

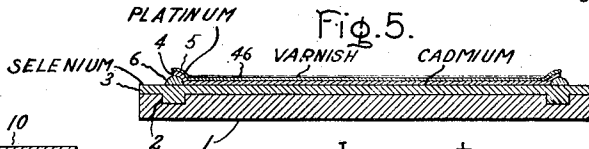
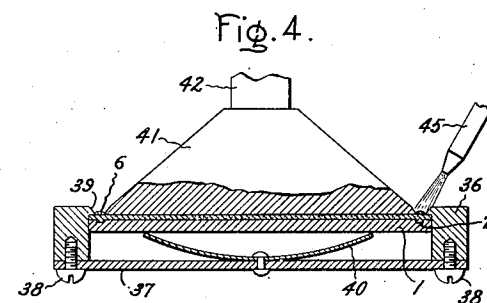
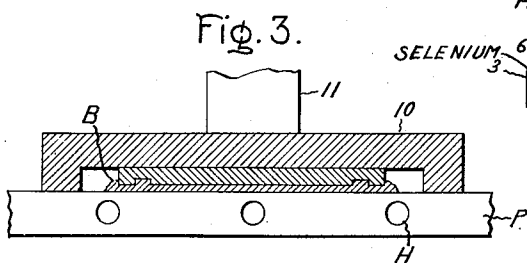
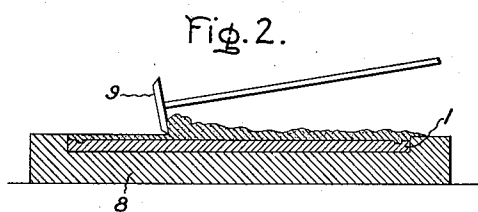
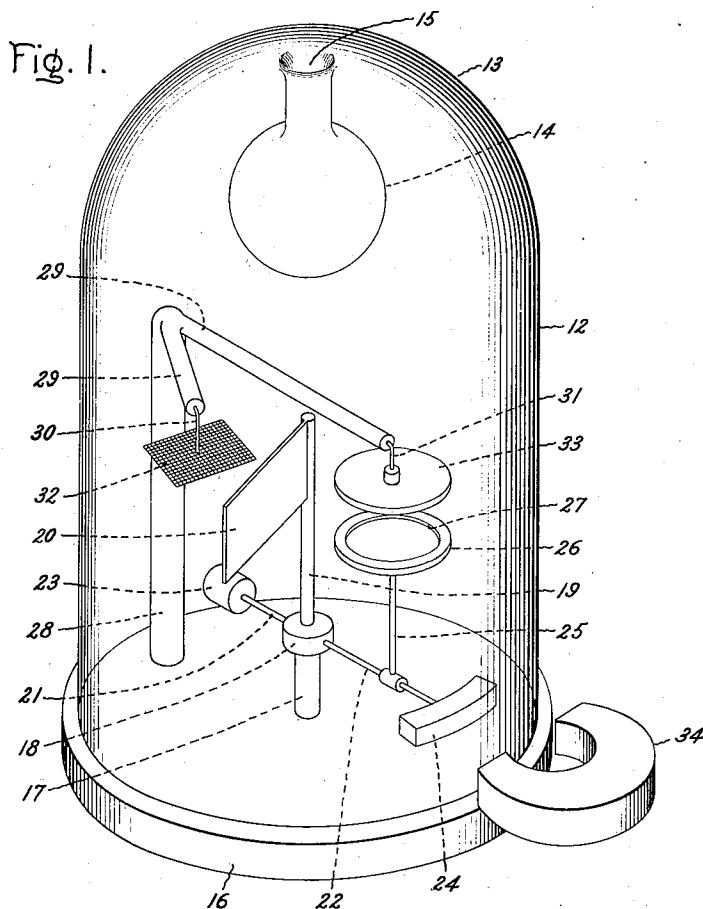
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METHOD OF MAKING A PHOTOELECTRIC CELL

Filed May 29, 1937



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METHOD OF MAKING A PHOTOELECTRIC CELL

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Application May 29, 1937, Serial No. 145,539

4 Claims. (Cl. 136—89)

The present invention relates to light-sensitive devices, more particularly to photoelectric cells, which generate a measurable electromotive force when subjected to light of practical intensities.

5 In my application Serial No. 716,677, filed March 21, 1934, I have disclosed and claimed a photo-voltaic cell which consists of a metal plate or base member coated first with selenium and then with cadmium and a relatively non-oxidizable metal such as platinum in order. The cadmium and platinum layers are preferably laid down by sputtering and are so thin as to be semitransparent to light. When light shines on the double metal layer, an electromotive force is generated between this layer and the selenium, and the current produced may be conducted away from the cell by conductors secured in any suitable manner to this semitransparent metal layer and to the base member. This current is of sufficient intensity to be measured by a microammeter which may be calibrated in foot candles to indicate the intensity of the light impinging on the metal. The present invention concerns devices of this character, and the objects are to increase the sensitiveness of photo-voltaic cells and to improve their manufacture. Another object is to provide a practical method of making a rigid contact between one of the current-carrying conductors and the thin metal layer. In accordance with these objects, the sensitiveness of the cell is increased by controlling the vapor content of the gaseous chamber in which the sputtering takes place. In order to provide the rigid contact between the conductor and the thin metal layer, a metal ring of substantial thickness is integrally joined, for example, by spraying, to the selenium surface and the sputtered film overlays the ring and the selenium surface. Then the conductor is pressed in any suitable manner against this ring. The objects and the manner in which they are attained will be more clearly understood when reference is made to the following specification and the accompanying drawing in which Fig. 1 is an elevational view of a sputtering chamber for depositing metal layers on the selenium; Fig. 2 is a sectional view of a cell in the process of making and the fixture for holding the same; Fig. 3 shows another step in the process; Fig. 4 shows an improved method of applying a contact ring to the cell; and Fig. 5 is a sectional view of the completed cell, ready for mounting.

Referring to Fig. 5, numeral 1 designates a flat metal plate of any configuration, for example, circular, and made preferably of iron or nickel. One side of the plate, the upper as shown, is provided with an annular groove 2 and on top of the plate, filling this groove, is a layer of selenium 3. As is pointed out in the said application referred to hereinbefore, there are two metal layers de-

posited on the selenium. The first, which is designated by reference character 4, is preferably of cadmium, and the uppermost metal layer 5 is a relatively non-oxidizable metal preferably platinum. A contact ring 6 of any suitable metal such as cadmium is applied in any convenient manner either to the selenium layer 3 before the sputtered layers have been deposited, or to the platinum 5 after both metal layers have been deposited. In case the ring is applied to the selenium layer, the sputtered layers are deposited not only over the selenium layer but also over the cadmium ring. The contact ring and the manner of forming the same constitute one of the features of the present invention and will be described presently. The groove 2 is preferably positioned directly under the ring 6 and is slightly wider than the ring as is explained in my copending application Serial No. 145,538, entitled "Photoelectric cells." The purpose of this groove as pointed out in the said application is to provide an excess of selenium and thereby increase the resistance of the path of the current which flows from the sputtered layer back to those portions of the selenium from which it started under the influence of the light. The selenium contained in the groove also serves to prevent a striking-through of the selenium layer when the contact ring is deposited in the manner described hereinafter.

In the manufacture of these cells, the first step is to provide the metal plate 1 with the annular groove or channel referred to hereinbefore. The side of the plate which is grooved is then roughened by sandblast in order to provide a good gripping surface for the selenium which is to be deposited. The plate is then heated and wetted with selenium, the latter being thoroughly rubbed into the surface. The selenium may be scraped off the plate or disk, leaving the channel full and only a thin layer of selenium on the surface. The plate is then chilled. This thin wetting layer of selenium is then recrystallized by heating the plate. The plate with the grooved side up is then placed in a heated heavy metal fixture 8, shown in Fig. 2, which has a countersunk or depressed portion of a size snugly to receive the plate. This countersunk portion is of a depth greater than the thickness of the plate 1 by an amount representing the thickness of the selenium layer which is to be deposited on the plate. Selenium, in paste form, is spread on the disk 1 and the excess is scraped off by a tool 9 which bridges the countersunk portion of the fixture 8 and leaves a layer of selenium of the proper thickness depending upon the depth of the recess in the fixture. After a smooth surface has been obtained on the selenium by drawing the scraper in several directions across the upper surface of the fixture 8, the selenium coated plate 1 is then removed from

the fixture and the element is chilled. The next step in the process is to obtain a smooth, glassy appearing, compact layer of selenium of uniform thickness on the plate, and this is conveniently accomplished by a hot press treatment.

A suitable fixture for this treatment is shown in Fig. 3 and consists of a metal plate P containing heating elements (not shown) let into holes H, and a die 10 containing a recess of a depth corresponding to the finished thickness of the selenium coated plate. Before placing the selenium plate on the press, the apparatus is heated to a temperature of about 140° C., and the selenium coated plate 1 is then placed, selenium side down, against the plate P. The die 10 is then placed on top of the selenium coated plate, and pressure applied in any suitable manner, for example by means of a clamp. At the temperature mentioned, the selenium softens and flows, the excess being exuded around the edges of the plate as indicated at B. Although as stated hereinbefore, the selenium at first softens and flows, in a few minutes it begins to harden, and after 10 to 30 minutes the pressure may be relieved and the plate removed from fixture. The selenium layer is now hard, smooth, and of uniform thickness, and the excess exuded selenium may be removed from the edges. The selenium coated plate 1 which has thus been treated is then baked at a temperature near the melting point of selenium.

The plate 1 is then placed in a fixture similar to that shown in Fig. 4 for the deposition of the contact ring. This fixture comprises a heavy metal ring 36 which has a metal back 37 secured thereto by screws 38. The front or upper portion of the ring 36 is provided with an inwardly extending lip 39 against which the selenium coated disk 1 can be pressed by a spring 40 riveted to the back plate 37. A conically shaped metal shield 41 provided with a handle 42 is provided for protecting the central portion of the metal or selenium coated disk from the heat effects of a Schoop gun 45. The shield 41 has an outer diameter less than the lip 39 so as to leave an annular space. A heavy metal layer of cadmium is laid down in this space by the gun 45, in the form of a ring. As stated hereinbefore, this ring is positioned directly above the selenium-filled groove 2 formed in the plate 1 and is slightly less in width than the width of the channel. This contact ring is for the purpose of readily permitting a connection between a conductor (not shown) and the metal layer which is to be sputtered over the selenium surface, as will be described presently, and lapping over the contact ring. After the contact ring has been built up to its proper thickness, the cell is removed from the fixture by unscrewing the plate 37, and it is then ready to be sputtered with the metal layers. While I prefer to apply the contact ring directly to the selenium surface, I may, under certain circumstances, deposit the ring on the sputtered metal layer.

The sputtering apparatus is shown in Fig. 1 and consists essentially of a large bell jar 12 which terminates at the top in a hemispherical portion 13. A reentrant bulb 14 having an opening 15 is secured to the hemispherical portion 13. The lower end of the bell jar is temporarily closed in any suitable manner, for example, by being inserted within a close-fitting recessed plate member 16 which is well known in the art. Secured to the plate member 16 and centrally positioned, there is a metal upright or standard 17 which

carries a rotatable drum 18 and a stationary rod member 19. A flat metal plate 20 is secured to the upper end of the rod 19. The purpose of this plate will be explained presently. The drum member 18 carries a pair of oppositely extending shafts 21, 22, one of which (element 21) terminates in a counterweight 23. The other shaft 22 carries a magnetic member 24 of arcuate form, and at a position intermediate the ends of the rod, also carries an upright shaft 25. A carrier 10 fixture 26 provided with a central recess 27 is secured to the upper end of the rod 25. This recess has a diametral size and thickness sufficient to accommodate the selenium coated disk 1. In addition to the upright 17, the base 16 is also provided with a glass upright 28 which terminates at the top in a pair of forked arms 29. The arms 29 contain a pair of conductors 30, 31, one of which is secured to a mesh member 32 composed of platinum, and the other carries a disk 33 of cadmium which lies directly above the carrier 26.

The arrangement is such that by means of a magnet 34, which is adapted to be moved around the bell jar, the armature 24 is caused to move within the chamber and this movement serves to rotate the carrier 26 from a position directly under the disk 33, as shown in Fig. 1, to a position directly under the mesh member 32. When it is desired to deposit a metal layer on the selenium-coated disk 1, the bell jar is temporarily removed and the disk 1 is placed in the recess of the carrier 26. A mask (not shown) is placed about the periphery of the cell, the purpose of which is to shield the edges of the cell from the sputtered deposit. This mask allows the sputtered deposit to cover the central portion of the selenium surface and partly to overlap the sprayed-on cadmium ring. After the bell jar is placed in position and properly sealed, the jar is evacuated in any suitable manner. Argon or any other inert gas is introduced into the bell jar at about 240 microns. By means of the leads 30 and 31 which pass to the exterior, either of the electrodes 32 and 33 may be made cathode of a circuit (not shown), and by means of a lead (not shown) the plate 16 may be made the anode. The selenium plate is then sputtered under the cadmium cathode in one-second flashes separated by 20-second intervals until a sputtered layer which permits about 30% of the incident light to pass through is obtained. The selenium plate is then adjusted under the platinum cathode by moving the magnet 34 around the bell jar, and sputtered with platinum for about three-fifths the length of the time of sputtering the cadmium. It is apparent that the metal plate 20 serves as a partition to prevent sputtered deposits from one cathode being deposited on the other cathode.

During the sputtering operation, liquid air may be poured into the flask 14, causing condensible vapors such as water to condense on the surface of the flask, thereby removing them from the gaseous atmosphere. While satisfactory results have been obtained by causing the condensation to take place simultaneously with the start of the sputtering operation and even before, I have found, and in accordance with the present invention, that outstandingly good cells may be obtained if the introduction of liquid air and the condensation are delayed until an appreciable time after the sputtering of the cadmium layer has started. I prefer to delay the introduction of the liquid air until from one to five flashes of

the cadmium sputtering have been carried out. After the liquid air has been introduced in this manner and the cadmium sputtering has been continued until the proper thickness of layer has been obtained, the platinum layer is sputtered in the usual manner, as explained above. It has been found that when the refrigeration of the gaseous atmosphere has been delayed for a short time and is not produced simultaneously with the beginning of the cadmium sputtering, the resulting cell is more satisfactory than those cells in which the refrigeration is initiated simultaneously with the sputtering. The improved cell will deliver more power in an external circuit of higher resistance, and the temperature coefficient of output and the fatigue under action of illumination are both considerably smaller. As a matter of fact, a cell so produced will have approximately double the open circuit electromotive force of one in which the refrigeration has not been delayed.

After the sputtering operations described above, the plate 1 is removed from the carrier 26 and the selenium surface up to the contact ring is lacquered or varnished as indicated at 46, Fig. 5. The cell is now complete and laid aside to mature or age.

While I do not wish to be limited to any theory as to why such a marked improvement is brought about by simply delaying the application of the refrigerant, I believe that the action might be as follows. It is of course well known that the so-called "blocking layer" of a cell of this character and its ability to generate electromotive force when exposed to light depend on the character of the material at the junction between the selenium surface and the semitransparent layers of cadmium and platinum. In my improved cell, this intervening layer of material is probably composed of selenium dioxide, cadmium oxide, or a mixture of these two oxides with cadmium. There are several methods by which this end can be obtained: (1) By exposing the selenium surface in a glow discharge of oxygen, in which case the selenium surface may or may not be made cathode of the discharge, (2) by evaporating selenium dioxide and cadmium oxide onto the selenium surface (in this case some decomposition of cadmium oxide may occur so that the resulting deposit includes a mixture of cadmium and cadmium oxide), (3) by the preferred method of dampening the cadmium electrode before exhausting the sputtering apparatus and then sputtering for a short time before refrigeration (by liquid air or other suitable refrigerant placed in the reentrant flask 14) in the sputtering space. This preliminary sputtering using the cadmium electrode as cathode liberates the residual water from the cadmium cathode, and the water vapor becomes ionized in the discharge. The resulting oxygen ions oxidize the selenium and the cadmium, resulting in a layer of selenium dioxide and sputtered cadmium oxide and cadmium on the selenium surface. The sputtering space is then refrigerated to remove vapors from the sputtering discharge and the cadmium sputtering proceeds, after which the platinum layer is produced. Regardless of whether this theory is correct or not, the fact remains that when foreign substances such as water vapor are permitted

to remain in the argon atmosphere during the initial stages of the sputtering process, some action takes place which causes the selenium surface to be more light-sensitive or causes a more effective barrier layer between the selenium surface and the cadmium to be formed so that a cell in which the refrigeration has been delayed for a predetermined length of time is much more sensitive than a cell in which the refrigeration has been provided simultaneously with the initial sputtering stages.

As was pointed out in my application Serial No. 716,677, a cell of this kind may be inserted in a casing of hard rubber and when connections have been made to the contact ring and the metal base 1, the cell will generate an electromotive force upon exposure to light which is sufficient to operate a microammeter. This meter may be calibrated in foot candles to indicate or measure the intensity of light falling on the metal layers.

What I claim as new and desire to secure by Letters Patent of the United States, is:

1. In the method of fabricating a light-sensitive device, the steps of coating a metal plate with selenium, then sputtering a semitransparent layer of cadmium onto said selenium in a chamber containing argon and water vapor, then condensing out the water vapor by cooling said chamber, then sputtering an additional semitransparent layer of cadmium onto the first layer of cadmium, and finally sputtering a semitransparent layer of platinum onto the cadmium.

2. In the method of fabricating a selenium cell the steps of coating a metal plate with a layer of selenium, then sputtering a semitransparent layer of cadmium onto said selenium from a dampened cadmium surface and then sputtering a semitransparent layer of platinum onto the cadmium layer.

3. In the method of fabricating a light-sensitive device, the steps of coating a base member with selenium, positioning the base member in a closed chamber in proximity to a source of cadmium, evacuating the chamber, introducing a quantity of an inert gas into the chamber, producing an electrical discharge within the chamber to cause sputtering of a thin layer of cadmium on the selenium, cooling a portion of the chamber to a temperature comparable with that of liquid air, thereby to remove any condensable constituents contained in the said inert gas, and thereafter sputtering a further layer of cadmium on the first layer thereof.

4. In the method of fabricating a light-sensitive device, the steps of coating a base member with selenium, positioning the base member in a closed chamber in proximity to a source of cadmium, evacuating the chamber, introducing a quantity of argon into the chamber, producing an electrical discharge within the chamber to cause sputtering of a thin layer of cadmium on the selenium, cooling a portion of the chamber to a temperature comparable with that of liquid air, thereby to condense any condensable constituents contained in the chamber, thereafter sputtering a further layer of cadmium on the first layer thereof, and finally depositing a thin layer of a relatively non-oxidizable metal on the cadmium.

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