Jan. 14, 1947. E. LIDOW 2,414,233

PHOTOELECTRIC CELL

Filed Aug. 3, 1942

Fig. 1.

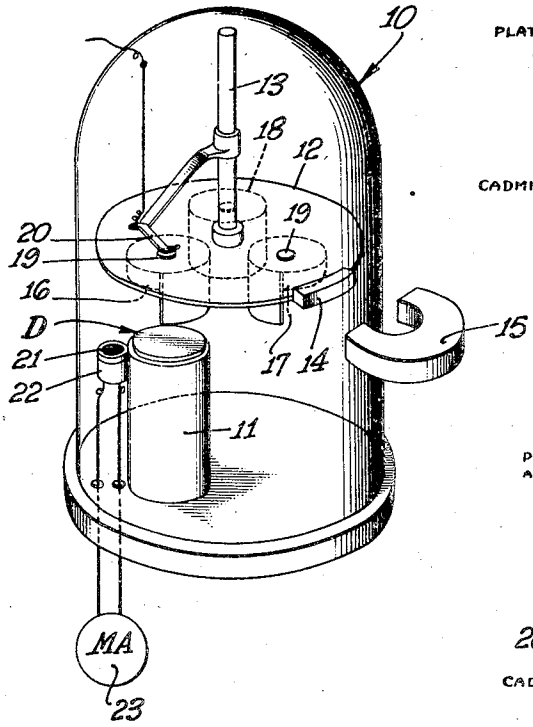


Fig. 2.

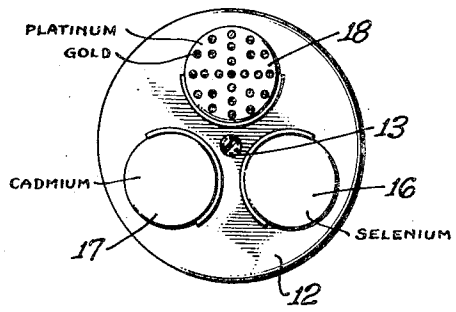
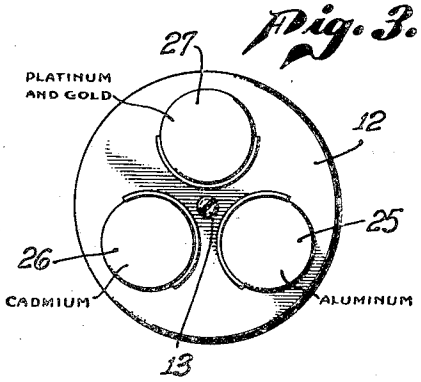


Fig. 3.



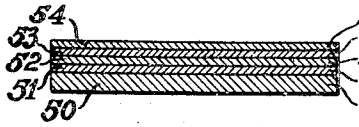
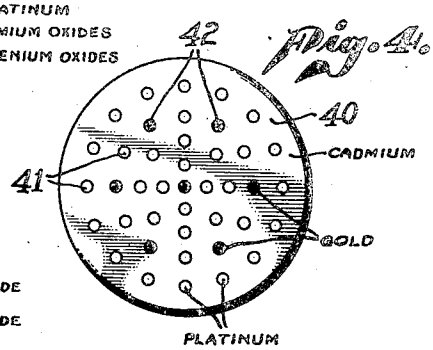


Fig. 5.

Fig. 4.



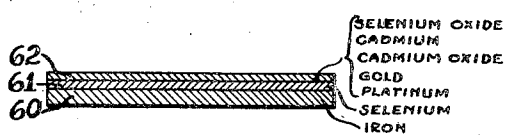


Fig. 6.

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PHOTOELECTRIC CELL

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Application August 3, 1942, Serial No. 453,392

3 Claims. (Cl. 136—89)

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This invention relates to photoelectric cells of the barrier- or blocking-layer type.

In the manufacture of cells comprising a base plate of iron, a layer of selenium, a layer of cadmium, and an outer electrode of platinum or other noble metals, difficulty is experienced in producing cells of uniform characteristics, despite the greatest care. The uniformity of cells of this type has been found to vary from cell to cell, and the previous manufacturing processes for cells of this type result in a large number of discards because the cells produced do not have the required characteristics.

It is therefore an object of the present invention to increase the uniformity of photoelectric cells of this type.

One of the reasons for this non-uniformity of the product is the existence of internal shorts, either extending from the outer layer to the selenium layer or else merely penetrating through the blocking layer between the selenium and the cadmium applied thereover. Some of these shorts can be removed by treatment of the cell after it has been produced by subjecting it to an electric current of high enough intensity to burn out the shorts. However, this treatment is not always positive in its results.

It is therefore a further object of the present invention to provide a method for the production of photoelectric elements of the type described which does not have a tendency to produce shorts during the process of manufacture.

One of the most important factors in the production of these cells is the formation of the so-called barrier layer between the selenium and the cadmium. Various methods of causing the formation of this barrier layer have been proposed and practiced and from what is known of the action of the cells it would appear that a very large proportion of the non-uniformity of the response of the cells is a result of a non-uniform barrier layer.

It is therefore a further object of the present invention to provide a method for production of a barrier layer of greater uniformity than has been produced in the past.

It is a further object of the present invention to provide a method of producing photoelectric cells of the barrier layer type which will assure uniformity of the barrier layer both on the same cell and from cell to cell.

Another aspect of the present invention lies in the improvement of the translucent electrode. Platinum, which is of neutral gray by transmitted light, is often used for this electrode. Cells

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utilizing gold electrodes have a comparatively high output. This has been attributed to the high conductivity of gold and its position in the contact potential table. However, a gold electrode acts as a green filter, and therefore alters the spectral characteristics of the cell in which it is used. Another disadvantage of gold, in this connection, is the high temperature coefficient of cells with gold electrodes, as compared with those employing platinum electrodes.

It is therefore a further object of the present invention to provide a new type of outer electrode which has satisfactory spectral characteristics, and in which the resistance of the outer electrode is comparatively low.

It is a further object of the present invention to provide a cell of the nature described with a small temperature coefficient.

This invention possesses many other advantages and has other objects which may be made more easily apparent from a consideration of the embodiments thereof, shown in the drawing accompanying and forming part of the present specification. These forms will now be described in detail, illustrating the general principles of the invention; but it is to be understood that this detailed description is not to be taken in a limiting sense, since the scope of the invention is best defined by the appended claims.

Referring now to the drawing:

Figure 1 is a view of one form of apparatus for practicing the present invention;

Figure 2 is a bottom view of a cathode utilized in the practice of the present invention;

Figure 3 is a similar view of another form of cathode;

Figure 4 is a similar view of still another form of cathode;

Figure 5 is a section of one form of cell produced by the present invention; and

Figure 6 is a similar section of a modified form of cell.

The preliminary treatment leading to the manufacture of the present cell is similar to that practiced in the past. A plate of metal, preferably of the iron group, is sandblasted or chemically roughened, and selenium is applied thereto. The selenium is most conveniently applied by heating the plate to a temperature greater than 220° C. Selenium in either powdered or molten form is applied to the heated plate. The plate is thereafter quickly cooled and then subjected to mechanical pressure at a temperature of between 80 and 140° C. This pressing operation is carried out in a press which presents a smooth pressure

surface to the selenium, resulting in the development of a smooth surface on the selenium, and is carried on for a sufficient length of time to convert the amorphous selenium into a semi-metallic form and cause it to adhere strongly to the base plate. In this condition the unit is easily removed from the press.

The next step as taught by the prior art is the annealing of the cell by heat treatment at a temperature between 170 and 220° C., in a suitable oven. Such annealing results in the conversion of the selenium into a crystalline form. It also results in the development of part of the blocking layer, because of oxidation of the selenium surface. However, the variable humidity of the air within the oven, together with lack of control over its composition, circulation, and other factors results in an extremely variable barrier layer at this point. For this reason, the barrier layer is often increased in uniformity by treatment of the selenium in a glow discharge chamber with oxygen. As a variation or supplement to this procedure, a cadmium layer is often sputtered onto the selenium surface in the presence of water vapor, which results in the development of a layer of selenium and cadmium oxides.

The present invention contemplates a new method of producing a highly uniform blocking layer. The process may be carried out in an apparatus such as that shown in Figure 1. The chamber **10**, which is a vacuum jar properly equipped for sputtering operations, contains a support **11**, upon which the selenium coated disc D is placed, with its selenium surface facing upwardly. The cathodes used in sputtering are mounted on a disc **12** of heat resisting glass or other suitable insulating material mounted by means of the pivot **13** for rotation within the jar. A segment **14** of magnetic material is mounted on the disc **12** to facilitate rotation of the disc by means of a magnet **15** exterior of the jar.

As shown in Figure 2, the sputtering cathodes may be in the form of metallic discs **16**, **17** and **18**, and are mounted on the underside of the disc **12**, so that by rotating the disc, any one of these cathodes can be moved into sputtering position over the cell supported on the table **11**. The cathodes are connected to contact elements **19** on the reverse side of the disc. A brush **20** selectively engages the contacts **19**, to conduct the sputtering current to the element directly above the support **11**.

After the selenium coated disc D is placed on the table **11**, the jar is sealed off and the pressure brought down to about 300 microns, and the sputtering current applied to one of the cathodes. For the first operation, the sputtering is carried on by means of the cathode **16**, which is of selenium. The sputtering is done by flashes, the current and intervals being selected to raise the temperature of the disc to about 140° C. This elevated temperature and subsequent operations cause the formation of a highly satisfactory blocking layer including selenium oxides.

It has been found that in order to produce a satisfactory blocking layer, this step, and others, must be regulated in such a manner that the transparency of the film laid down can be controlled. For this reason, a glass disc **21** is placed immediately adjacent the table **11**. A photoelectric cell **22**, beneath the glass plate is utilized to measure the transparency of the film sputtered on the glass plate by means of a suitable meter **23**, and a source of light. This first sputtering action is carried on to produce a transparency of the deposited film of about 70%.

After the deposit of the selenium, the disc **12** is rotated to bring the cadmium element **17** above the support **11**. The sputtering potential is applied to the cadmium cathode, the current density and flashing intervals being selected to bring the temperature of the disc to 140° C. This causes a laying on of a film of cadmium and cadmium oxides.

The 140° C. temperature may be measured in various conventional ways. For instance, a small strip of metal, such as Newton's alloy, with melting point at approximately 140° C., may be placed on the upper side of the disc **12**. The melting of the metal, clearly visible through the glass jar, will indicate when the temperature of 140° C. is reached. An alternate method is to use colored wax marks, which change colors at specified temperatures. These waxes are commercially available. Other temperature measuring means could be employed, such as a thermo-couple connected to the plate, or a thermometer in contact with the plate could be used with little difficulty.

After the completion of the cadmium sputtering, the disc **12** is again rotated to bring the third cathode **18** in place. The composition of this cathode is a novel feature of my invention. It has essentially a platinum and gold surface, obtained by the use of gold inserts in the platinum, the area of gold being about 20% of the area of the platinum. Application of a sputtering potential results in a deposit of the gold and platinum together. This sputtering action is carried on by timing the flashes to avoid extensive heating of the cell. The transparency of the three sputtered on layers is not permitted to drop below about 20%.

The resulting cell is shown in Figure 5. A base of iron **50** carries a selenium layer **51** which is applied by the conventional methods well known in the art. Immediately overlying this is a sputtered on layer of selenium and selenium oxides **52**, and on top of that a similar layer **53** of cadmium and oxides thereof. The top layer **54** is a homogeneous layer of platinum and gold.

In the above description, the step of annealing was mentioned. This annealing, practiced in the past in a thermostatically controlled oven at atmospheric pressure resulted in the formation of the nucleus of the blocking layer. However, the conditions within a thermostatically controlled oven are difficult to control; and the variations in humidity, contamination of the air and other factors seriously affect the character of the blocking layer nucleus formed in the oven. These factors result in non-uniform nuclei, and the resulting cells are as a result very irregular. A large number of them have very little output, only a few being extremely efficient.

As the conditions within the vacuum jar **10** are readily adjustable, and must be accurately controlled to permit the proper sputtering, it is proposed to perform the annealing in the sputtering chamber, utilizing the heat developed during the sputtering process. For this purpose the selenium coated disc is placed in the sputtering jar after being removed from the press. The jar is then exhausted, and gases, such as oxygen, hydrogen, or argon may be introduced at the proper pressure, it being understood, however, that minute quantities of oxygen are present in the jar, even though it has been exhausted and filled with hydrogen, argon, or the like. The cathode shown in Figure 3 is utilized. Instead

of a selenium electrode, an aluminum electrode 25 is utilized together with a cadmium electrode 26 and a combination platinum and gold electrode 27. The selenium coated disc is supported about an inch from the cathode. The aluminum cathode is positioned opposite the selenium disc and a potential applied to this cathode. The potential should be high enough to raise the temperature of the selenium coated disc to 200° C. It has been found that the pressure in the jar, the sputtering potential, and the duration of the flashes, determine the length of time necessary to complete the annealing process. Subjecting the selenium coated disc to this potential does not result in the deposit of any material, but merely changes the nature of the selenium on the disc. Aluminum is selected for the cathode as it does not sputter under the potentials and current densities suitable for raising the temperature of the disc to the necessary point. After completion of annealing, the turn table may be rotated to bring the cadmium opposite the selenium coated disc, and the sputtering carried on as above described. The cell may then be sputtered with the gold and platinum.

As a modification of the above described process I have found that the sputtering can be carried on with an electrode such as that illustrated in Figure 4. A cadmium disc 40 is provided with platinum inserts 41 and gold inserts 42. In the use of such an electrode, the sputtering current and other variables are controlled to bring the temperature of the disc above 200° C., thus accomplishing the annealing and the sputtering simultaneously.

The cell shown in Figure 6 results from this method of forming the layers on the selenium.

A base 60 carries a layer of selenium, 61, overlaid by a homogeneous layer 62, which consists of a selenium oxide overlaid by a mixture of cadmium, cadmium oxide, gold and platinum. This final layer can be considered as a combination barrier and electrode, as it performs both functions. The usual connections can be made to this layer in the usual way.

I claim:

1. A photoelectric cell of the selenium type including a selenium coated back electrode, and a translucent counter electrode overlying the back electrode and including a homogeneous mixture of platinum and gold in the ratio of substantially five to one.

2. A photoelectric cell of the selenium type comprising a selenium coated back electrode, a blocking layer thereon comprising a semi-transparent layer of selenium and selenium oxides, a semi-transparent layer of cadmium and cadmium oxides overlying said blocking layer, and a semi-transparent layer of a homogeneous mixture of platinum and gold overlying the layer of cadmium and cadmium oxides, forming a counter electrode.

3. A photoelectric cell of the selenium type comprising a selenium coated back electrode, a blocking layer thereon comprising a semi-transparent layer of selenium and selenium oxides, a semi-transparent layer of cadmium and cadmium oxides overlying said blocking layer, and a semi-transparent layer of a homogeneous mixture of platinum and gold in the ratio of about five to one overlying the layer of cadmium and cadmium oxides, forming a counter electrode.

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