oven-baking (at 500°C) and metal outgassing (liquid nitrogen having been placed around the liquid-air trap with the tube oven hot) continuing until the pressure read by an ion gauge failed to improve. The tubes were gettered with Ba-Al getter, and special attention paid to long and thorough outgassing of the getter ring and to pre-heating of the seal off constriction (losing one-half its cross section) before sealing the tube off. After standing for about twelve hours, tubes sealed off with the ion gauge attached showed pressures as low as 5×10^{-9} mm Hg.

B. Preparation of Points

Electrolytic etching of the end of a 0.003-inch diameter General Electric "218" tungsten wire in a 30 g/liter NaOH solution to produce a sharp, microscopically smooth point seemed to give superior and more reliable results than chemical etching with molten sodium nitrite. The use of 60-cycle a.c. seemed to give more uniform macroscopic shapes than could be obtained with d.c. The initial determination of proper conditions was a matter of somewhat tedious trial and error. Excellent and consistent results were obtained by using 4.4 volts, 60 cycles, applied through a

[9] E. W. Müller, Zeits. f. Physik **108**, 668 (1938).
[10] E. W. Müller, Naturwiss. **49**, 820 (1939).
[11] M. Benjamin and R. O. Jenkins, Proc. Roy. Soc. **A176**, 262 (1940).
[12] R. Haefer, Zeits. f. Physik **116**, 604 (1940).
[13] K. K. Darrow, Rev. Sci. Inst. **12**, 53 (1941).
[14] S. T. Martin, Phys. Rev. **56**, 947 (1939).
[15] F. V. Hunt and R. W. Hickman, Rev. Sci. Inst. **10** 6 (1939).
[16] W. B. Nottingham, J. App. Phys. **8**, 762 (1937).

20-ohm resistor in series with the electrolytic cell. Figure 2 shows typical points.

Although these points could be made so fine as to be unresolved by the microscope (magnification 315×), heating[17] to 2900°K for several minutes in vacuum always dulled them to estimated diameters of about 4 to 10×10^{-5} cm. Observations of the voltages required to produce given currents in projection tubes indicated by their reproducibility that if a point were flashed at 2900°K for a minute, it could be held at 2600°K for long periods without altering its diameter or shape. The relative sizes and intensities of crystallographically identical parts of the projector pattern were good indicators of symmetry of point shape. Heating the point for long periods (of the order of ten hours) at 2700°K was found to remove asymmetries without appreciably changing the diameter of the point as measured under the microscope, or its emission for a given voltage. About nine out of ten points so constructed proved to be perfect single crystals.

With the aid of the electron microscope, it has been established by Heafer[12] that the surfaces of points thus "heat smoothed" exhibit no faceted structure, and are smooth down to atomic irregularities. These should not affect field emission because of their smallness compared to the surface potential barrier thickness.

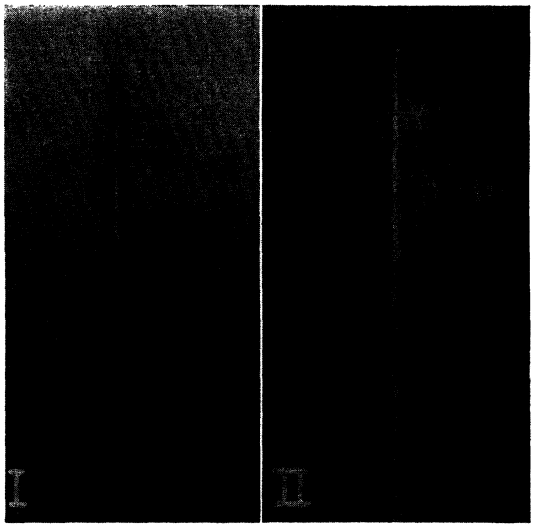

FIG. 2. Top illumination photomicrographs of typical electrolytically-etched tungsten "points." Ten scale divisions = 7×10^{-3} cm. I. Blunt-shaped point immediately after etching. Note glassy-smooth appearance. II. Long, thin point (not the same point shown in I) after heating in vacuum to 3300°K for 4 minutes has produced a ball-like tip. Before heating, the tip was so fine as to be unresolved by the microscope (magnification 315×).

OBSERVATIONS ON TUNGSTEN SINGLE CRYSTALS

Figures 3-I and 3-II show the field emission pattern of an almost clean single crystal tungsten point. The central dark region is along the 110 direction, which normally lies parallel to the axis of drawn tungsten wire. The three smaller dark spots arranged on vertices of an equilateral triangle to the right and also to the left of the 110 region are the 211 directions, with the bright 111 directions of threefold symmetry at the center of the triangles. The two large bright areas immediately above and below the 110 direction are symmetrical about the small 100 dark spots.

The pattern of a clean tungsten surface differs from that of Figs. 3-I and 3-II only in its completely smooth texture, and in the disappearance of the suggestion of dark areas forming a cross which is centered at the 110 spots and connects the adjacent 211 spots. Under the best vacuum

[17] Heating of the point was accomplished by passing current through the point wire and another wire of the same diameter welded on about a millimeter distant from the point tip, as shown in Fig. 1. Temperatures, calculated from the Jones-Langmuir tables [H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310, 354, 408 (1927)], with the wire diameter and current input, could be checked at the junction of the wires with a micropyrometer. This method cannot be relied upon for wire diameters less than 10^{-3} cm, however, and it is thus impossible to measure the temperature of the emitting surface of the point. This might well be appreciably below that of the junction since the conduction area along the wire decreases as the square of the point radius, while the radiation area decreases roughly only as the first power, and it is chiefly by conduction that the temperature of the tip is maintained against radiation losses. Rough calculation [J. H. Daniel, "Studies of field emission," Sc.D. Thesis, Massachusetts Institute of Technology (1940), Appendix II], with approximations in the direction to increase the effect, show that at worst the temperature drop between junction and tip would amount to 6°, 100°, and 500°K for junction temperatures of 1000°, 2000°, and 3000°K, respectively. Since radiation from the tip has been assumed to take place with the tip at junction temperature, the calculations made for a blackbody, and the effect of Joule heating by field currents as well as the effect of radiation in heating the tip neglected, we can expect this temperature difference for temperatures below 2000°K to be negligible for the purposes of this article. The flashing temperatures quoted, however, since they are uncorrected for any such temperature differences, are probably one or two hundred degrees too high as given. In view of such considerations, Haefer's reported temperature measurements may well be too low, perhaps by several hundred degrees at reported temperatures of 2400°K.

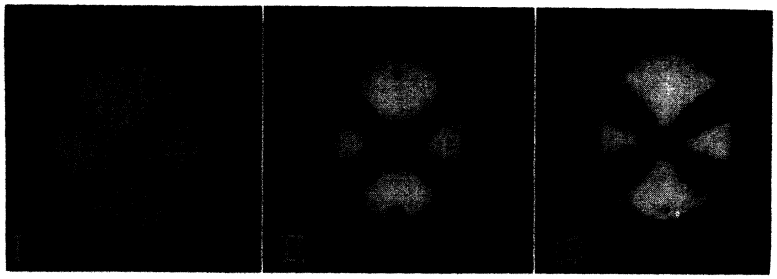

FIG. 3. Field emission patterns from tungsten single crystals at room temperature. I. "Almost clean" pattern. Photograph was taken immediately after "flashing" the point at 2800°K. Exposure time 10 seconds. II. Same pattern as in I, but different crystal and 15-second exposure. III. Pattern of II 30 minutes after flashing.

conditions ever attained in these experiments this clean pattern could be maintained at room temperature only for a period of a second or so immediately after flashing the point at high temperature.

Following this short-lived clean state, a dancing commotion of fine bright spots spreads over the light areas. After a number of seconds this commotion becomes less in evidence, the activity decreasing, and the bright spots appearing somewhat larger. After a minute or less a sort of background with the mottled appearance of Fig. 3-III sets in, and finally, after several minutes, this background becomes fairly stable, with, however, some motion still taking place. After ten minutes or less the pattern appears completely stable insofar as this "atomic" motion is concerned.

If the pattern of a point which has not been previously heat treated be observed between periods of heating at successively higher temperatures, the erratic phenomena of "anomolous" field emission occurring before "blackout," described elsewhere,[18] will appear up to temperatures of 2000°K. Around this temperature, electro-positive surface impurities causing the anomolous emission are removed. The relatively stable patterns occurring immediately after blackout exhibit a large dark region around the 100 direction. This transforms into the brightest region of the pattern of Fig. 3-I only after several minutes heating at 2800°K (see Fig. 4). This same phenomenon, as well as the comparative darkness of the 111 region evidenced in Fig. 4, was noted in Nichols' quantitative measurements of thermionic emission from tungsten as a function of crystallographic direction.[19]

If before such severe heating has caused the area around the 100 to change to a good emitter (and, therefore, presumably while the point surface is strongly contaminated by adsorbed gases, but probably not by electro-positive impurities[18]), the temperature be raised while the field producing the pattern remains on, the following will be observed: At 1100°K, the mottled spots of the pattern begin to stir sluggishly, quickly reaching a state of violent agitation at 1200°K which becomes more and more rapid until smoothed into a restless haze at 1500°K. From 1500°K to 2000°K, where the pattern is finally obliterated by the light of thermionic emission from other parts of the wire, a perfectly smooth appearance is presented. During this temperature rise, however, the striking changes illustrated in Fig. 4 take place. The transfer from the pattern of Fig. 4-II to that of Fig. 4-IIA occurs in the neighborhood of 1150°K. At any time during these phenomena, the existing pattern may be "frozen" in position by reducing the point to room temperature. Figure 4-IIB represents the "freezing" of Fig. 4-IIA, and the mottled aspect again appears. If, however, the field be removed before the temperature is reduced, and then applied again with the point at room temperature, the pattern of Fig. 4-II is found. Such phenomena can be explained by the assumption that surface atoms which change emission properties have one set of more stable positions on the crystal in the absence of the field, and another in its presence, a temperature

[18] J. H. Daniel, J. App. Phys. 12, 645 (1941).

[19] M. H. Nichols, Phys. Rev. 57, 297 (1940).

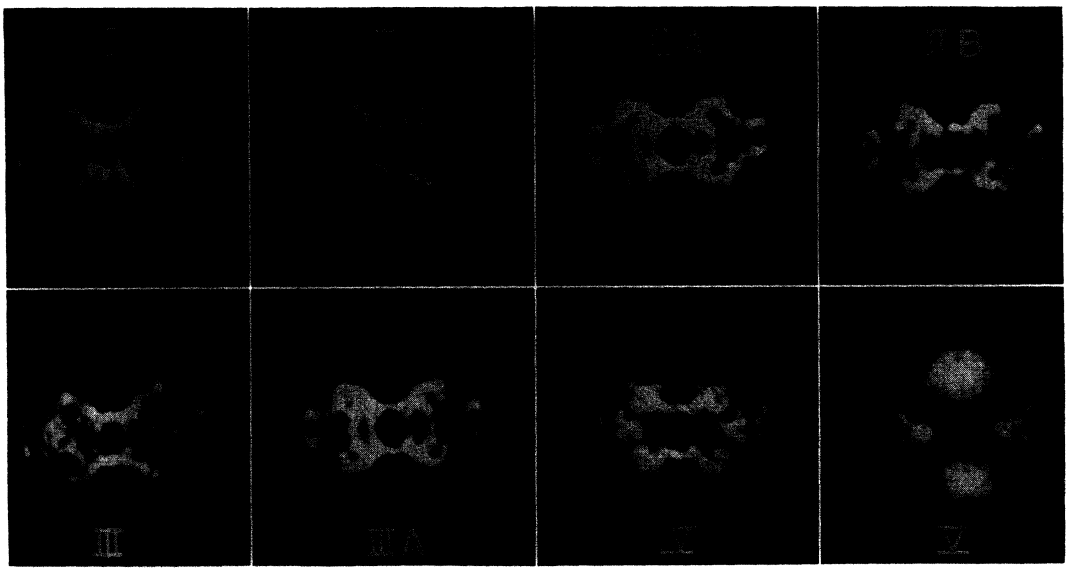

FIG. 4. Field emission patterns illustrating successive stages in "clean up" of a tungsten crystal by heat treatment. Electro-positive impurities were removed by temperatures in excess of 2000°K before the getter was flashed and the tube sealed off. I. Point at room temperature 20 hours after seal off of tube. II. Point at room temperature after 20 seconds at 1700°K and 20 seconds at 2100°K. IIA. Point raised to 1700°K from condition of II. If the field be removed and the point then reduced to room temperature, the pattern of II returns. IIB. Point reduced to room temperature from condition of IIA, field remaining on. If the field now be removed and reapplied, the pattern of IIB will still be found. The pattern of IIA and IIB is designated as the "temperature pattern" of the "normal pattern" II. III. Point at room temperature after 20 seconds at 2600°K. IIIA. Point raised to 1400°K from condition of III. IV. Point at room temperature after 20 seconds each at 2760°K, 2840°K, and 2900°K. V. Point at room temperature after 3 minutes (including 20 seconds in IV) at 2900°K.

of between 1100°K and 1200°K being necessary to allow the atoms to change from one set to the other. That the temperature at which the "reorientation" occurs is so definite is due to the fact that the field necessary for producing a pattern for observation is relatively constant; a slight lowering of the transition temperatures in the case of strong fields is believed to have been detected.

To promote further discussion, a "normal pattern" will be defined as that pattern existing before temperature (in excess of 1100°K) and field have been applied simultaneously; e.g., Fig. 4-II. A "pattern change" is then the change of pattern occurring when temperature and field are applied simultaneously to give what will be defined as the "temperature pattern" corresponding to the normal pattern. Figure 4-IIA (or Fig. 4-IIB) is thus the temperature pattern corresponding to the normal pattern Fig. 4-II. The normal pattern may be returned by heating to 1200°K in the absence of field.

Figures 5-IA, 5-IIA, 5-IIIA, and 4-IIA in that order illustrate the typical time sequence found in temperature patterns. The patterns of this sequence were much more striking in their differences than the corresponding normal patterns.

DISCUSSION

A. Mechanism of Pattern Changes

The change of projector pattern with heating in external field has been attributed[9, 11, 12] to a surface migration of tungsten atoms over the underlying crystal. The following considerations suggest that such changes are due instead to reorientation or migration of surface impurity atoms:

With increasing pressures in the tube, the time sequence of temperature patterns is speeded up, the patterns themselves remaining the same. The pattern of Fig. 4-IIA is obtained easily with points which have not been thoroughly outgassed. With points which have been thoroughly outgassed, this pattern can be obtained only by leaving the point at room temperature for weeks or months. The better the vacuum, the longer the time before the pattern returns.

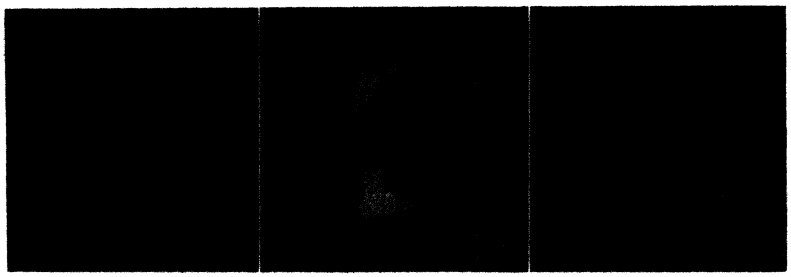

FIG. 5. Time sequence of temperature patterns observed with tungsten crystals. The crystal of this point is unusual in having the 100 region rather than the 110 region near the center of the pattern. The faint dark line running horizontally through the 100 region is an imperfection due possibly to twinning. Areas below this line are displaced slightly to the right of corresponding areas above. The bright 111 region of the threefold symmetry in the extreme left of IIA and IIIA appears where the 100 would be expected if the entire point surface were composed of a single crystal. The crystal boundary was visible in the actual pattern. The pattern of IA offers a striking illustration of how asymmetry of point shape can be detected by the variation in size of crystallographically identical dark spots. IA. Temperature pattern obtained a few seconds after thorough flashing. This pattern would become practically identical to that of clean tungsten if the bright lines connecting the 110 spots to adjacent 211 spots were absent. IIA. Temperature pattern obtained 30 minutes after flashing. IIIA. Temperature pattern obtained 2 hours after flashing. The final temperature pattern of this sequence is that of Fig. 3-IIA, and can only be obtained weeks after flashing.

If the various temperature patterns were caused by migration of tungsten atoms under the influence of temperature and field, rather than by accumulation of adsorbed atoms, comparatively little change in any existing temperature pattern should occur over a reasonable time with the field removed and with the point below 1100°K. Instead, the sequence of temperature patterns proceeds at substantially the same speed whether the point is at room temperature or well above 1100°K, and whether the field remains on or off (i.e., off except when observing the pattern).

If pattern change were due to the migration of surface tungsten atoms under the influence of temperature and field, a temperature pattern well advanced in the time sequence should be present immediately after reducing the point from a high temperature, with field applied, to room temperature. Instead, each flashing, with or without field, for any length of time, starts the pattern sequence over from its beginning.

The dependence of the speed of temperature-pattern sequence on pressure, its relative independence of temperature (below 1500°K) and of field, and the effect of high temperatures (above 2000°K) in returning a temperature pattern occurring early in the sequence—all are consistent with the gas adsorption hypothesis and not easily explained by the tungsten migration hypothesis.

To fit the findings of Benjamin and Jenkins[11] into the picture presented here, it is necessary to conclude that their surface conditions were considerably more stable than those considered here, although total gas pressures are presumably of the same order of magnitude. Total pressure, of course, cannot be relied upon for a true indication of surface condition since the partial pressures of active gases responsible for contamination may be many orders of magnitude less than the total pressure. Recently Moore[20] has shown that the evacuation schedule used here, while excellent for thermionic work, is not suitable for low temperature work. Thus the relatively rapid appearance of successive temperature patterns in the sequence observed here is explained.

Such vacuum conditions made the pattern sequence quite apparent when it might otherwise have escaped attention. They do not allow the arguments (given above) against migration of surface tungsten atoms to be applied with certainty to the pattern of Fig. 5-IA, however, because of the rapid appearance (within about a second under the most stable conditions obtained) of this pattern. Thus the possibility

[20] N. H. Moore, Ph.D. Thesis, Massachusetts Institute of Technology (1941).

that the bright lines of Fig. 5-IA may be due to repositioning of surface tungsten atoms instead of adsorbed gas atoms cannot be excluded on the evidence presented here.

It has been suggested[11] that the crystal-symmetric, step-like structure often observed in projector patterns of field emission is due to etched ridges which are subsequently removed by heating. Such structure was obtained in these experiments (e.g., Figs. 5-IIA and 5-IIIA) from points which had been heated many hours at 2800°K—enough to remove all ridges. It was obtained, however, only with the temperature pattern of gas contaminated surfaces. It might be inferred that such structure occurs because of layer-like gas adsorption on a smooth surface.

It is probable that the large dark region about the 100 direction in early stages of heat treatment (see Figs. 4-I through 4-IV) is due to adsorbed atoms rather than to etching effects which are removed by surface tension at high temperatures. The dark region occurs with points which have not been outgassed in sealed-off and gettered tubes, but which have been thoroughly heat treated previous to sealing off, so that any etched flat surfaces have been removed if they are ever to be removed by heat treatment. The dark region was also observed to return in the space of a month to two points which had been sealed off in a vacuum of not so low a pressure as was usually the case.

B. Other Aspects of Single Crystal Field Emission

On the strength of the adsorbed gas hypothesis, the temperature pattern sequence may be used as a sensitive indicator of surface and of vacuum conditions. From the normal pattern it appears that regions connecting the 110 to adjacent 211 directions are first contaminated. Whether contamination then spreads to the 111 regions and finally to the regions around the 100, as might be suggested by the greatly enhanced temperature-pattern emission from these regions, cannot be determined with certainty until what takes place in the "repositioning" of adsorbed atoms is understood in detail.[21]

Rough tests seemed to indicate that the amount of gas contamination occurring in four hours on a thoroughly outgassed point held at temperatures above 1600°K was not of sufficient importance to affect the total emission more than five percent, although the effect on the projector pattern was quite apparent for temperatures below 2000°K. Points left at room temperature for long periods first showed a rapid decrease (for perhaps half an hour), then a gradual increase (several days) over the "almost clean" tungsten emission.

Aside from any explanation of pattern change, there is the perplexing problem of accounting for the apparently excessive variation in field emission between bright and dark areas of the normal pattern. A quantitative measurement of the emission variation would be more satisfactory than estimates based on the brilliancy of the projector image. However, Benjamin and Jenkins[11] (as well as Müller[9]) have estimated this variation to be of the order of at least 100 to 1, and have given several suggestions in attempting to account for such large variation. In this connection, the following comments are in order: In confirmation of Benjamin and Jenkins' objections to Müller's proposed theory of internal reflection of electrons between the crystal atomic lattice planes, it might be pointed out that in extending the theory to Martin's thermionic pattern for a clean tungsten single crystal, Müller was able to explain results (concerning relative brilliancy in projector patterns of the 110, 211, and 100 directions) attributed to Martin[14] which are not the results Martin obtained, and which are irreconcilable with those results. This theory has never been supported by the discovery of band structure in energy distribution measurements in thermionic, photoelectric, or field emission measurements.

The field emission pattern of clean tungsten is identical in configuration to the thermionic pattern Martin obtained from a polished single-crystal tungsten ball, but the light contrast is much greater. There is also strict qualitative or relative agreement between field emission pattern intensities in various crystallographic directions and the thermionic emission in the corresponding directions determined quantitatively by Nichols.[19] As will be seen in the next section, the transformations produced in the clean tungsten

[21] It might be pointed out, however, that a darkening of these areas does occur in the contaminated normal pattern.

pattern by evaporation of thorium on the crystal are qualitatively the same in thermionic[14] and in field emission. Such agreement[22] may be considered to strengthen the evidence that field emission, like thermionic, is predominantly a surface phenomenon, and not governed by reflection of electrons within the metal.

OBSERVATIONS ON THORIATED TUNGSTEN SINGLE CRYSTALS

A. Experimental

To extend electron projector investigations of field emission to simple composite surfaces, the same tubes described above were used. In two of these were mounted points formed by electrolytic etching from 0.005-inch diameter tungsten wires in which about one percent thoria had been incorporated during manufacture (981328 Westinghouse "B" wire). These points will be referred to as "thoriated tungsten points." The third tube contained a close spaced coil of this 0.005-inch thoriated tungsten wire about an inch and a quarter in length and a tenth of an inch in diameter, mounted just within the collector ring, on the level of the General Electric 218 "pure" tungsten point. Electrical connection and mechanical support were furnished by an extension of one filament lead and by an extra lead incorporated in the tube stem. From this coil thorium could be evaporated externally on more than half the surface of the tungsten point. This type of point will be designated as a "thoriated 218 point."

The vacuum technique described above was again employed, and observations made only on gettered tubes with total pressures less than 10^{-8} mm Hg. As shown above, under such conditions no appreciable contamination takes place on simple tungsten surfaces above 2000°K. It is therefore possible, though by no means certain, that in the 15- or 20-minute period required for activation of thoriated tungsten points (during which the points were held at 2100°K following a "flash" at 2900°K) there was little chance for contamination.

As compared to the simple tungsten patterns described above, all patterns from both thoriated tungsten and thoriated 218 points were remarkably stable. It was not found possible to produce any marked changes by rearrangement of adsorbed atoms upon application of the field at high temperatures. About the only effect ever produced was to form or intensify a sort of dark ring around the 111 region which is evident in Fig. 6-IV.

B. Thoriated Tungsten Points

Figures 6-I through 6-VIII are explained by their captions. Activation for long periods at temperatures below 2100°K produced no essential changes in the patterns. It was found impossible by any amount of flashing to obtain a pure tungsten pattern.

The patterns of Figs. 6-I through 6-V were obtained many times, and were reproducible and comparatively stable until the points had remained at temperatures in excess of 2700°K for a total time of between one and two hours. Then a change took place, and these patterns were not again obtained. Instead, the pattern of Fig. 6-VIII appeared. As will be seen presently, this is the same pattern as was obtained from thoriated 218 points. Figures 6-VI and 6-VII show transition stages. Such a transition suggests the elimination, by a process of decomposition and diffusion to the surface, of metallic impurities which are not present in the 218 wire.

C. Thoriated 218 Points

In evaporating thorium on the pure tungsten 218 point, a schedule developed by Coomes[23] to give an oxygen-free layer of thorium, and one to give an oxygen-impregnated layer were used. Differences in resulting patterns were too minor to warrant any conclusions.

Before the evaporating coil had been raised

[22] It appears that Benjamin and Jenkins are not justified in stating that they do not find similar agreement between thermionic and field emission work functions. First, their estimated order of increasing work function based on field emission patterns is actually the order of decreasing field emission intensities, and agrees perfectly with Nichols' experiments if compared with his order of decreasing thermionic emission intensities. Second, in referring to the work function of the 100, 111, and 110 regions, Benjamin and Jenkins must actually mean for what they call the 100 region, the region surrounding the 100 dark spot, since if this spot itself were taken as the 100 region, their order of increasing "work function" would surely have been given as 111, 100, and 110 instead of 100, 111, and 110. However, they compare this region surrounding the 100 spot with Nichols' data for the 100 spot itself.

[23] E. A. Coomes, Phys. Rev. **55**, 519 (1939).

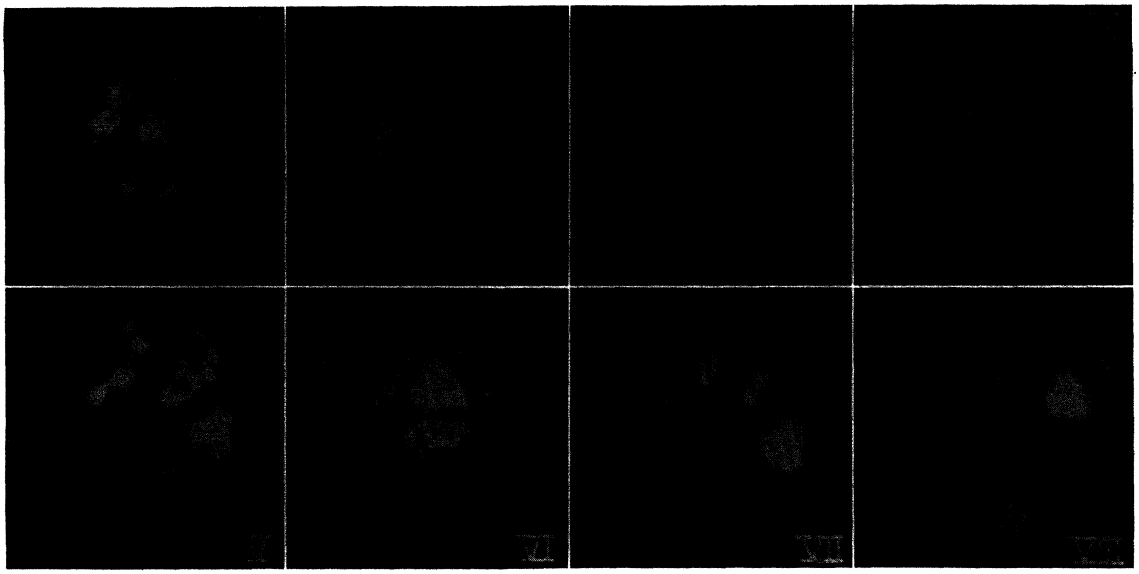

FIG. 6. Field emission patterns from a thoria-incorporated tungsten point which has been activated at 2100°K, thus giving a thorium coverage corresponding to maximum thermionic emission in the polycrystalline state. I. Initial semi-permanent pattern, point at room temperature. The bright 111 triangle is at the center. The three 100 regions resemble dark centers of a daisy with twelve bright radial petals, the four petals bordering the 211 regions being much darker than the rest, so that eight bright petals are symmetrically arranged in four groups of two's (better seen in V). II. Pattern of I after 3 hours at room temperature. The bright 111 region has been completely blacked out. III. Pattern of I after 15 minutes at room temperature. In the meantime the point has been flashed at temperatures in excess of 2700°K for about 10 minutes total. After such treatment, the bright 111 triangle could not be blacked out by long standing at room temperature as in II, but developed instead a six-sided star appearance as in III. IV. Pattern of III when point is raised to 1200°K. The dark circle appearing in the 111 triangle is the only evidence found of anything suggesting a "temperature pattern" differing from the "normal patterns" with thorium coverages. V. A second thoriated tungsten point, not a single crystal, but exhibiting one 100 area and one 111 area, the regions affected by thorium adsorption. The pattern is a late stage of III. VI. Crystal of I at room temperature, showing an early stage of transition to the final permanent pattern of VIII and Fig. 7. This transition occurred after approximately one and one-half hours total at temperatures in excess of 2700°K. VII. Crystal of V showing a later stage of the transition of VI. VIII. Final pattern of crystal of V. Point at room temperature after activation for one hour at 2100°K.

above 1800°K in the presence of the point, simple tungsten patterns with their characteristic time sequence were obtained. After evaporation of thorium, however, attempts to remove it from the point by severe heating[24] gave rise to a pattern not greatly different from that of Fig. 7-I, though with less marked separation of the 111 region into three bright spots. While this pattern was very similar to the normal pattern of contaminated tungsten (Fig. 4-V), it was much more stable, and over a period of days showed none of the striking temperature pattern variations (except for the presence of slight bright ridges along the dark cross connecting the 211 spots through the 110) through which a simple tungsten surface is transformed by adsorption of gases.

[24] Periods as long as 18 hours at 2600°K with intermittent flashes amounting to a total of thirty minutes at 2850°K were tried.

DISCUSSION OF RELATED PHENOMENA

Placed in logarithmic form, Eq. (1) becomes:

$$\log_{10}(I/V^2)=\log_{10}[1.55\times10^{-6}(\beta^2A/r^2w)]-2.98\times10^{7}(rw^{\frac{1}{2}}/\beta V)\phi(y), \quad (2)$$

where I is the field emission current in amperes from an area $A=kr^2$, r being the point radius in centimeters, and k a proportionality constant; V is the applied voltage, giving a surface field $F\doteq\beta V/r$, where β is a constant depending on the shape or smoothness of the point; w is the work function in electron volts; ϕ is a function of $y=3.62\times10^{-4}(\beta V/rw^2)^{\frac{1}{2}}$. Thus a plot of $\log_{10}I/V^2$ *vs.* $1/V$, which will be termed a field emission characteristic, should give a straight line, the

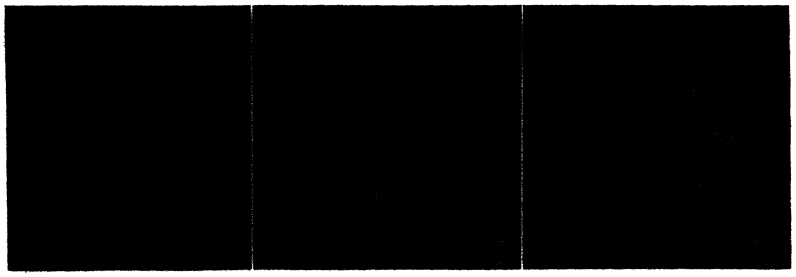

FIG. 7. Field emission patterns from a tungsten single crystal point upon which thorium has been evaporated externally from a coil of thoria-incorporated tungsten wire. Unsymmetrical light flares near the 111 area on the left are caused by stray field emission from the evaporating soil. The evaporation schedule: With point at 1600°K, the evaporating coil is held at 2500°K, flashed at 2850°K for two minutes every three hours. I. After evaporation for 1 hour, point at room temperature. II. After evaporation for 5 hours, point at room temperature. III. After evaporation for 30 hours, point at room temperature.

effect of $\phi(y)$ being, to close approximation, a vertical displacement of the line.[7] The slope is given by:

$$S=\frac{d(\log_{10} I/V^2)}{dV^{-1}}=-2.98\times10^7\frac{r}{\beta}\phi(y)w^{\frac{1}{2}}. \quad (3)$$

In an extensive series of experiments, Müller[5] varied w by evaporating layers of different materials on the surface of both points and wires, measured w thermionically, and plotted $\log_{10} S$ *vs.* $\log_{10} w$, where S is the slope of the field emission characteristic obtained for the corresponding value of w. From Eq. (3) this should give a straight line with slope equal to $\frac{3}{2}$. However, for films of Ba, Mg, Th, and O_2 on tungsten, and Cs on WO_3, in thicknesses ranging from zero ("pure" tungsten) to layers having the properties of the "massive" film material, Müller consistently obtained a linear relation with slope magnitude equal to three.[25]

To account for the discrepancy on the basis of a variation in β, it is necessary that β be proportional to $w^{-\frac{1}{2}}$ over the entire range of work function used by Müller—a factor of at least ten in β. Müller ruled out this possibility on the ground that the w^3 law held in the transition from a tungsten surface over to sufficient atomic layers of adsorbed material to give in effect "massive" metal of the material. Under such conditions no orientation or repositioning of adsorbed dipoles, which might give an effective β variation, would be expected.

On the other hand, assuming values for the average work function and width of the Fermi band in tungsten, calculating the field from the shape of the point as observed with the electron microscope, and estimating the emitting area, Haefer[12] found the experimentally obtainable numerical values in Eq. (2)[26] to agree with the theoretical values to within 10 percent. This he takes as confirmation of the $w^{\frac{1}{2}}$ law for pure tungsten. The significance of such agreement becomes less clear in view of Benjamin and Jenkins' finding[11] from a rubber membrane potential model that β may be about $\frac{1}{2}$ instead of unity[27] on account of the presence of the heating wire and the point wire itself.

Haefer's experiments with Ba, K, and Cs layers on tungsten appear to confirm the $w^{\frac{1}{2}}$ law. He suggests that Müller's results were due to crystallite formations of the evaporated materials which effectively altered β, and which he avoided by careful evaporation. In view of the picture of adsorption well-established by thermionic experiments on activation of thoriated tungsten,[28] however, it does not seem probable that such crystallites could exist, unless by "crystallite" is meant a grouping of adsorbed atoms only one

[25] That Ahearn [A. J. Ahearn, Phys. Rev. **50**, 238 (1936); see also footnote 2 of reference 18] found no change in field emission upon activation of a thoriated tungsten wire would seem to indicate that thorium atoms were not present on the sharp irregularities which must have comprised the emission centers.

[26] A simplified equation was used.

[27] β = unity for a geometrically perfect and microscopically smooth sphere.

[28] I. Langmuir, J. Frank. Inst. **217**, 543 (1934).

atom thick in the dimension perpendicular to the surface. There is good evidence[29] that such a grouping (patch effect) does exist, particularly at low temperatures, and it seems to offer an explanation of the "mottled" pattern aspect often observed with adsorbed layers.[30] However, because of the small thickness of such a group relative to the thickness of the surface potential barrier, it does not seem probable that such atomic irregularities could affect field emission through a local intensifying of field (or change in β).

It is difficult to see how the apparently excessive variation of field emission with crystallographic direction could be directly concerned in giving a high exponent for w in Müller's experiments. However, there are objections to all field emission experiments so far reported which, though they might not be expected to have great influence on the results, nevertheless should be removed in order to establish conclusively the exponent of w in Eq. (1). Müller's measured thermionic work function presumably did not apply to the comparatively minute single-crystal area giving rise to field emission, but rather to a much greater area. Haefer used values from the literature for w which were obtained for large polycrystalline surfaces. Nichols has found[31] that the average thermionic work function of a single crystal wire differs from that of a polycrystalline wire. Measurements should be made under proper vacuum and surface conditions upon a well-defined area of a single-crystal surface small enough to have an essentially constant value of w and uniform value of surface field,[32] so that a value of w obtained as a thermionic average will not be compared with one obtained by a field emission averaging process.

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[29] W. B. Nottingham, Phys. Rev. **49**, 88 (1936).

[30] Benjamin and Jenkins (see reference 11) give a calculation, based on diffraction effects, which relates the size of a spot on the fluorescent screen of a projector to the number of atomic diameters across the "aperture" of a group of atoms on the point surface which might be causing the spot. Their implicit assumption that the emerging parallel electron beam, at the "aperture" of surface atoms, has a wave-length corresponding to the energy attained after falling through the total potential difference between point and screen, seems unjustifiable.

[31] M. H. Nichols, Phys. Rev. **59**, 944 (1941).

[32] The non-uniformity of field produced by certain types of surfaces has been shown by calculation [C. C. Chambers, J. Frank. Inst. **218**, 463 (1934); also reference 7] to be relatively unimportant, merely introducing a higher power of V in the first term of Eq. (2). This results in a slight curvature of the field emission characteristic, which, as in the analogous case of the effect of the temperature exponent in plots of Richardson's thermionic equation, is difficult to detect experimentally.