Dec. 22, 1931. V. K. ZWORYKIN 1,837,746

PHOTO ELECTRIC TUBE

Filed March 3, 1928

Fig. 1.

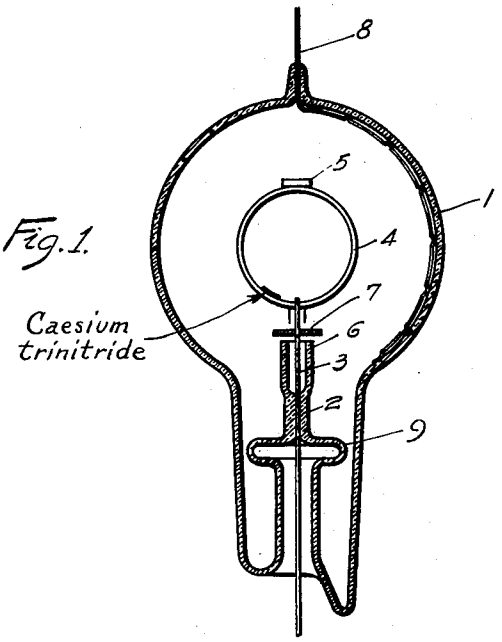
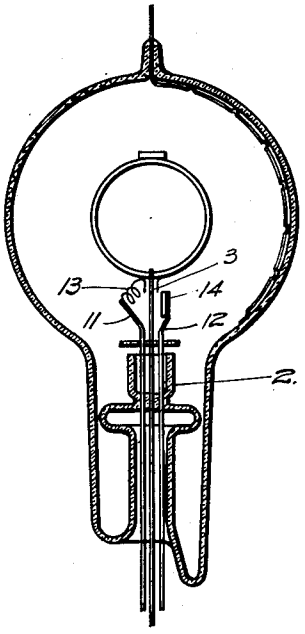


Fig. 2.



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UNITED STATES PATENT OFFICE

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PHOTO-ELECTRIC TUBE

Application filed March 3, 1928. Serial No. 258,706.

My invention relates to vacuum electrical discharge devices and particularly to devices of the foregoing character in which discharge is adapted to be varied in accordance with the intensity of light falling upon a predetermined surface within the apparatus. Devices of such character are commonly called photo-electric cells.

One object of my invention is to provide a photo-electric cell which shall be sensitive to small variations in the amount of light to which it is subjected.

Another object of my invention is to provide a photo-electric cell in which the intensity of the electrical discharge corresponding to a given incident illumination shall remain invariable over a long period of time.

Another object of my invention is to provide a photo-electric cell in which the maximum response lies in the yellow and red part of the spectrum.

Still another object of my invention is to provide a method whereby the curve connecting electron emissivity with wave length of incident light may be given a wide variety of forms and the maximum thereof caused to occur at almost any wave length desired.

A further object of my invention is to provide a photo-electric cell which shall be simple and cheap to manufacture and which will require only methods of manufacture and apparatus for producing the requisite vacuum which are well known in the vacuum-tube art.

Other objects of my invention will become apparent upon reading the following specification, taken in connection with the appended drawings, in which

Figure 1 is a sectional view of a vacuum tube embodying one modification of my invention; and

Fig. 2 is a similar view of a vacuum tube embodying another modification of my invention.

A photo-electric cell of the usual early type comprised a surface of an alkali metal, such as potassium, in electrical contact with one of the terminals and adapted to emit electrons in accordance with the amount of light to which it was subjected. Such surfaces usually constituted parts of the interior wall of a tube exhausted to a high vacuum.

In accordance with another development, it was found that the intensity of the electrical discharge current produced by a given illumination was increased if the alkali metal were subjected to a treatment with hydrogen, the formation of a hydride of the alkali metal probably resulting. However, cells of this character suffered from the disadvantage that the sensitivity decreased with the course of time so that, while the cells were much more efficient than those of the vacuum type, when first put into use, in the course of several hundred hours, their sensitivity had fallen so that it was not much greater than that of a cell formed with a simple alkali metal surface. Such a variable electrical characteristic as the foregoing constituted a bad effect in such cells when used for certain kinds of service.

In accordance with my invention, I have discovered that by forming the photo-electric surface of a composite layer comprising a base layer consisting of certain metals later specified, upon which is deposited an extremely thin film, which may even be invisible, of a metal which emits electrons strongly in response to radiation within the visible range of wave lengths. A photo-electric cell may be obtained having a higher sensitivity than any of the prior-art cells and which maintains this sensitivity apparently indefinitely, so far as can be seen. This we believe is due to the fact that the deposited film of alkali metal is not more than one or a few molecules deep. I have further observed that the film will withstand a temperature far in excess of the normal melting point of the metal composing it, and that the wave length for maximum sensitivity has been shifted from its normal position corresponding to the work function of the superposed metal, when used as in the prior art, toward the low frequency end of the spectrum.

Still further, I have discovered that, by superposing, not one but a number of different substances in the thin, probably monomolecular, layer, it is possible to obtain a resultant electron emission which varies with

wave length of incident radiation in almost any desired way. Thus, if rubidium alone, let us say, is the superposed substance, the maximum electron emission is produced when radiation of about 4800 Angstrom units wave length is incident. If potassium alone is used, there is a fairly sharp maximum of electron emissivity when the radiation is of about 4200 Angstroms. But if both potassium and rubidium are employed, in proper proportions, a curve with a broad flat maximum region results. Thus, by combining a number of different superposed materials in proper proportion, almost any desired relation between electron emissivity and wave length of radiation is attainable. It will be obvious that this is a very important result. As further features of my invention, I have devised apparatus by which the layers of metal above described may be formed very quickly and cheaply without the necessity of employing either methods or apparatus other than those now usual in the vacuum-tube art.

With the foregoing principles and objects in mind, my invention may be readily understood by reference to the accompanying drawings, in which the Fig. 1 modification comprises a vacuum-type container which is provided with a stem 2 through which an inleading wire 3 is sealed. The inleading wire 3 supports a metallic electrode 4, preferably of annular form, to which a small piece of magnesium 5 is attached.

In order to properly insulate the inleading wire 3 in a manner which will be described in more detail below, a sleeve 6 projects a short distance above the stem 2, and a disk 7 of glass may be affixed to the wire 3 a short distance above the end of the sleeve 6. At the opposite end of the container, an inleading wire 8 is sealed through the glass wall and bent to lie closely against it for a considerable distance. A flange 9 is provided on the stem 2 and arranged to nearly fill the cross section of the neck of the cell below the point where the wire 3 is sealed therein.

The tube constructed in the foregoing manner is first exhausted by methods well known in the vacuum-tube art. In accordance with such methods, the tube is heated to as high a temperature as the glass wall thereof will stand without collapsing. It may then be sealed off from the vacuum pump. Such having been done, a high-frequency magnetic field is produced in the vicinity of the electrode 4, and the latter is heated to such a temperature that the magnesium 5 thereon is vaporized. It immediately deposits on the walls of the tube, making contact with the wire 8 and forming the base for the photo-sensitive film. At the same time, it acts as a getter for any gases or vapors remaining or liberated during the sealing-off process. The flange 9 prevents magnesium from depositing in the neck of the cell below it and thus confines that material to the chamber walls in the vicinity of the wire of the lead 8, the location most desired for it. The sleeve 6 and the flange 7 prevent the vapor of magnesium from depositing on the inner end of the cell 2 and thereby insure the insulation of the lead 3 from the magnesium coating.

It may be noted that, while I have described magnesium as the metal to be vaporized, other metals such as those of the alkali earth group, and even aluminum alloys and the well known alloy "misch metal", may be utilized for this purpose. The metal to be used depends upon convenience of manufacture and the particular characteristics of the photo-electric cell which are desired.

In order to provide the other element of the pair of metals which are combined in the photo-electric surface which I have invented, several methods and materials are available. In accordance with one method, a small amount of the vapor of a metal or metals may be introduced, after a high vacuum has been produced in the cell, by heating a small tube containing the desired metal. As previously indicated, the metals chosen should be such as have a maximum on their emissivity versus wave length curve in the region of the wave length of the radiation to which response is desired. Usually response is desired to radiation in the visible spectrum; hence, potassium, rubidium and caesium which have maxima of emissivity in the visible region are usually preferable for use.

A way which I prefer, however, consists in painting a weak solution of an alkali-metal trinitride such as caesium trinitride on the portion of the electrode 4 considerably removed from the magnesium 5.

Still another method of setting free the required alkali metal is to place a small amount of some salt thereof which will not yield a deposit when heated in vacuum to about 500 degrees C., on an electrode within the tube and producing a discharge which shall bombard the salt with ions and consequently decompose it.

After the vaporization of the magnesium, it will, in general, be necessary to heat a small portion of the cell wall to clear a window so that light may enter and strike upon the photo-sensitive surface.

However, when it is desired to decompose a salt in order to furnish the alkali metal, it will usually be found preferable to employ the cell illustrated in Fig. 2. This cell is similar to that shown in Fig. 1 except that it has a pair of additional inleading wires 11 and 12 sealed through the stem 2. Between one of these wires 11 and a suitable point of the inleading wire 3, is connected a filament 13 which is suitable for heating to provide an incandescent cathode. The other inleading wire 12 is provided with a small

auxiliary electrode plate 14, upon which a small amount of the required alkali-metal salt has been deposited. When it is desired to decompose the latter, the filament 13 is heated to incandescence, and the plate 14 is supplied with a positive potential. In consequence, the salt is bombarded with electrons and decomposes to furnish the necessary alkali metal. The decomposition of the salt in this manner may be carried out subsequent to the deposition of the magnesium, but a small portion of the cell wall should afterward be heated in order to clear a window to permit entrance of light.

As examples of alkali metal salts which are suitable for treatment in the foregoing manner, carbonates, cyanides, chromates, borates, phosphates and tungstates have been found to give satisfactory results. While I have specifically mentioned cæsium trinitride, it will be understood that trinitrides of other alkali metals may be used in a similar manner.

While, in the foregoing, I have described the manufacture of a vacuum-type photo-electric cell with a composite photo-electric surface, certain features of this invention are likewise applicable to cells in which a gaseous atmosphere is employed. In such cases, the desired inert gas, which may, for example, be argon, helium or neon, may be introduced before the cell is sealed off from the pump. Vaporization of the magnesium in the manner previously described causes it to act as a purifying agent to remove gaseous impurities evolved when the glass of the tube is heated in sealing it off from the pump. The noble gases appear not to be carried down by the condensation of the magnesium in anything like an equal degree to the gaseous impurities aforesaid which it is desired to remove.

It will be evident that, by means of the apparatus and processes above described, I have provided a way of producing a photo-electric cell of superior sensitivity, range and constancy in action to those of the prior art.

While I have described the foregoing particular embodiments of my invention, it will be evident to those skilled in the art that many modifications thereof can be arranged to meet special problems without departing from the broad principles which I have described. Accordingly, I desire that the claims shall be given their broadest reasonable interpretation to which their terms are susceptible in view of the prior art.

I claim as my invention:

1. A photo-sensitive device comprising a vacuum-type container having a surface therein covered with a metal of the alkaline earth group and a metal of the alkali metal group superposed on said first metal to form a cathode, and a cooperating electrode therefor.

2. A photo-sensitive device comprising a vacuum-type container having a surface therein covered with magnesium and metallic cæsium superposed on said magnesium to form a cathode, and a cooperating electrode therefor.

3. In combination a vacuum-type container, an electrode adapted to be heated by a high-frequency magnetic field, magnesium metal on one portion of said first electrode, cæsium trinitride on another portion of said first electrode and an inleading wire in contact with the surface within said container.

4. A photo-sensitive device comprising a vacuum-type container, an annular electrode therein, a second electrode in operative relationship with said first electrode, magnesium metal on a portion of said first electrode and cæsium trinitride on another portion of said first electrode.

5. The method of forming a photo-sensitive cathode comprising the steps of depositing a metal of the alkaline earth group within an envelope and vaporizing a metal of the alkali group thereon.

6. A photo-sensitive device comprising a plurality of cooperating electrodes, a plurality of thin layers of photo-electric material on one of said electrodes, the substances forming said layers having a maximum on their emissivity versus wave length curve in the region of the visible spectrum.

7. A photo-sensitive device comprising a plurality of cooperating electrodes, a plurality of thin layers of various alkali metals on said electrode, said metals having a maximum on their emissivity versus wave length curve in the region of the visible spectrum.

8. A photo-sensitive device comprising a plurality of cooperating electrodes, a thin film comprising two or more substances on one of said electrodes, said substances individually having maximum electron emissivity at different places on the visible spectrum, the electron emissivity curve of said film being substantially flat between the maximum electron emissivity of said substances individually.

In testimony whereof, I have hereunto subscribed my name this 28th day of February, 1928.

VLADIMIR K. ZWORYKIN.