

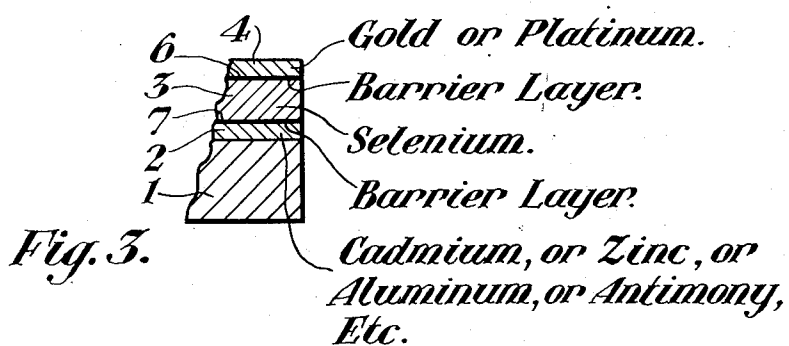
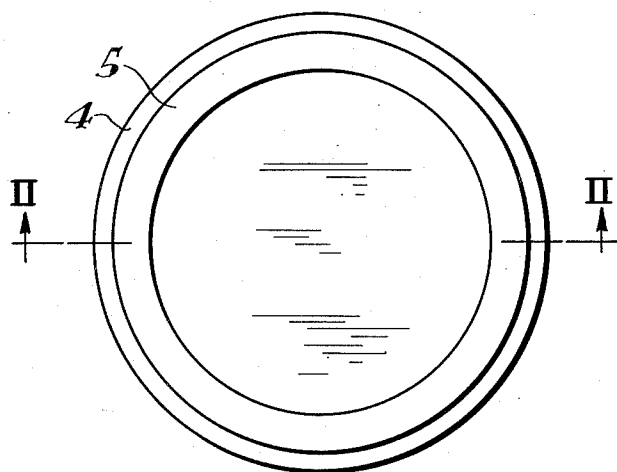
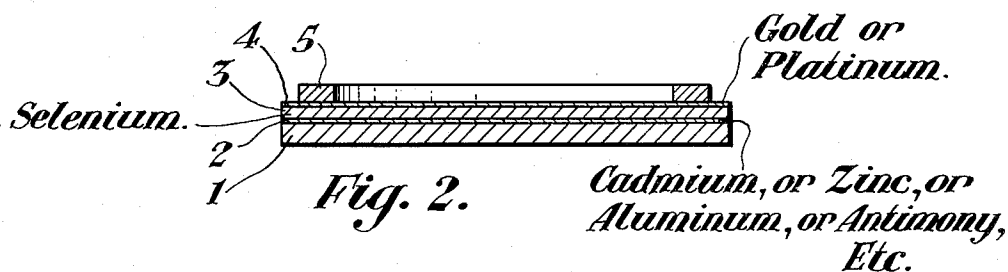
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PROCESS OF MANUFACTURING PHOTOELECTRIC CELLS

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PROCESS OF MANUFACTURING
PHOTOELECTRIC CELLS

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1 Claim. (Cl. 201—63)

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A barrier layer photo-electric cell consists, like a dry rectifier, of a thin layer of a semi-conductor, interposed between two metallic electrodes. In the rectifiers one of the electrodes, the base plate, serves as a mechanical support for the semi-conductor, with which as perfect as possible an electrical connection is made. The phenomena of asymmetric conductivity are localized at the contact of the semi-conductor and the second electrode, called the counterelectrode. It is agreed that this asymmetry is due to the existence, at the interface between the metal of the counterelectrode and the semi-conductor, of a very thin layer of high resistivity, called the barrier layer, which is formed in the course of the manufacturing treatment. This layer is traversed much more easily by the conducting electrons in the direction from the metal to the semi-conductor, than in the reverse direction. In consequence, the direction of the greater conductivity corresponds to the flow of current from the base plate to the counterelectrode through the semi-conductor.

The photo-electric cell differs from the rectifier in that the counterelectrode, consisting, for example, of a thin layer of gold or platinum, allows light to pass while remaining conductive. If the surface of the semi-conductor is illuminated through the counterelectrode, the appearance of an electrical difference of potential may be observed between it and the base plate, the positive pole being the base plate. This difference of potential on open circuit is not proportional to the illumination but increases less rapidly and appears to tend toward a saturation value with very intense illumination.

If now the counterelectrode and the base plate are connected to the two terminals of a galvanometer, a current may be measured, when the resistance of the galvanometer is low, which is sensibly proportional to the illumination. Since the cell constitutes a rectifier, it will be seen that the photo-electric current which flows from the negative pole to the positive pole through the cell, that is to say, from the counterelectrode to the base plate, flows in the high resistance direction through the rectifier.

These phenomena may be explained, as for the rectifier, by the existence of a barrier layer between the semi-conductor and the counterelectrode. The light, traversing the latter, liberates some electrons in the semi-conductor. Those which have sufficient energy traverse the barrier layer and pass into the counterelectrode. On open circuit the latter is charged negatively. An

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equilibrium is established between the electrons passing from the semi-conductor to the counterelectrode and those which recombine with their ions in taking the reverse path, and a sort of saturation intervenes. On short circuit, on the contrary, this manifestation practically does not appear, the current forcing the electrons to move all together and they recombine with their ions after having entered the exterior path including the load circuit and the base plate. Under these conditions, the current delivered is proportional to the number of electrons liberated per second in the semi-conductor by the primary photo-electric effect.

It will be seen that on the one hand the useful photo-electric current traverses the barrier layer in the direction corresponding to the blocking resistance of the contact between the semi-conductor and the counterelectrode; on the other hand the currents of direct recombination of electrons with their positive ions take the reverse path, which is that of the low resistance of the contact. However, in addition to this recombination, which has its location in a space very close to the barrier layer, there exists some leakage currents which are not negligible which flow directly from the counterelectrode to the base plate perhaps due to defects in the surface, or through the non-illuminated portions of the cell (collector ring, for example). Finally, certain photo-electrons, which, moreover, are more numerous when the illumination is very intense, flow directly from the semi-conductor to the base plate. In effect, the semi-conductor is not rigorously opaque and the region of emission of photo-electrons approaches closer to the base plate when the illumination is very intense.

These different defects contribute each in part to the diminution of the potential difference on open circuit with strong illumination. Now it is evident that the power capable of being furnished by the cell to a load device will moreover be greater, for the same short circuit current, if the difference of potential of the cell on open circuit, which may be likened to an apparent electromotive force, is increased, under the condition that the apparent resistance of the load apparatus is adapted to the apparent internal resistance of the cell.

The present invention, due to the work of Messrs. Roger Millet and Léon Dubar, obtains cells of definitely increased electromotive force by reduction of the leakage currents of which the origin will be explained thus: This result is obtained according to the invention by creating

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a barrier layer between the semi-conductor and the base plate. Thus a second rectifying contact is obtained, in opposition to the rectifying contact of the semi-conductor and counterelectrode. This back contact allows however the useful photo-electric current to pass easily and notably reduces the leakage currents in the reverse direction. Moreover, it efficiently blocks the photo-electrons, strongly retarded by their passage through the semi-conductor, which are emitted directly toward the base plate.

By way of example, and not as a limitation, as applied to the selenium cell, the use may be indicated of a base plate of a metal capable of forming with the selenium a non-conducting compound. This metal can be, for example, cadmium, zinc, aluminum, antimony, etc., used as a solid plate or an electrolytic deposit. The barrier layer is formed by association of the selenium with the metal after the heat treatment which transforms the selenium to a conducting variety. The duration and the temperature of this heat treatment can be regulated to obtain the optimum properties at the same time for the selenium and the barrier layer, the other treatments remaining unchanged.

Experience has shown that besides a notable increase in the difference of potential on open circuit, which can reach up to 0.5 volt at 1.200 lux, there is obtained with certain metals such as cadmium a remarkable adherence of the layer of selenium to the base plate sufficient to enable optionally the omission of the usual roughening of the base plate by a sand blast. This property should likewise be considered as one of the results accomplished by the invention.

It is obvious that the example of realization given is not limited by the invention but may be applied to any barrier layer cell whether it is of selenium or not and, finally, that the second barrier layer between the semi-conductor and the base plate or back layer can be realized in any known manner. This consists of a deposit on the base plate, previous to the addition thereto of the semi-conductor, of an appropriate insulating film, organic (such as varnish) or mineral (such as quartz, fluorite, cryolite, the deposit being made by evaporation in vacuum).

Moreover, the invention by no means depends upon the theoretical considerations disclosed above. It rests uniquely upon the actual observation of the increase in the difference of potential on open circuit by means of strong illumination following the creation of a rectifying contact between the base plate and the semi-conductor and not to the explanations which may be given for this result.

By reason of the present invention, having regard to the direction of rectification, the useful photo-electric current is not sensibly affected while the undesired leakage currents are notably attenuated. The result is an increase in the internal resistance and in the electromotive force of the cell permitting the latter to deliver a larger power to a receiver.

In the accompanying drawing, Fig. 1 is a plan view, and Fig. 2 is a cross-section view of a photo-electric cell constructed according to our invention; and Fig. 3 is a view showing an enlarged portion of the cross-section view shown in Fig. 2.

Referring to the drawing, a base plate 2 is provided, of a metal which can be, for example, cadmium, zinc, aluminum, antimony, etc., used

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either as a solid plate, or an electrolytic deposit on a supporting base plate 1. A layer 3 of a semi-conductor selenium material is then applied to the exposed or upper side of base plate 2, as shown in the drawing. By means of a heat treatment, in an oven at a temperature above 150° centigrade but not exceeding the melting point of selenium, the layer 3 of semi-conductor selenium material becomes transformed into a conducting variety.

A counterelectrode consisting, for example, of a thin layer 4 of gold or platinum, is applied to the exposed side of selenium layer 3, and a suitable collector electrode, such for example as a ring shaped electrode 5 may be applied to counterelectrode 4.

In Fig. 3, the usual barrier layer 6 is shown between selenium layer 3 and counterelectrode 4. A second barrier layer 7 is also formed between the base plate 2 and layer 3 of selenium. Barrier layer 7 has higher resistance to the flow of current in the direction from base plate 2 to selenium layer 3 than in the opposite direction from selenium layer 3 to base plate 2, whereas barrier layer 6, as is well known, has higher resistance to the flow of current in the direction from counterelectrode 4 to selenium layer 3, than from layer 3 to counterelectrode 4.

Having thus described our invention, what we claim is:

A process of manufacturing a photo-electric cell which comprises depositing an organic film such as varnish, or a film of a mineral selected from the group consisting of quartz, fluorite and cryolite on a base plate of a metal capable of forming a barrier layer with a semi-conductor material such as selenium, then depositing a layer of said semi-conductor material on said film, providing a thin layer of metal such as gold or platinum in contact with the opposite side of said layer of semi-conductor material, applying heat to transform said semi-conductor material into a conducting state, in which said barrier layer is formed between said base plate and said layer of semi-conductor material, said barrier layer having high resistance to electric current of a given polarity and having low resistance to electric current of the opposite polarity, and in which a second barrier layer is formed between said thin layer of metal and said opposite side of said layer of semi-conductor material, said second barrier layer having low resistance to electric current of said given polarity, and having high resistance to electric current of said opposite polarity.

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ROGER PHILIPPE MILLET.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
420,884	Mercadier	Feb. 4, 1890
1,827,016	Joffe	Oct. 13, 1931
2,476,042	Hewlett	July 12, 1949

FOREIGN PATENTS

Number	Country	Date
109,730	Australia	Feb. 15, 1940
500,094	Great Britain	Feb. 2, 1939