THE PHOTOELECTRIC PROPERTIES AND CONTACT RESISTANCES OF THIN CATHODE FILMS.

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INTRODUCTION.

THE relation between the velocity of the electrons emitted by the action of light on metals and the frequency of the light was deduced by Einstein[1] on the unitary theory of light and was expressed by the equation

$$\tfrac{1}{2}mv^2 = eV = h\nu - w_0.$$

Here m is the mass, v the maximum velocity and e the charge of the electrons liberated by light of frequency ν. V is the difference of potential in electrostatic units, which is just sufficient to prevent these electrons from reaching the receiving electrode. h is Planck's constant and w_0 is the work done in the escape of an electron from the metal. Recently this same equation has been derived by Richardson[2] by thermodynamic and statistical methods which do not necessarily involve the unitary light hypothesis. Richardson's theory further enables the constant w_0 to be interpreted and calculated by the relation[3]

$$w_m - w_p = \frac{e}{300}\left\{ V_p - V_m - \theta\frac{\partial}{\partial\theta}(V_m - V_p) \right\},$$

where $w_m - w_p$ is the difference between the amounts of work required to liberate an electron from each of two metals m and p, and $V_p - V_m$ is the contact difference of potential, between the metals, expressed in volts. The last term, which expresses the Peltier effect, is so small in comparison with the contact difference of potential that it may be neglected in this work. w_0 has been measured directly for platinum[4] and for osmium[5] and is not far from $e/300\cdot5$ volts for platinum. From this value, w_0 for any other metal may be calculated from a knowledge of their contact differences of potential.

[1] Ann. der Physik, Vol. 17, p. 146 (1905).

[2] PHYS. REV., Vol. 34, p. 146 (1912); Phil. Mag., Vol. 23, p. 615 (1912); Science, Vol. 36, p. 57 (1912).

[3] Phil. Mag., Vol. 23, p. 620 (1912).

[4] O. W. Richardson, Phil. Trans., A, Vol. 201, p. 497 (1903); Vol. 207, p. 23 (1906). H. A. Wilson, Phil. Trans., A, Vol. 202, p. 243 (1903). F. Deininger, Ann. der Physik, Vol. 25, p. 396 (1908). O. W. Richardson and H. L. Cooke, Phil. Mag., Vol. 20, p. 173 (1910).

[5] H. L. Cooke and O. W. Richardson, PHYS. REV., Series 2, Vol. 1, p. 71 (1913).

These relations have been tested[1] for a large number of different metals and frequencies, and have been found to be consistent with the experimental results, within the probable limits of accuracy of the experimental methods employed.

Several investigators have succeeded in obtaining electron velocities considerably higher than those ordinarily obtained in photoelectric measurements. Most of these high velocities have been obtained when sparks were used as the source of light. These have been shown to be due to secondary action from electro-magnetic radiation accompanying the spark discharge. However high velocities have also been obtained in other ways. Von Baeyer and Gehrts[2] obtained velocities equivalent to 6.3 volts for electrons from copper, gold and aluminium after passing an induction coil discharge between the emitting and receiving electrodes. Recently Dike[3] has published results of experiments in which he obtained values of the maximum initial kinetic energy equivalent to as much as 44 volts for electrons liberated from thin platinum cathode films when illuminated by light from a quartz mercury arc. These results were repeated by Dike and Brown,[4] who obtained values as large as 52 volts under conditions similar to those in Dike's first experiment.

It is evident that if these results are correct they render Richardson's theory untenable. From the relation $V = 300/e \cdot (h\nu - w_0)$ discussed above, we may calculate the maximum potential possible according to the theory. 180 $\mu\mu$ is the shortest wave-length of light that will pass through the air and quartz interposed between the source of light and the illuminated metal. Take w_0 for platinum to be approximately 5 volts. Substituting these values in the above equation we find $V = 1.95$ volts. Even if the work done on an electron in escaping from the metal were zero we would still have V equal to only 9.95 volts. This is the upper limit allowed to any substance by Richardson's theory. It is an impossibly favorable case but it still falls far short of explaining the high velocities found by Dike.

It seems necessary, then, either to reject Richardson's theory or to discover some error in the results or the interpretation of the results given by Dike. It was with the purpose of discovering whether these high velocities are real or only apparent photoelectric velocities that we undertook this investigation.

[1] Richardson and Compton, Phil. Mag., Vol. 24, p. 575 (1912); A. L. Hughes, Phil. Trans., A, Vol. 212, p. 205 (1912).

[2] Ber. d. D. Phys. Gesell., Vol. 21, p. 870 (1910).

[3] PHYS. REV., Vol. 34, p. 459 (1912).

[4] PHYS. REV., Series 2, Vol. 1, p. 254 (1913).

One of the writers[1] has shown that the velocity actually measured in photoelectric experiments consists of two parts, (1) the true initial velocity with which the electrons are liberated and (2) a velocity acquired after emission due to the force exerted on the electrons, arising from the contact difference of potential between the emitting and receiving electrodes. Of these two parts, only (1) has anything to do with the photoelectric effect and it is only this part of the measured potential which should be considered as due to photoelectric action. It seemed probable that the great increase in the photoelectric potentials following an induction coil discharge might be due principally or entirely to a great increase in the contact difference of potential. Thus the initial kinetic energy with which the electrons leave the metal film may have the ordinary value predicted by Richardson's theory. But after emission this velocity may be greatly increased by the repulsion due to an absorbed negative charge in the sputtered plate or due to their passage through a charged insulating layer, deposited on the surface by the induction coil discharge. With the object in view of testing these explanations of the apparent high velocities, these experiments were undertaken.

APPARATUS.

Our apparatus, shown in Fig. 1, is essentially the same in size and arrangement as that used by Dike,[2] with the addition of an arrangement for testing the contact difference of potential between the emitting

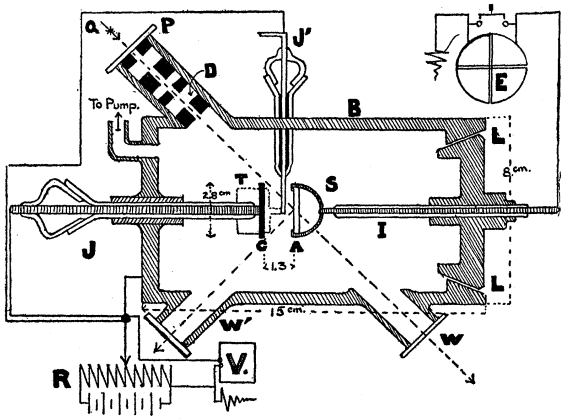

Fig. 1.

electrode and the surrounding vessel. *BB* is a cylindrical brass vessel 15 cm. long and 8 cm. in diameter. It is closed at one end by an accu-

[1] K. T. Compton, Phil. Mag., Vol. 23, p. 579 (1912).

[2] PHYS. REV., Vol. 34, p. 465 (1912).

rately turned and ground lid, and wax could be poured into the grooves LL to render the vessel airtight. Through this lid extends an insulated rod I, which carries on its end a stirrup S, supporting the plate A on which the film under investigation is to be deposited and tested. This plate is about 2 cm. square and is connected to an electrometer E giving a deflection of 180 divisions per volt at a scale distance of one meter. The films were sputtered on the plate A from a platinum cathode C, which, when not in use, could be turned out of the way by rotating the ground glass joint J through half a revolution.

Light from a quartz mercury arc Q entered the vessel through a quartz window P and a side tube provided with diaphragms D. When a quartz plate was in position at A the transmitted light passed out of the vessel through a window W, and the reflected light escaped through W'. In this way the reverse stream of electrons due to light incident upon the sides of the vessel was practically eliminated. The vessel could be charged to any desired potential from a potentiometer circuit R. The maximum initial kinetic energies of the electrons, expressed in equivalent volts, were determined by charging the vessel to such a negative potential that the electrometer showed no deflection. The voltmeter V then gave the maximum potential directly. By this *null* method we avoided possible errors due to faulty insulation. When saturation currents were to be measured, the vessel was charged to a sufficiently high positive potential and the rate of deflection of the electrometer noted.

As pointed out above, it is necessary to apply a correction for contact difference of potential to the measured values of the maximum potential in order to find the true photoelecrtic potentials. This contact difference of potential between the metal film on A and the vessel BB was determined by the Kelvin method.[1] The contact difference of potential tester T consisted of a brass plate, of the same dimensions as the plate A, fixed on a movable arm to the end of a brass rod which extended to the outside of the vessel through the ground glass joint J'. By rotating this joint the test plate could be moved close to A or back against the side of the vessel. The tester T was raised to various potentials from the divided circuit R, and the potential was so adjusted that no kick of the electrometer was produced by moving T back and forth in front of A. The voltmeter, under these conditions, gave a direct measure of the contact difference of potential between T and A. An objection to this arrangement is that it measures the contact difference of potential between the emitting electrode and *only a particular part* of the receiving electrode. If the inside of the vessel always remains a polished brass

[1] Kelvin, Phil. Mag., Vol. 56, p. 82 (1898).

surface this arrangement would introduce no error. However, if the induction coil discharge, during the process of sputtering, changes the condition of the inside surface of the vessel and changes it more in some regions than in others, the above method will not be accurate, because it is not certain that the contact difference of potential actually measured is the true difference of potential between the emitting electrode and that portion of the vessel to which most of the electrons are escaping. Nevertheless, if any considerable changes in the contact difference of potential occur, this method should give at least an approximate measure of these changes. For this reason the contact potential measurements should be considered as indications of what surface changes are produced by the electrical discharge rather than as accurate quantitative measures of these changes. It will be seen, however, that these indications are fairly accurate, especially in the case of the larger effects measured.

The sputtering was all done at a pressure of $(10)^{-4}$ cm. of mercury by means of the discharge from a small induction coil capable of giving a spark of about 4 cm. in air. The thickness of the deposited film may be taken to be proportional to the time of sputtering. The photoelectric measurements were all made at a pressure of $5(10)^{-6}$ cm. or less.

Effect of Reflected Electrons.

A number of investigators[1] have assumed that electronic reflection at the receiving electrode causes a reverse stream of electrons which reduces the measured value of the maximum acquired photoelectric potential. Dike and Brown[2] offered this as one of the possible reasons for the high potentials obtained in their experiments. They further suggested that Robinson,[3] who also worked with sputtered films, did not obtain high velocities like they did because the construction of his apparatus may have made a difference in the amount of electronic reflection. It is hard to see, however, how electron reflection can have any effect on the maximum photoelectric potential. Suppose that fifty per cent. of the fastest electrons which strike the receiving electrode are reflected and return to the plate from which they started. This will not prevent the electrode from charging to the same maximum potential which it would attain were there no reflection. Under these conditions the final potential will be attained just half as rapidly, but it is inconceivable that the final potential will be altered. Especially is this true when the maximum potential is measured by a *null* method which eliminates errors

[1] Ladenburg and Markau, Verh. d. D. Phys. Ges., p. 562 (1908); Von Baeyer and Gehrts, loc. cit.; Klages, Ann. der Phys., Vol. 31, p. 343 (1910).

[2] PHYS. REV., Series 2, Vol. 1, p. 254 (1913).

[3] Phil. Mag., Vol. 23, p. 542 (1912).

due to imperfect insulation. Electronic reflection certainly must be prevented in case "distribution of velocity" curves are to be obtained, but its influence may be neglected in measurements of maximum potentials or of saturation currents. The apparent increase in the maximum potentials when electron reflection has been reduced by a perforated gauze and an auxiliary field has been shown to be a spurious effect.[1] For these reasons we have, in these measurements, made no effort to measure or prevent electronic reflection.

ORDINARY PHOTOELECTRIC POTENTIALS.

(*a*) *No Evidence of Absorbed Charge.*—In our first trials the cathode films were deposited on quartz in a separate sputtering vessel, which consisted of a large glass bell-jar waxed on a brass base plate, with the electrodes sealed in. The contact difference of potential was then tested in air by the ionization method,[2] which is more accurate than the Kelvin method but which may only be used while the films are in contact with the air. Then the sputtered plate was placed in position in the apparatus, the vessel exhausted and the maximum photoelectric potential measured. This process was repeated for three films of different thicknesses. The results are shown in Table I.

TABLE I.

Potential.	Platinum Film.		
	Very Thin.	Medium.	Thick.
Maximum.....	1.45 volts	1.65 volts	1.85 volts
Contact.....	−0.15	−0.15	−0.15
Corrected.....	1.30	1.50	1.70

Evidently this method does not yield the high potentials found by other investigators. On the other hand these maximum potentials are of the order of magnitude predicted by Richardson's theory. While the potential apparently is higher for the thicker films, the differences are small and may be due to experimental error, since the apparatus is not well designed for measuring potentials accurately to a fraction of a volt.

The results are, however, of some interest. The contact differences of potential are practically identical with that between brass and ordinary platinum. The photoelectric potentials are also what one might expect from platinum foil. It is quite certain, therefore, that these films consist of true platinum. The photoelectric potentials showed a

[1] Compton, Phil. Mag., Vol. 23, p. 277 (1912).

[2] Kelvin, Beattie and Smolan, Phil. Mag., Vol. 45, p. 277 (1898).

tendency to increase slightly with time, the increase amounting to one or two tenths of a volt in several hours. This "aging" effect has been noticed before by Dike and by one of the writers.[1] The saturation currents were larger than those usually obtained from platinum. This was true for all the sputtered films investigated. An important result bearing on the problem under investigation is that the induction coil

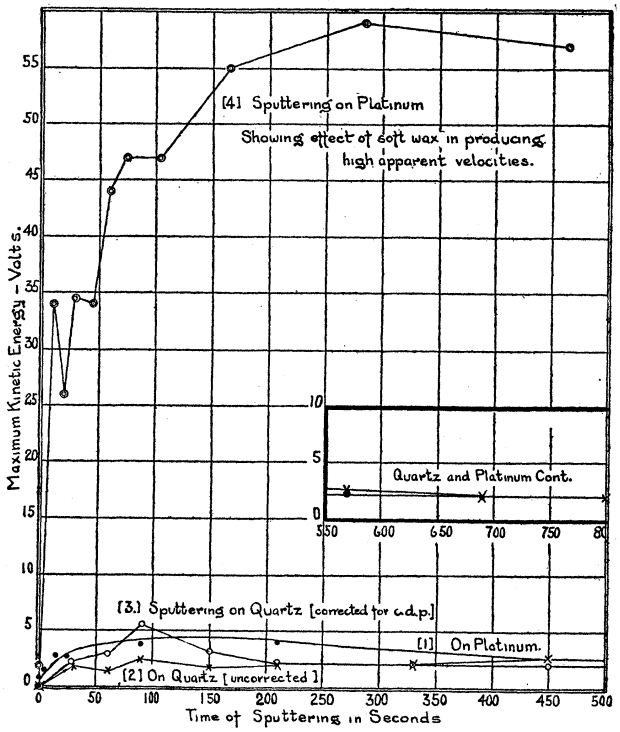

Fig. 2.

discharge evidently produces no "absorbed" charge in the quartz. Hence the high potentials obtained by Dike cannot be ascribed to this cause. An absorbed charge in the quartz, if it existed, would not have vanished immediately on contact with the air and would have been easily detected by the contact difference of potential measurements.

(*b*) *Films Sputtered and Investigated in Vacuo.*—Films sputtered on quartz and on platinum foil in the apparatus (Fig. 1) were tested for contact difference of potential and for photoelectric potentials and saturation currents without allowing the films to come in contact with the air.

[1] Stuhlmann, PHYS. REV., Series 2, Vol. 4, p. 330 (1913).

Results as shown in Fig. 2, curves 1, 2 and 3, were obtained. Curve 1 represents the variation of maximum potential with the time of sputtering, for films sputtered on a platinum plate. The highest measured potential is 3.9 volts. Since the contact difference of potential remained too small to be detected accurately by the Kelvin method no corrections for contact difference of potential were made. Curve 2 represents the photoelectric potentials for various thicknesses of films deposited on quartz. In this case the contact differences of potential were measurable and the corrected potentials are shown in curve 3.

Several facts are evident from these results. The potentials were rather irregular, most of the irregularities occurring in the early stages of sputtering. The contact differences of potential also varied, and further experiments showed that they varied also in different parts of the vessel. These photoelectric potentials are distinctly higher than those for ordinary platinum, although they still fall far short of those obtained by Dike and Brown.[1] Since the following experiment throws light on these results they will not be discussed further at this point.

SPURIOUS HIGH PHOTOELECTRIC POTENTIALS.

Up to this point it appeared that, although we had followed closely the method used by Dike, we were unable to duplicate his high velocities. Following a suggestion from Professor Richardson, however, we made another trial and succeeded in obtaining the high potentials, even exceeding the highest values obtained by either Dike or Brown.

TABLE II.

Time Sputtered.	Contact Potential.	Photoelectric Potential.
0 sec.	− 0.1 volt	1.8 volt
10	−16	35
10	−22	26
10	−28	34.5
15	−28	34
15	−37	44
15	−40.5	47
30	−40	47
60	−57	55
120	−57	59
180	−57	57

A tiny bit of soft wax was placed on the sputtering cathode and the above experiments were repeated. From the first the measured potentials were high, and are here shown graphically in Fig. 2, curve 4. After

[1] Loc. cit.

a film due to five minutes of sputtering had been deposited the corresponding maximum observed potential had risen to 59 volts. Further sputtering did not increase this value.

That these high potentials do not indicate high photoelectric velocities is shown by the fact that the contact difference of potential between the film and the vessel increased parallel with the photoelectric potential, in such a direction as to make the emitting film electro-negative and repel the electrons after they were emitted. The parallelism between these quantities is shown in Table II.

This enormous contact difference of potential is not the true contact difference of potential between the film and the chamber of the apparatus. If these high values represented true contact differences of potential, no photoelectric effect would be possible with light of the frequency used, since under these conditions $h\nu$ would be smaller than w_0. The effect is evidently due to a charged layer of soft wax covering the platinum film, within which layer the escaping electrons experience an enormous acceleration. This charged layer persisted for about 24 hours after air had been let into the apparatus. During this time the apparent contact difference of potential gradually fell to its normal value of $-$ 0.15 volt. The saturation currents under these conditions were a little more than half as large as in the similar tests where the soft wax had been omitted. This again gives evidence of some sort of layer through which the electrons were obliged to pass while escaping.

It is evident from these results that the high potentials observed by Dike and later also by Dike and Brown must be ascribed to the presence of oil or grease introduced while making the metal apparatus, to vacuum wax in the ground joints or to some other material which could produce such layers as suggested. Doubtless the small increase in potential which we observed before we intentionally introduced the soft wax was due to wax or grease unavoidably present in any form of metal apparatus.

There is therefore no evidence in these experiments to show that the photoelectric velocities should be different from those predicted by Richardson's theory. There are certain theoretical reasons for believing in the possibility of small variations in the saturation currents and maximum potentials from very thin films; but these effects, if they exist, will probably not exceed a fraction of a volt and will be taken into account by a variation in the quantity w_0 for very thin films.

SATURATION CURRENTS AND CONTACT RESISTANCES.

Several interesting phenomena are exhibited by the relations between saturation photoelectric currents and thickness of films, which are shown graphically in Fig. 3.

One of the most striking things about these curves is the influence of the nature of the contacts on the shape of the curves. In curve 5 the film was deposited directly on a platinum plate. The saturation curve under these conditions is a smooth curve of logarithmic form. Contact between the sputtered film and the platinum plate was evidently established from the very beginning, as is indicated by the lack of certain characteristic phenomena which appear in all curves for saturation

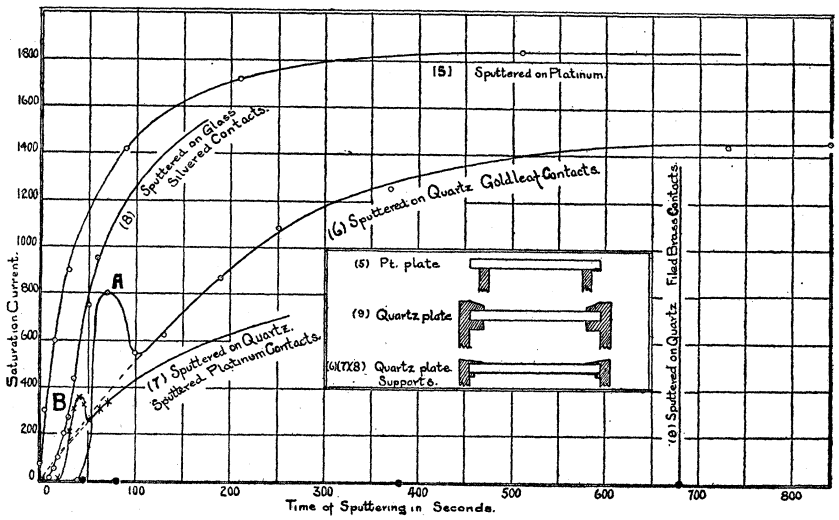

Fig. 3.

currents from films sputtered on glass or quartz. In curve 7 the contact between the sputtered film and the supporting stirrup was made as follows. A thick opaque platinum film was first sputtered on the quartz and a central strip was removed, leaving two strips of film about 3 mm. wide on the two opposite edges. The clamps of the stirrup were now fastened to these edgings and the films to be investigated were sputtered over this prepared surface. This was done with the idea in view that the film to be deposited would spread in a uniform layer over the cleaned quartz and the sputtered contacts alike, and in this way the preliminary film would serve as an intermediate contact between the sputtered film and the contact clamp. It is evident in this case that contact was not perfect from the beginning as in the case of curve 5, and that no contact with the film was established until the sputtering had continued about 25 seconds.

To show that the absence of photoelectric currents in the early stages of sputtering is really due to the absence of electrical contact rather than

to some inherent photoelectric property of very thin films, various other methods of making contact were employed. These methods, with their differences greatly exaggerated, are shown in Fig. 3. For curve 6 we used gold leaf contacts. Strips of gold leaf were placed firmly adhering to the two opposite edges of the quartz plate and the contacts were clamped down on this leaf. In this case the discontinuity of surface between the quartz and the gold leaf would be more pronounced than between the quartz and the sputtered film used previously. The preliminary film used for contact in the case of curve 7 was much thinner than the gold leaf and therefore a less abrupt discontinuity was found between the film under investigation and the contacts. As might be expected, the contact in this case was more difficult to establish, and was not obtained until the sputtering had continued for about 55 seconds.

A still greater degree of difficulty in establishing contact between film and holder is shown by curve 9. In this case a clean quartz plate was simply held in a brass clamp whose edges had been filed down to a very sharp angle, whose vertex rested flush on the quartz plate. The bounding surface was much more abrupt in this case than in the others. This time sputtering continued for at least 680 seconds before contact was made and currents obtained from the film. In fact this film was of such a thickness as to be quite opaque.

It is evidently a very difficult matter to make good electrical contact with very thin films. The less abrupt the boundary between the surface of the contact film or plate and the quartz surface on which the film is deposited, the more perfect will be the contact. At first sight it may seem unlikely that a contact edge as thin as gold leaf would prevent uniform deposition and perfect contact with the film. But when one remembers that these thinnest films are many times thinner than a wave-length of light, it is easy to believe that the deposited molecules must "bank up," so to speak, at the edge of the contact before continuity is obtained.

There are two applications of this experiment on the effect of the method of making contact with the films, to which we would call attention. In the first place it explains why, in our results and also in the recent results of Robinson,[1] little or no photoelectric current was observed until the film had reached a certain thickness, where the current showed a sudden increase. The above results seem to show that this is due to imperfect contact rather than to any inherent property of very thin films.

It also offers a possible explanation of some of the results obtained by

[1] Phil. Mag., Vol. 25, p. 115 (1913).

Patterson[1] on the specific resistance of thin metal films. He found for very thin platinum films that the specific resistance increased more rapidly than was predicted by the electron theory of conduction suggested by J. J. Thomson.[2] It seems possible that all or part of this unpredicted increase may be due to high contact resistance superposed on the regular resistance of the film. If this is true it would explain the discrepancy between theory and experiment in the case of very thin films. We also tested photoelectrically a film with contacts very similar to those used by Patterson, with the results shown in curve 8. The contact between film and holder was here established by sputtering the platinum film over a quartz plate whose two opposite edges had been covered by means of a semitransparent silver film, deposited by the Rochelle salt method. This method of establishing electrical contact between film and holder was evidently the most perfect yet tried. As seen from the curve, contact was established soon after 10 seconds' deposition. Had contact been made from the first it is probable that the resistance which Patterson measured would have been found to conform more closely to the theory discussed in his paper.

[1] Phil. Mag., Vol. 4, p. 652 (1902).

[2] Proc. Camb. Phil. Soc., Vol. 11, 2, p. 119 (1901).