Dec. 23, 1958 D. DE NOBEL 2,865,793

METHOD OF MAKING ELECTRICAL CONNECTION TO SEMI-CONDUCTIVE SELENIDE OR TELLURIDE

Filed Nov. 29, 1955

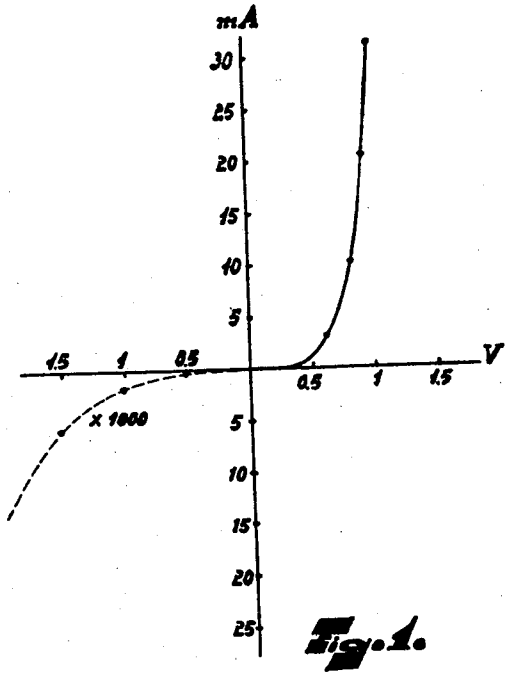

Fig. 1.

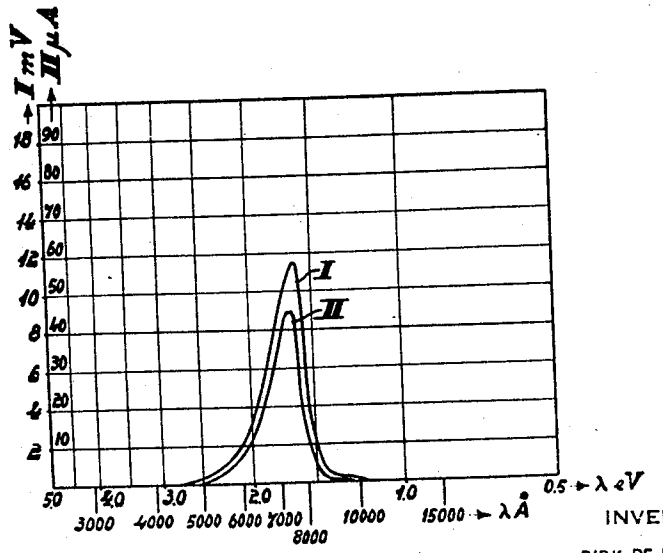

Fig. 2.

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United States Patent Office

2,865,793

Patented Dec. 23, 1958

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METHOD OF MAKING ELECTRICAL CONNECTION TO SEMI-CONDUCTIVE SELENIDE OR TELLURIDE

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Application November 29, 1955, Serial No. 549,754

Claims priority, application Netherlands December 6, 1954

9 Claims. (Cl. 117—200)

This invention relates to a method of making an electrical connection to a semi-conductive body, and, in particular, to the application of precious-metal layers to bodies of a semi-conductive selenide or telluride of a bivalent metal.

The compounds concerned are the selenides and tellurides of the metals Zn, Cd, Hg, Sn and Pb.

For the application of precious-metal layers various methods are known, for example application by evaporation, by burning on suspensions of silver or decomposable silver compounds and by electrolytic means.

With such metal layers the nature of the contact, i. e. whether it is ohmic or rectifying, is of minor importance. The invention permits of producing ohmic or rectifying contacts in a very simple manner and under particular circumstances.

In accordance with the invention the aforesaid selenides and tellurides of bivalent metals are brought into contact with a solution of an elementary precious-metal salt, so that ions of the bivalent metal emerge from the body, i. e., are dissolved in the solution, and a precipitate of the precious-metal is formed on the surface depleted of the bivalent metal. Naturally only those precious metals can be used which are lower in the electromotive series than the bivalent metal in the compound that is affected.

It is found that the contact obtained is ohmic on p-type material and rectifying on n-type material.

If with such rectifying contacts the properties of the precious-metal are less favourable, for example if the specific resistance is too high, or if the permeability for particular wavelengths of the light is too small, the precious-metal may be removed wholly or partly and a different metal, for example iridium, may be applied, since the ohmic or rectifying connection resulting actually exists between the surface layer of the body that has lost bivalent metal ions by reason of reaction with the solution, and the subjacent semi-conductive material.

This method is performed in a very simple manner if mercury is applied, since the mercury, subsequent to its deposition, can be removed in a very simple manner.

The strength and pH of the precious-metal solution is of minor importance. Solutions of ½, 5 and 50% of precious-metal salt, acidified or not, even to a HCl-content of 20%, yield the same results. For carrying out the invention use may be made for example of solutions of $AgNO_3$, $AuCl_3$, $PtCl_4$, $RhCl_3$, $OsCl_3$, $PdCl_2$, or $IrCl_4$. Salts, in which the precious-metal ion is contained in complex form, for instance $KAuCl_4$, K_2PtCl_6, do not yield, however, the desired precious-metal layer.

In the alkaline salts, the precious-metal ion is contained in complex form, or the precious-metal precipitates in the form of a hydroxide. As is the case with many such processes, organic salt solutions are dissociated too little for obtaining a good result. Thus these are also not satisfactory.

The time of treatment is not important for the nature of the contact, whether it is ohmic or rectifying. As the time of treatment is longer, the contact penetrates deeper into the semi-conductive body. Solutions of salts of Hg and Au yield rapidly a satisfactorily adhering layer at room temperature. With a treatment with a solution of salts of Pt, Rh, or Ir it is desirable to carry out a slight heating, for example to 50° C. for a few minutes.

Several specific examples are described below, with some of the results obtained described in connection with the two graphs in the accompanying drawing.

Example I

A plate of p-type CdTe is provided on both sides with a gold contact by applying thereto a drop of a 10% $AuCl_3$ solution, by causing it to react for about one minute, and by rinsing it off subsequently. The contacts obtained appear not to have any deviation from the ohmic nature even at low voltages. A like result is obtained by means of a solution of 0.5% of $AuCl_3$, even if it is acidified to for example 20% of hydrochloric acid.

Example II

To a plate of the kind referred to in Example I is applied a drop of a 5% $RhCl_3$ solution. Subsequent to heating for a few minutes at about 50° C. and subsequent to rinsing, a rhodium contact is obtained, which exhibits ohmic characteristics. A like result is obtained by means of a 10% $PtCl_4$ solution, acidified to 20% of hydrochloric acid or not acidified.

Example III

A plate of p-conductive HgSe is provided with a gold contact by causing a drop of a 10% $AuCl_3$ solution to react therewith.

Example IV

An n-conductive CdTe-crystal plate with about 3×10^{17} charge carriers per $cm.^3$ is provided on one side with an ohmic contact by fusing thereto indium in a nitrogen atmosphere with 10% of hydrogen. The other side of the plate is treated with a 10% $AgNO_3$ solution. Subsequent to the reaction of the solution for one minute a silver layer is formed and a rectifying connection.

In this manner a rectifier is obtained, which has a current voltage characteristic curve as shown in Fig. 1.

Upon exposure to about 2700 lux from a tungsten tape lamp (colour temperature 2800° K.) the silver layer or underlying rectifying connection exhibits a photo-electromotive force and/or a photo-current. The short-circuit current is 140 $\mu a.$ and the voltage is 395 mv. with an infinite external resistance.

As is evident from Fig. 2, which shows the relationship of the photo-electromotive force (referred to by I) and of the photo-current with (referred to by II) respect to the wavelength of the incident light, the maximum sensitivity lies at a wavelength of about 7800 A.

Example V

To a plate of CdTe with n-conductivity and a specific resistance of 0.1 ohm cm. is applied, by treating it with a solution of $AuCl_3$, a layer of gold. This layer is removed with the aid of a solution of potassium-cyanide, after which such a thin layer of iridium is applied that 80% of the visible light is permitted to pass. It is found that a short-circuit current may be obtained, which is five times higher than that obtainable by means of a gold electrode.

What is claimed is:

1. A method of making an electrical connection to a semiconductive body constituted of a member selected from the group consisting of a bivalent metal selenide

and a bivalent metal telluride, said bivalent metal being selected from the group consisting of zinc, cadmium, mercury, tin and lead, which comprises bringing said body into reactive engagement with a solution of a precious metal selected from the group consisting of gold, silver, mercury, platinum, rhodium, osmium, palladium and iridium thereby to dissolve out some bivalent metal from a surface portion of said body and precipitate on the said surface portion from which bivalent metal was dissolved said precious metal.

2. A method of making an electrical connection to a semi-conductive body constituted of a member selected from the group consisting of a bivalent metal selenide and a bivalent metal telluride, said bivalent metal being selected from the group consisting of zinc, cadmium, mercury, tin and lead, which comprises bringing said body into reactive engagement with an elementary, inorganic, salt solution of a precious metal selected from the group consisting of gold, silver, mercury, platinum, rhodium, osmium, palladium and iridium thereby to dissolve out some bivalent metal from a surface portion of said body and precipitate on the said surface portion from which bivalent metal was dissolved said precious metal.

3. A method as set forth in claim 2, wherein a p-type semi-conductive body is employed, thereby to produce an ohmic connection to said body.

4. A method as set forth in claim 2, wherein an n-type semi-conductive body is employed, thereby to produce a rectifying connection to said body.

5. A method as set forth in claim 2 wherein at least part of the precipitated precious metal is thereafter chemically removed from the body and replaced by a different electrically conductive metal.

6. A method of making an electrical connection to a semi-conductive body constituted of a member selected from the group consisting of a bivalent metal selenide and a bivalent metal telluride, said bivalent metal being selected from the group consisting of zinc, cadmium, mercury, tin and lead, which comprises bringing said body into reactive engagement with a gold salt solution at room temperature thereby to dissolve out some bivalent metal from a surface portion of said body and precipitate gold on the said bivalent-metal-depleted surface portion.

7. A method of making an electrical connection to a semi-conductive body constituted of a member selected from the group consisting of a bivalent metal selenide and a bivalent metal telluride, said bivalent meatl being selected from the group consisting of zinc, cadmium, mercury, tin and lead, which comprises bringing said body into reactive engagement with a silver salt solution at room temperature thereby to dissolve out some bivalent metal from a surface portion of said body and precipitate silver on the said bivalent-metal-depleted surface portion.

8. A method of making an electrical connection to a semi-conductive body constituted of a member selected from the group consisting of a bivalent metal selenide and a bivalent metal telluride, said bivalent metal being selected from the group consisting of zinc, cadmium, mercury, tin and lead, which comprises bringing said body into reactive engagement with a platinum salt solution at a temperature of about 50° C. thereby to dissolve out some bivalent metal from a surface portion of said body and precipitate platinum on the said bivalent-metal-depleted surface portion.

9. A method of making an electrical connection to a semi-conductive body constituted of a member selected from the group consisting of a bivalent metal selenide and a bivalent metal telluride, said bivalent metal being selected from the group consisting of zinc, cadmium, mercury, tin and lead, which comprises bringing said body into reactive engagement with a rhodium salt solution at a temperature of about 50° C. thereby to dissolve out some bivalent metal from a surface portion of said body and precipitate rhodium on the said bivalent-metal-depleted surface portion.

References Cited in the file of this patent

UNITED STATES PATENTS

2,677,715	Auwarter	May 4, 1954
2,710,813	Forgue	June 14, 1955

OTHER REFERENCES

Schwartz: Proc. Phys. Soc. (London), 63B (1950), pp. 624–5.

Schwartz: Nature, vol. 162 (1948), pp. 614–15.