

PHOTOELECTRIC EMISSION FROM DIFFERENT METALS

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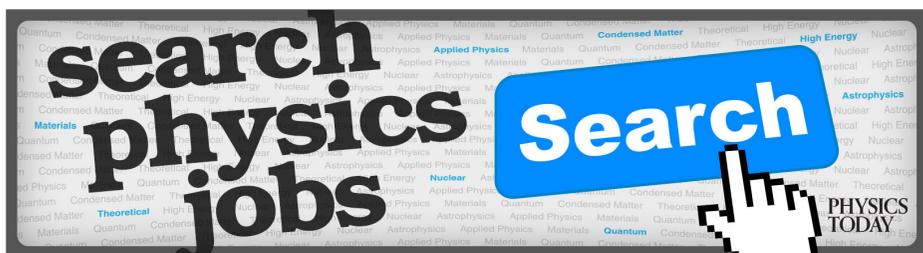
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PHOTOELECTRIC EMISSION FROM DIFFERENT METALS

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A method is described for preparing photoelectric cells of any metal which can be made in wire form. The characteristic curves for different cells of the same metal are exceedingly uniform. The method appears to give metal surfaces capable of giving the true photoelectric effect of the metal under test. The values of the photoelectric work function for tungsten and tantalum agree with the values of the thermionic work functions for these same metals. The photoelectric work functions for solid thorium, uranium, zirconium and calcium are higher than the thermionic work functions reported for monomolecular layers of these metals on tungsten, apparently supporting the commonly accepted theory that the thermionic emission of such a thin layer is higher than that for the solid metal. The photoelectric data for barium and for materials present in oxide coated cathodes used in radio tubes indicate that the activated oxide coated cathodes contain something which has a lower work function than that of pure barium alone. A simple method is described for making photo-cells sensitive to radiations of wave length 2500A or shorter without the use of quartz, which is expensive and difficult to work. Also a simple design is given for constructing cells in quartz where it is essential to use the more transparent container.

INTRODUCTION

About two years ago one of us¹ described a uranium photoelectric cell for measuring the ultraviolet output (in the biologically active region of wave lengths) of a light source. Since then a number of such cells has been constructed. The color sensitivity curves for the different cells made in this manner are remarkably uniform. The same method is suitable for making cells of practically any metal as the active surface. A number of different metals have been tested in this way and the relative response curves for the various metals tested are given below.

Everyone who has worked with photoelectric effects realizes how essential it is to have a perfectly clean surface of the metal under test

¹ Rentschler, *Trans. Am. Inst. Elec. Eng.*, 49, p. 576; 1930.

and to have this in a space free from any contaminating influences. With some metals this condition is more easily attained than with others; thus tungsten and molybdenum oxides are removed from the respective metals by heating them to a sufficiently high temperature to vaporize the oxides and at the same time degas the metals thus leaving clean surfaces. Certain other metals such as zinc, cadmium, etc., may be purified by distillation. When working with such metals as iron or aluminum and more particularly thorium, uranium, zirconium, titanium, etc., the problem is not so easy. Again it is often difficult to remove all impurities from the bulb and parts without at the same time contaminating the metal surface.

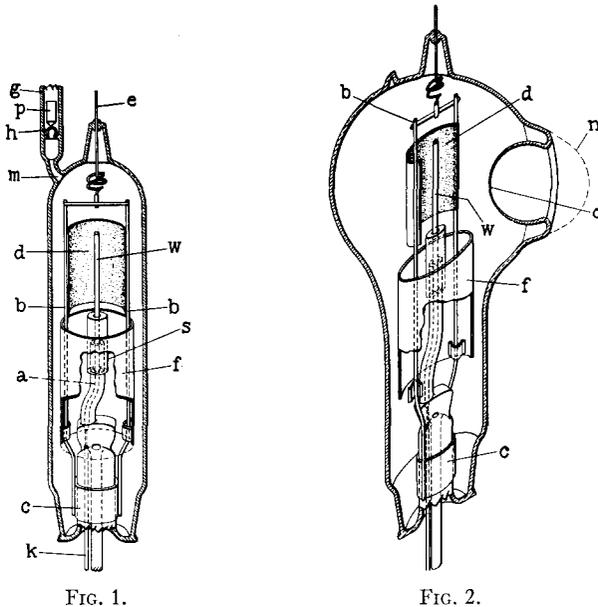


FIG. 1.

FIG. 2.

CELL CONSTRUCTION

The metal whose photoactivity is to be tested is mounted in the form of a wire *w* on a lead passing through a press as shown in Fig. 1 at *a*. A lavite insulator *s* surrounds the lower end of the wire and completely shields the lead wire. A frame *b* consisting of two heavy guide wires is mounted on a collar clamped around the stem at *c*. This frame carries a semi-circular nickel electrode *d* on which the active metal is later deposited. This is connected to a lead wire sealed into the top of the bulb as shown at *e*. A cylinder *f* of nickel or other suitable metal, slides on the frame. This shields the glass or quartz around the semi-

circular electrode d during the process of forming the photoelectrically active deposit.

The bulb is thoroughly exhausted and baked at about 400°C for about fifteen minutes. The metal parts are heated by high frequency to out-gas them as thoroughly as possible. An inert gas at a few millimeters pressure is introduced and the tube is sealed off. The metal of the wire w is then sputtered until a sufficiently thick layer has been deposited on the electrode d . During this sputtering process the sleeve f surrounds the wire w and the plate d to prevent the metal from depositing on the glass wall. In some of the tests the shield f was so constructed that during the first stage of sputtering the plate d also was shielded so that any contamination that happened to be on the wire could not reach the plate. This precaution was found unnecessary and was eliminated in later cells.

The sputtering at first cleans off all metal parts and permanently removes the impurities by the reactions that take place. Finally the discharge takes on the appearance characteristic of the pure gas, and a fairly rapid transfer of metal from the wire to the electrode d takes place. After a sufficiently heavy deposit has been formed on d , the bulb is again sealed to a high vacuum pump at g . An iron plunger p is placed in the exhaust tube before sealing to the pump. After the tube is thoroughly exhausted, the thin glass bubble h is broken by raising the iron plunger by means of an electromagnet and again allowing it to drop. After the gas is again completely pumped out, the bulb is sealed off at m and the cell is ready for test.

The cell bulb may be regular glass for visible or the longer ultraviolet radiation. For investigation further into the ultraviolet region Corex D glass is quite suitable. If the wave-length region to be investigated extends to about 2500Å, a special bulb of Corex D glass as shown in Fig. 2 serves very well. The bulb is first blown out as indicated by the dotted contour n . This thinner wall is again heated and sucked in thus producing a very thin walled window o which may transmit as much as 70 percent or more of 2500Å radiation. The cell structure is clear from Fig. 2. A great many of the photoelectric properties of most metals may thus be investigated without the use of quartz, which is expensive and difficult to work. If, however, it is necessary to use quartz, a simple design shown in Fig. 3 serves very well. A single graded quartz to Pyrex seal shown at i serves to connect the quartz container j to the glass tube t through which the leads and exhaust tube are sealed. The cell structure is introduced through the end of the quartz bulb before this end is

closed up. The collar *c* presses against the tube wall and supports the frame *b* with the assembled cell structure. The lead *e* connects the frame, etc., to the outside while the lead *k* passes through the glass tube which in turn supports the wire *w* and connects with it.

RESULTS

The relative response of a cell to different wave lengths was determined by measuring the current from a battery (50 to 100 volts or higher) passing through the cell when illuminated by the different lines from a quartz mercury arc, obtained by means of a large quartz monochromator. The energy for the individual lines was measured by a

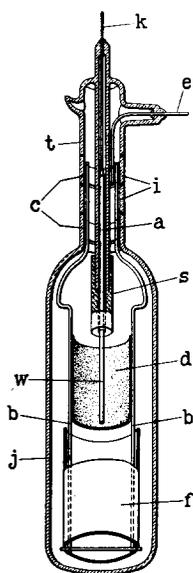


FIG. 3.

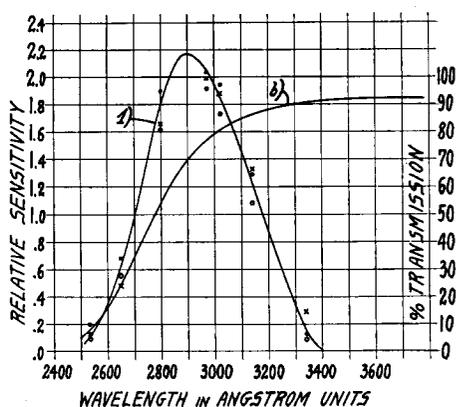


FIG. 4. (1) Average sensitivity curve for three uranium cells in Corex D glass; (b) transmission for 1 mm thickness of Corex D glass.

thermopile thus giving the response for equal energy for the different wave lengths. In Fig. 4 the average response curve for three uranium cells in Corex D glass is shown. The peak of the curve and the short wave cut-off are determined by the thickness and absorption of the glass and are not properties of the uranium. The transmission for 1 mm thickness of this glass for the different wave lengths is also shown. The curves of Fig. 5 show the relative response for cerium, magnesium and thorium in Corex D glass. The curves of Fig. 6 show similar response for uranium, zirconium and titanium again in Corex D. The curves of Fig. 7 are the relative response for the metals zinc, cadmium, silver,

aluminum, tantalum, tungsten and copper in Corex D glass with thin windows. Here again the falling-off in sensitivity for the short waves is due to the absorption by the windows. The windows of the different

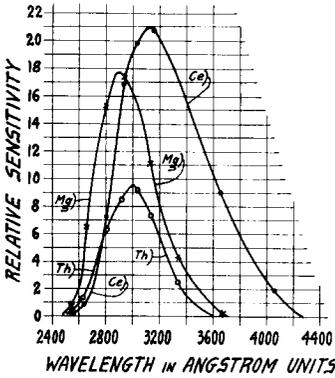


FIG. 5. Ce, average sensitivity curve for cerium in Corex D glass; Mg, average sensitivity curve for magnesium in special-corex glass; Th, average sensitivity curve for thorium in Corex D glass. Black dot, cerium; cross, magnesium; circle, thorium.

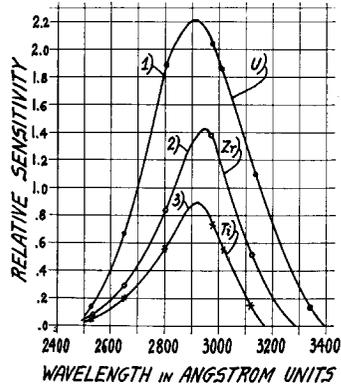


FIG. 6. U, average sensitivity curve for uranium in Corex D glass; Zr, average sensitivity curve for zirconium in Corex D glass; Ti, average sensitivity for titanium in Corex D glass.

cells are not of uniform thickness and hence some show the effect more than others. The curves of Fig. 8 show the relative response for cerium,

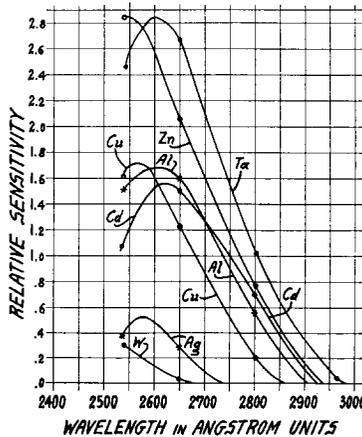


FIG. 7. Sensitivity curves for tantalum, zinc, cadmium, aluminum, copper, silver and tungsten in Corex D glass with thin windows. (The windows differ in thickness for the different bulbs.)

thorium and uranium in quartz. The relative response curves for calcium sputtered in a pure inert gas and for calcium similarly sputtered in the presence of a trace of hydrogen are shown in Fig. 9. The hydride

cell is considerably more sensitive, has a longer wave-length threshold value and shows the selective photoelectric effect while the pure calcium cell shows only the normal effect.

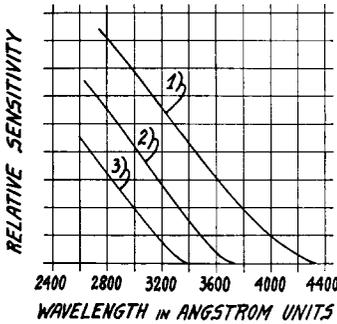


FIG. 8. (1) Sensitivity curve of cerium in quartz; (2) sensitivity curve of thorium in quartz; (3) sensitivity curve of uranium in quartz.

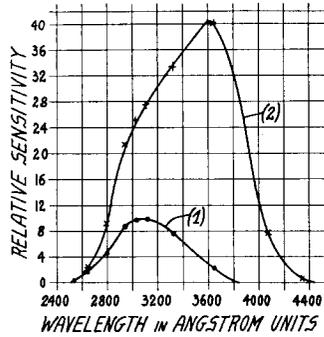


FIG. 9. (1) Sensitivity curve for calcium metal in Corex D glass; (2) sensitivity curve for calcium sputtered in the presence of a trace of hydrogen in Corex D glass.

In Fig. 10 is shown the relative response for barium metal and also a representative curve for the material evaporated from an oxide coated, indirectly heated cathode and deposited on a nickel or other

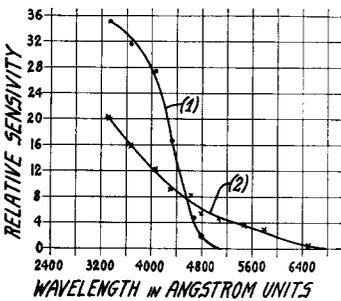


FIG. 10. (1) Sensitivity curve for barium metal in Corex D glass; (2) sensitivity curve for vaporized deposit from barium-oxide coated cathode.

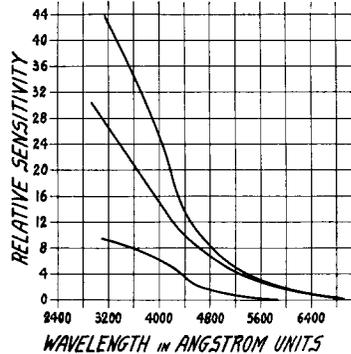


FIG. 11. Sensitivity curves from vaporized deposits from barium-oxide cathodes.

metal plate. This is the same whether barium carbonate or a mixture of barium and strontium carbonate is used as the coating. The process followed in making these deposits is practically that described by Case²

² Case, *Photoelectric Cells and their Applications*. Published by the Physical and Optical Societies, London, 1930; p. 54.

of the Case Research Laboratory. In Fig. 11 are shown several curves showing variations of the photoelectric activities obtained for such evaporated coatings, depending upon the temperature of the cathode for vaporizing the active material, etc.

At first it was thought that photoelectric cells of a number of metals could be made by vaporizing the metal by high-frequency heating of a plate to which the metal in question was attached. The results obtained in this manner were extremely variable and unreliable in some cases. This is particularly true for such metals as aluminum, etc., while such metals as uranium, titanium, thorium, etc., cannot thus be vaporized. To determine further the possible influence of the gas used during the sputtering upon the cell characteristics, cadmium and zinc cells prepared by careful distillation were compared with similar cells made by the sputtering process. The relative response curves for the two types are in no way different. Most of the compounds of silver such as the oxide, etc., are easily decomposed by heat. The sensitivity for a cell with a heat treated silver cathode is found to be the same as that for a cell with a sputtered silver cathode. One can therefore conclude as was suspected that the presence of the inert gas used during the sputtering process has no influence upon the final relative response of the cell. It appears therefore that the process used in the present tests affords a method for preparing surfaces of practically any metal capable of giving the true relative response characteristic of that metal.

If the cell on the second exhaust is again baked at even 150°C for any length of time, the sensitivity is diminished although the character of the response curve is not changed. This was tried with several uranium and several titanium cells. This change is probably brought about by the liberation of slight impurities from the glass wall, etc., reacting to a slight extent with the active surface.

WORK FUNCTION FROM PHOTOELECTRIC DATA

From the work of Warner³ with tungsten and Du Bridge⁴ on platinum, the value of the photoelectric work function is the same as the value of the thermionic work function for the same metal. From the curves of Fig. 7 the threshold wave lengths for tungsten and tantalum are approximately 2680Å and 2990Å, respectively, giving the calculated values of the photoelectric work function of 4.60 volts for tungsten and

³ Warner, Nat. Acad. Sci. Proc., 13, p. 56; 1927.

⁴ Du Bridge, Nat. Acad. Sci. Proc., 12, p. 162; 1926; Phys. Rev., 29, p. 451; 1927; Phys. Rev., 31, p. 236; 1928.

4.12 volts for tantalum. This value of the photoelectric work function for tungsten agrees very well with the value of the thermionic work function 4.54 volts given by Dushman.⁵ The value of the photoelectric work function for tantalum 4.12 volts is somewhat lower than Dushman's value of the thermionic work function 4.31 volts reported in 1923, but agrees very well with the calculated value of about 4.12 volts obtained from Dushman's⁶ later data reported in 1925 on thermionic emission from tantalum. This further indicates the reliability of the present method for producing surfaces of metals from which the true photoelectric activity of a metal may be obtained. The threshold wave length 2990A for tantalum agrees very well with 3020A obtained by Fowler.⁷

From the curves of Figs. 5, 6 and 9 the approximate threshold wave lengths for thorium, uranium, zirconium, cerium and calcium are approximately 3650A, 3400A, 3300A, 4300A and 3850A, respectively. From these the corresponding calculated values of the photoelectric work functions are 3.38, 3.63, 3.73, 2.84 and 3.20 volts, respectively. The values given by Dushman⁵ for the thermionic work functions for these metals as obtained from thermionic emission data obtained from activated tungsten filaments containing oxides of these elements are 2.94, 3.28, 3.28, 3.07 and 2.24 volts, respectively. The discrepancies in the values of the work function for thorium, uranium, zirconium and calcium are entirely too great to be attributed to experimental errors. This discrepancy seems to support the theory that the thermionic work function of an activated tungsten filament consisting of approximately a monomolecular layer of the metal on tungsten as pointed out by Langmuir⁸ is lower than the work function for the solid metal. The discrepancy for cerium is in the opposite direction. This may be due to a difficulty in obtaining the true work function from thermionic data or to a possible presence of a minute quantity of one of the other rare earth elements either in the cerium used for the photoelectric or the thermionic measurements. The material used for making the cerium photo tests shows the neodymium absorption band when in solution indicating that the cerium used in this test was not absolutely pure.

An attempt was made to detect the photoelectric emission from a coil of triple thoria doped tungsten and also from a doped ribbon

⁵ Dushman, *Phys. Rev.*, 21, p. 623; 1923.

⁶ Dushman, *Phys. Rev.*, 25, p. 328; 1925.

⁷ Fowler, *Phys. Rev.*, 38, p. 45; 1931.

⁸ Langmuir, *Phys. Rev.*, 22, p. 357; 1923.

of tungsten and measure the photoelectric threshold for such a surface. These were mounted in Corex bulbs, with magnesium getter and a second electrode sealed in the opposite end of the bulbs. The coil and ribbon were easily activated to show the thermionic emission characteristic of thorium on tungsten. In every attempt the photoelectric effect was exceedingly small, while the photoelectric emission from a thorium wire of approximately the same surface area as that of the coil or ribbon was very easily detected. Further experiments are in progress to determine whether the photoelectric and thermionic work functions for these thin deposits of one metal on another are the same.

EMISSION FROM BARIUM AND OXIDE COATED CATHODES

The curves of Fig. 10 show clearly that the vaporized deposit obtained from heating an indirectly heated oxide coated cathode such as is used in radio tubes, etc., at least contains something having a lower photoelectric work function than that for barium metal. From the curves of Fig. 11 one may easily conclude that this deposit may consist of a mixture of perhaps barium and another material perhaps a suboxide of barium as Case² suggests. Photoelectric tests on the cathode surface of the indirectly heated oxide cathode clearly show that the material with the lower work function is also found on the cathode. A careful study of the photoelectric effect from various cathodes treated in different ways may throw a great deal of light on the thermionic emission from such cathodes.

