The Photoelectric Sensitization of Aluminum*

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It is shown that the increase in photo-current from aluminum which had been subjected to hydrogen glow discharges, is dependent on the time of discharge and on the pressure of hydrogen. If the target is not outgassed a rapid decay is noted after sensitization, because of diffusion to the surface of gas contained in the body of the metal. Results indicate that this sensitization is due mainly to "clean-up" of the surface of the oxide coated aluminum. Glow discharges have little effect on the yield from freshly evaporated aluminum. Another type of sensitization is effected by exposing a freshly evaporated aluminum surface to minute quantities of dry air. The effect of the glow discharge upon a surface thus sensitized is one of desensitization. The current-voltage data from freshly distilled aluminum yield a curve which fits well upon the theoretical curve of the DuBridge theory. The curves from surfaces sensitized with air show no agreement with the theory. The threshold value obtained from a film of aluminum approaching bulk thickness is 2840A.

THE process of photoelectric sensitization of alkali metals by hydrogen glow discharges has been the object of a considerable amount of research. Data on this subject are relatively abundant and the theory of the factors involved has been advancing steadily. Meanwhile, investigation of the effect of glow discharges on metals outside the alkali group has been neglected to a great extent. The process has been used at times to sensitize metals in the latter class, but generally without much attention to the factors controlling sensitivity. The purpose of this paper is to report the results of preliminary experiments on the sensitization of aluminum by hydrogen glow discharges under various conditions. The experiments were undertaken with the hope of clarifying the uncertainties concerning the effect on the photoelectric emission of the duration for the discharge, its direction and the pressure of hydrogen. In the first set of trials the photoelectric emitter was un-outgassed aluminum and in the later experiments an evaporated aluminum surface sensitized by admission into the photocell of air in minute quantities.

The effect of the variation of film thickness upon the photo-current was observed, and also a test made of the DuBridge theory of the energy distribution of photoelectrons in pure aluminum.

APPARATUS AND METHOD OF PROCEDURE

The experimental photo-cell (Fig. 1) was a two-liter Pyrex flask with a quartz tubular window attached by means of a graded quartz-to-Pyrex seal. A thirty mil tungsten rod, led into the tube from the side opposite the window, carried the aluminum target 1.5 cm² in area. Freshly evaporated aluminum could be deposited on this target by passing heavy currents through three pairs of 60 mil tungsten leads, each supporting a 30 mil tungsten filament wound about a supply of aluminum from the same source as the target.[1] Hydrogen could be introduced into the system by flaming a palladium tube, and its pressure measured by ionization and McLeod gauges. Mercury vapors were trapped by means

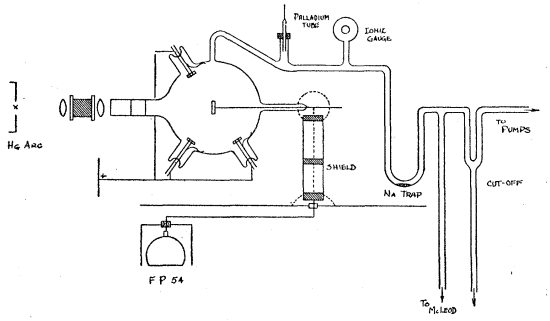

FIG. 1. The photo-cell.

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[1] The aluminum used was obtained from the Alcoa Laboratories through the courtesy of the chemistry department of St. Louis University. It was guaranteed to contain less than 0.1 percent impurities.

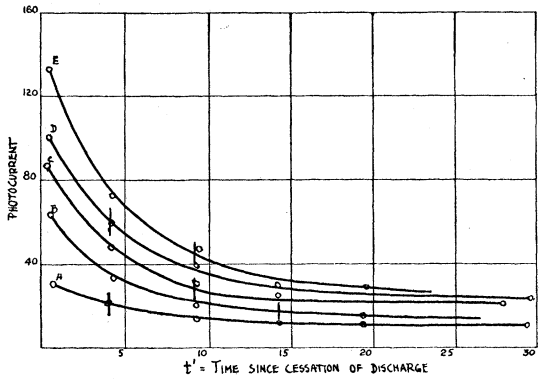

FIG. 2. Decay of sensitivity of un-outgassed aluminum.

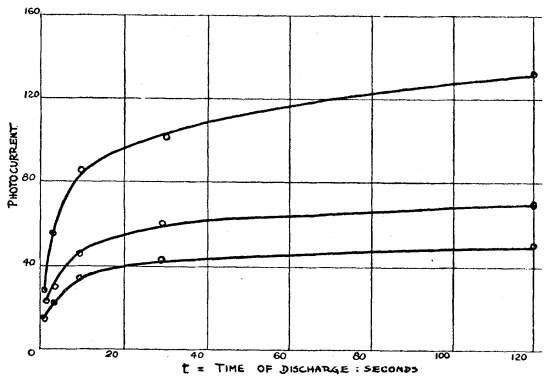

FIG. 3. Variation of sensitivity with time of discharge.

of triply-distilled sodium as described by Poindexter.[2] The photo-cell itself and the neighboring glass parts were outgassed by a seven-hour heating at a temperature averaging 350°C.

The circuit used for measuring the photo-electric current was that designed by Brown and DuBridge, using an FP-54 Pliotron.[3] With an input resistance of approximately 10^9 ohms, and a Leeds and Northrup high sensitivity galvanometer in the plate circuit currents smaller than 10^{-13} amp. were measurable. Light aluminum tubing was used in the shielding of leads. In the sensitization experiments the unresolved radiation from a G.E. mercury arc was focused upon the aluminum surface by a quartz lens. For the threshold measurements the predominant 2653A and 2536A lines of the same arc were used. The high voltage source consisted essentially of a filament transformer a high voltage transformer and an RCA 866 rectifier tube. With 3000 volts applied to the terminals, currents varying from 0.0005 amp. to 0.008 amperes were obtained.

A preliminary set of measurements of the effect of a 10 sec. hydrogen glow discharge, with the target which had not been outgassed as cathode, showed a twenty-fold increase in the photo-current measured one minute after the discharge ceased. The increase was only temporary; a rapid decay ensued, the current decreasing to half its value within a few minutes. Therefore, in addition to the anticipated factors affecting the sensitivity, the decay factor had also to be considered.

In the first group of experiments upon aluminum which had not been outgassed, the following order was observed:

1. The hydrogen pressure kept constant, the time of sensitization (t) varied, and the decay curves run for each (t).
2. The time of sensitization held constant and the decay curves plotted for various pressures of hydrogen.
3. The time (t') since the cessation of discharge held constant, and the sensitization curves plotted for various hydrogen pressures.

In the measurements made upon freshly evaporated aluminum which had been sensitized by the oxygen of the air, only the variation of sensitivity with time of discharge was recorded, since in this case no decay effects were in evidence.

Current-voltage curves, from which the threshold values were calculated, were run both for sensitized aluminum and for a freshly evaporated film approaching bulk thickness.

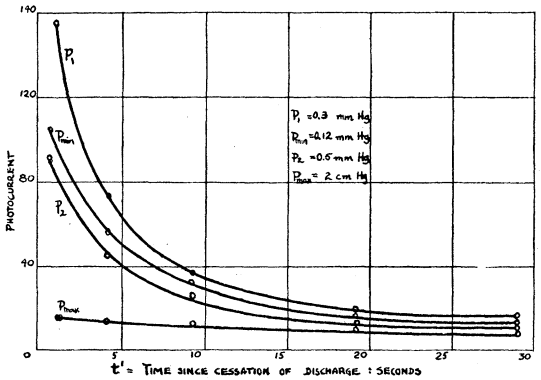

FIG. 4. Decay curves of un-outgassed aluminum. Various pressures.

[2] Poindexter, Phys. Rev. **28**, 208 (1926).
[3] Brown and DuBridge, Rev. Sci. Inst. **4**, 532 (1933).

Results

Sensitization of un-outgassed aluminum

In Fig. 2 the photo-current is plotted against the time of decay (t') the pressure being constant and the time of sensitization varying for each curve thus: A, 1 sec.; B, 3 sec.; C, 10 sec.; D, 30 sec.; E, 2 min. In these experiments the hydrogen was removed at different times during the run, as indicated by the small vertical bars of Fig. 2, but no decided deformation of the curves was noted. All the decay curves seem to be exponential in character.

Figure 3 illustrates the variations in photo-current with time of discharge (t), the pressure again being constant. In addition each particular curve has a constant (t'). The steep slope of all the curves at the beginning indicates that the initial short periods of sensitization are relatively more effective than the longer and later periods.

In Fig. 4, the time of sensitization was a constant (2 min.), and the individual curves show the decay in photo-current for the pressures: $P_{\min}$, 1.2×10^{-1} mm Hg; P_1, 3×10^{-1} mm Hg; P_2, 5×10^{-1} mm Hg; $P_{\max}$, 2 cm Hg. The outstanding feature of these curves is not their form (approximately exponential as in the previous case) but the order of their vertical arrangement: P_1, $P_{\min}$, P_2, $P_{\max}$. This order shows there is an optimum pressure in the neighborhood of P_1 (0.3 mm Hg), and that the higher pressures are ineffective in producing sensitization. By extrapolation of the P_1 curve a sensitization factor of about 80 was obtained for $t'=\frac{1}{2}$ min.

The occurrence of an optimum pressure in the region of 0.3 mm Hg is brought out more clearly in the curves of Fig. 5; the same data being plotted with current and hydrogen pressure as the coordinates.

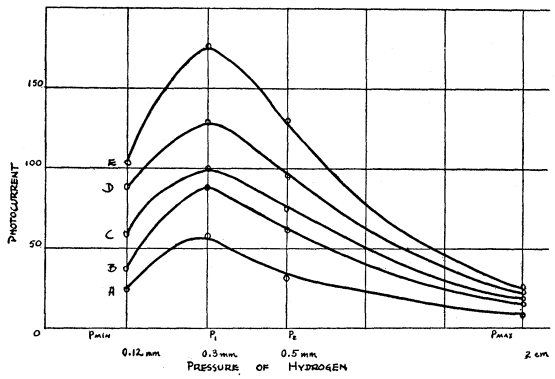

FIG. 5. Optimum pressure curves. Un-outgassed aluminum.

Glow discharges with the aluminum target as anode, produced only an extremely slight increase in the photoelectric sensitivity (Fig. 6).

A preliminary trial of the effect of the hydrogen discharge upon a freshly evaporated film of aluminum yielded a negligibly small decrease in the photoelectric current. An extended set of such tests which had been planned were prevented by the exhaustion of the aluminum in the spirals.

Effect of hydrogen glow discharges on complex surfaces

Pure aluminum was deposited on the target by slow evaporation in a high vacuum (10^{-6} mm Hg) and the new surface was then sensitized by admission of air in minute quantities. The procedure and the results were similar to those obtained by Cashman and Huxford[4] on the sensitization of magnesium by air and oxygen. Successive admissions of air up to the pressure 10^{-3} mm Hg increased the photo-current to a value about 800 times that obtained from the original un-outgassed specimen. Further additions of air produced a decrease in the emission, the lowest value of the yield being characteristic of aluminum oxide. For the high sensitivity surface the threshold was shifted definitely into the visible region. An attempt to determine the exact threshold by the DuBridge graphical method was unsuccessful, since the data for such a surface do not follow the theoretical curve.

Figure 7 shows the effect of the hydrogen glow discharge upon the emission from an aluminum surface which had been highly sensitized by small amounts of dry air. The effect is a rapid desensitization. Although each successive discharge produced further decrease in the photoelectric

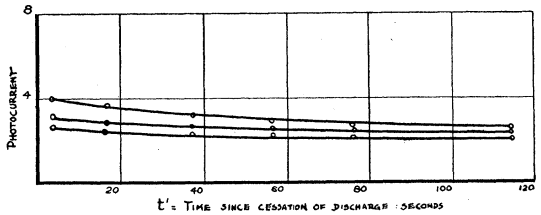

FIG. 6. Decay curves. Aluminum target as anode.

[4] Cashman and Huxford, Phys. Rev. **48**, 734 (1935).

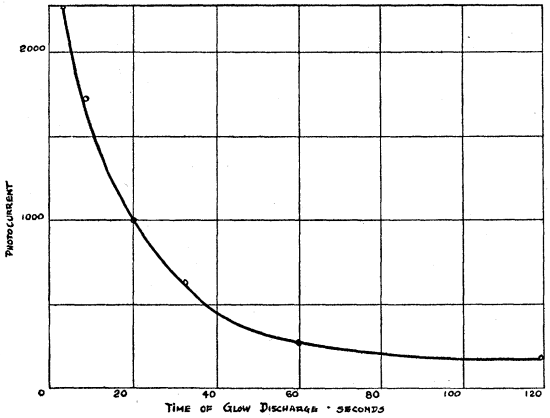

FIG. 7. De-sensitization of an air-sensitized aluminum surface.

current no decay was observed between discharge times. A complete pump-out of the hydrogen was made preceding each measurement of current. With the aluminum surface as anode in the discharge, the same desensitization effect was observed, but to a less marked extent, that is, the slope of the descending curve was less steep.

A surface which had been sensitized by air and subsequently de-sensitized by excess of air was also subjected to the glow discharge. The effect shown in Fig. 8 is a sharp increase to a maximum in the photoemission, followed by a steady decrease down to an end value, at which stage even protracted periods of discharge produced no further variation.

In the process of depositing aluminum by evaporation, the current-thickness curve of Fig. 9 was run. This curve shows a definite film effect with one intermediate maximum point. Readings were made after extended pumping. Analogous results had been observed by Stuhlmann[5] Compton and Ross[6] and others. In some cases a double maximum in the current thickness curve was obtained. The final stationary value of the emission from the freshly evaporated aluminum upon attaining bulk thickness was 135 times that obtained from the original un-outgassed specimen.

Threshold measurements

In the analysis of the current-voltage curves obtained from pure aluminum and from aluminum sensitized by air, the graphical method developed by DuBridge[7] in his theory of the energy distribution of photoelectrons, was applied in order to determine the threshold value. The expression he derived for the slope and tail of the curves of Figs. 10 and 11 is,

$$\log\,(I/x)=B+f(x-x_0),$$

where I is the photo-current, B a constant (including the temperature constant),

$$x_0=V_m e/kT$$

and $$f(x-x_0)=\log\,[e^{-(x-x_0)}-\tfrac{1}{4}e^{-2(x-x_0)}].$$

Plotting $f(x-x_0)$ *vs.* (x_0-x) yields a theoretical curve of the same form as that obtained experimentally by plotting log (I/x) *vs.* x. To bring the curves into coincidence a vertical and a horizontal shift are needed, the latter being x_0 from which V_m the maximum energy at 0°K, and also ν_0, the photoelectric threshold, are determined.

An attempt to apply the theory to the curve of Fig. 10, obtained from an aluminum surface

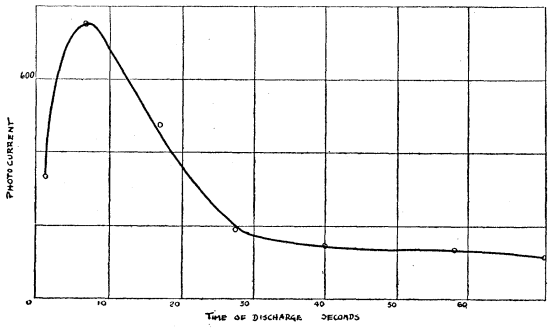

FIG. 8. Effect of the hydrogen glow discharge on a low sensitivity complex aluminum surface.

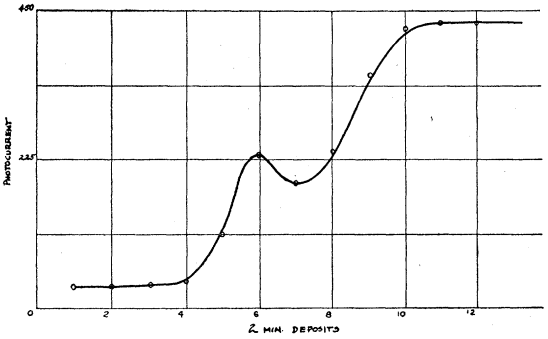

FIG. 9. Variation in photoemission with film thickness. Freshly distilled aluminum.

[5] Stuhlmann, Phys. Rev. **13**, 109 (1919).
[6] Compton and Ross, Phys. Rev. **13**, 374 (1919); Rosenthal, Zeits. f. Physik **99**, 607 (1931).
[7] DuBridge, Phys. Rev. **43**, 726 (1933).

sensitized by air, failed completely. It was not found possible to fit the experimental curve upon the theoretical. This curve exhibits the long "tail" which was found by Roehr[8] and others to be characteristic of high temperatures as well as of contaminated surfaces.

The Fig. 11 measurements were made using freshly evaporated aluminum, approaching bulk thickness, as the photoelectric emitter. The result of the DuBridge analysis is shown in Fig. 12. Although the experimental and theoretical curves do not coincide as closely as those obtained by Roehr in his analysis of molybdenum, nevertheless the agreement is good, considering the small number of readings taken and the fact that the incident light was only approximately monochromatic. The results seem to justify the conclusion that at 300°K the DuBridge theory is valid for a pure aluminum surface but not for the complex surfaces produced by air sensitization. The photoelectric threshold of aluminum as determined by the analysis was 2840A, in good agreement with recent measurements by Gaviola and Strong.[9]

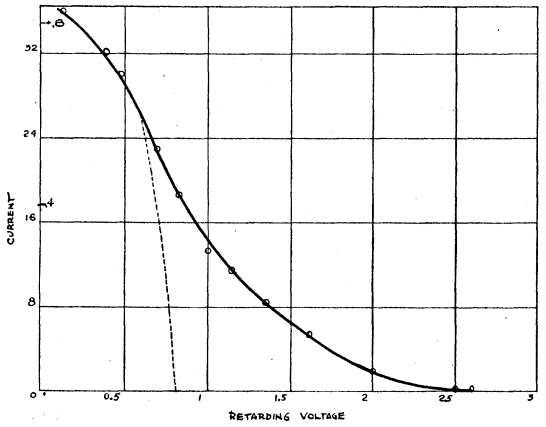

FIG. 10. Current-voltage curve. Complex aluminum surface.

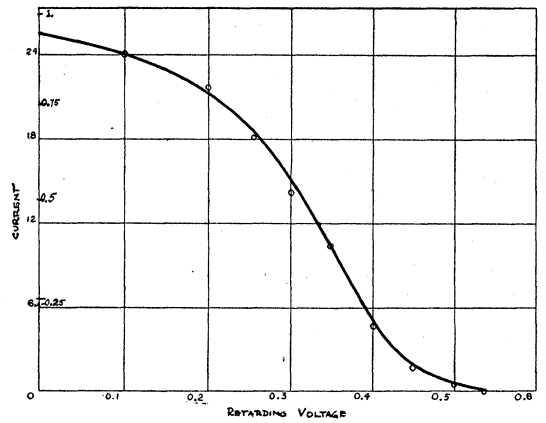

FIG. 11. Current-voltage curve for freshly evaporated aluminum.

INTERPRETATION OF RESULTS

Any attempt to picture the processes involved in the sensitization of aluminum by hydrogen glow discharges must take into account these possibilities:

1. A clean-up of the surface by dissociation of the aluminum oxide coating.
2. The sputtering effect, producing detachment of neutral aluminum atoms.
3. The formation of compounds of aluminum, oxygen and hydrogen.

All of these factors may enter into the process under a given set of conditions; or one may predominate to the practical exclusion of the others. The experiments on sensitizing unoutgassed aluminum, (Fig. 3) suggest that here the predominant action is the dissociation of surface oxide molecules, exposing more pure aluminum. This clean-up action should then proceed as the sensitization time is increased, until the photoemission reached is that of pure aluminum. This upper limit was never actually attained in the experiments described, but could be approached by longer treatment.

The temporary nature of the sensitization of an

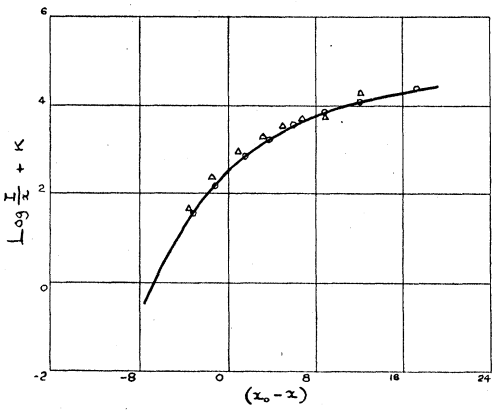

FIG. 12. DuBridge analysis for freshly evaporated aluminum.

[8] Roehr, Phys. Rev. **44**, 866 (1933).

[9] Gaviola and Strong, Phys. Rev. **49**, 441 (1936).

un-outgassed target may be attributed to the diffusion to the surface, of the oxygen contained within the body of the untreated metal. This is borne out by the fact that after the un-outgassed metal had been covered by a layer of fresh aluminum the decay ceased.

The current-pressure curves (Fig. 5), reveal the inefficiency of the higher pressures as well as the existence of an optimum pressure in producing sensitization. If the process is predominantly one of dissociation a fixed minimum amount of energy for dissociation is required. At the higher pressures, the bombarding hydrogen ions are relatively numerous but the velocity over the small mean free path is not sufficient. The optimum pressure would be that at which there would exist the largest number of hydrogen ions, each possessing energy sufficient to break up the surface molecules. In the light of this minimum energy requisite, the ineffectiveness of the discharge with the target as anode is also understandable. Dember[10] observed an increase in the photo-current from aluminum bombarded by electrons from a heated filament. This effect, however, took place only with light shining and electron stream bombarding simultaneously.

The phenomena observed in the experiments on the sensitization of pure aluminum by oxygen are in good accord with the similar observations on uranium, caesium, thorium[11] and magnesium[12] by other investigators. The results may be explained by assuming that the surface produced is one characterized by a sparse distribution of isolated aluminum atoms bound on all sides by aluminum oxide molecules; that is, the type of surface described by de Boer[13] and Kluge and Rupp[14] for alkali-metals and subsequently referred to as the "sensitive spot" type. For a pure surface with a Fermi distribution of electrons, the photo-current should be relatively low, since only the electrons in the highest states are available for ejection. In the complex surface produced by air-sensitization no Fermi distribution exists in the surface layer—individual atoms are exposed. Every quantum absorbed by these isolated atoms would free an electron either downward into the metal or outwards. This one-in-two chance is however greatly diminished by the fact that the great majority of incident quanta are absorbed not by the aluminum atoms but by the aluminum oxide whose work function is relatively high.

Either a detachment of these "sensitive spots" in the complex surface or their widening by dissociation of the surrounding aluminum oxide molecules should produce a decrease in the emission probability. The descending curve of Fig. 7 thus fits well into this tentative picture of the process. The sputtering effect, producing detachment of aluminum atoms may be the major factor in this case—the dissociation effect playing only a supporting role.

The rise and fall of sensitivity in the experiment on the effect of the glow discharge upon a surface desensitized by excess of air (Fig. 8) may be explained by assuming that the discharge first removes excess oxygen exposing individual atoms, and then detaches these by sputtering. Further discharges produce a decrease in the current down to a low limiting value, where the sensitivity remains constant, unaffected even by prolonged discharges. From the present results, the chemical nature of the photoelectrically insensitive end-product cannot be determined. A clue to its identity would probably be found in the exact measurement of the variations in threshold value.

The assumption that the complex surface formed by oxygen sensitization is of the "sensitive spot" type is in harmony with the current-voltage analyses. For the pure aluminum curve of Fig. 11 analysis yielded the agreement predicted by the DuBridge theory based on the Fermi distribution. No such agreement between the experimental and theoretical curves for air-sensitized aluminum could be found; indeed none is predicted by the DuBridge theory, since the Fermi distribution upon which the theory is based does not here exist.

In conclusion the author wishes to express his grateful appreciation to Dr. J. J. Brady who proposed this problem and whose helpful suggestions were of great value throughout the investigation.

[10] Dember, Zeits. f. Physik **33**, 529 (1925).
[11] Rentschler and Henry, J. Opt. Soc. Am. **26**, 30 (1936).
[12] Cashman and Huxford, Phys. Rev. **48**, 734 (1935).
[13] De Boer, *Electron Emission and Absorption Phenomena*, p. 210.
[14] Kluge and Rupp, Physik. Zeits. **32**, 163 (1931).