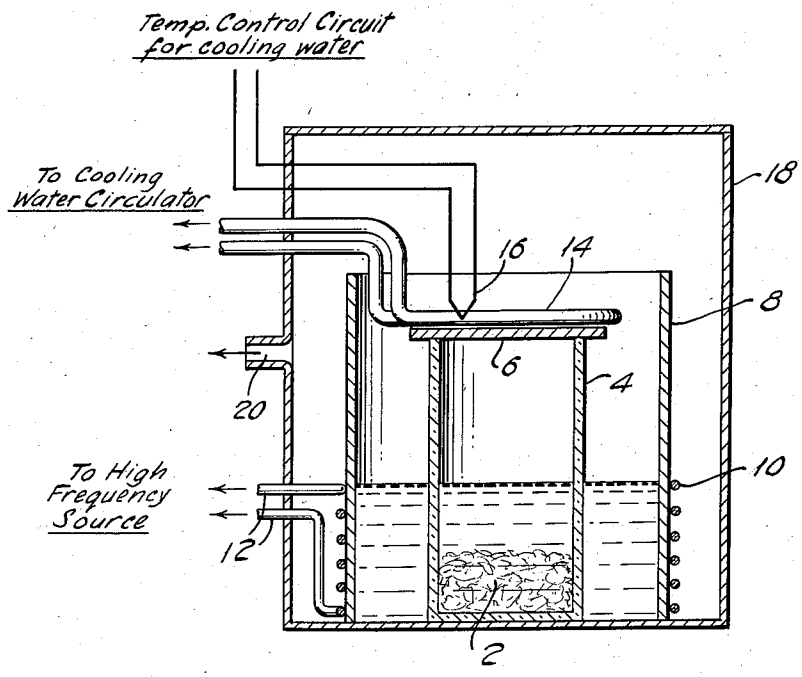
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PREPARATION OF PHOTOSENSITIVE CRYSTALS

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INVENTOR
OTTO WEINREICH
BY
Eyre, Mann & Burrows
ATTORNEY

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PREPARATION OF PHOTOSENSITIVE CRYSTALS

Otto Weinreich, East Orange, N. J., assignor to Tung-Sol Electric Inc., a corporation of Delaware

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The present invention relates to photosensitive compounds of the type that increase in electrical conductivity when subjected to light rays and comprises a novel method for preparing photosensitive compounds of cadmium or the like that is adapted for practice on a commercial scale and results in a product of substantially uniform electrical characteristics and of relatively high photosensitivity.

The process is applicable to starting compounds which have little or no initial photosensitivity. Examples of suitable starting materials are sulfides, selenides and tellurides of cadmium, indium, thallium, tin, lead, antimony and bismuth and combinations thereof, such as sulfides and tellurides of silver and thallium combined with silver, bismuth, tin or thallium. It is not necessary that the starting material be chemically pure. In fact superior results have been obtained when the starting material contains traces of impurities such as are to be expected in commercial products. The invention is directed primarily to the process whereby photosensitivity is enhanced in materials of the above type and not to any new chemical compound.

For convenience in the following description of the process of the invention, cadmium selenide is specified as the starting material. It will be understood that the process is equally applicable to other materials such as above indicated.

In general the process of the invention comprises vaporization of the starting material under vacuum and condensation upon a metal wall in which, or on the surface of which, is the activator for enhancement of the photosensitivity of the deposited crystalline material. The activator, preferably oxygen, may be adsorbed by the metal wall or it may comprise part of a coating on the wall. For example, the metal may contain occluded oxygen, or the metal may be oxidized or may be coated with an oxide of another material. By control of the amount of oxygen or other activator combined with the metal wall upon which the material is to be deposited and of the temperature difference between the wall and that applied for vaporization of the starting material, the quantity of activating material for combination with the compound may be controlled to yield optimum photosensitivity.

The activated crystalline material deposited upon the metal wall is readily removable by mechanical means and is suitable for use in manufacture of photoelectric cells.

For a better understanding of the invention reference may be had to the accompanying drawing of which the single figure is a diagrammatical representation of apparatus suitable for use in practicing the new process.

The starting material **2**, for example, commercial cadmium selenide containing traces of impurities, is placed in a quartz container **4** having a loose fitting lid **6** of tantalum, molybdenun or other metal of high melting point containing or carrying an activator for the material to be deposited thereon. A lid of oxidized molybdenum has been found particularly satisfactory in the process. The container **4** with its contents and the lid **6** is placed

within a platinum cylinder **8** about the lower end of which is a coil **10** to which radio frequency current is delivered through leads **12**. A cooling coil **14** is positioned about the lid **6** and temperature responsive means as, for example, a thermocouple indicated diagrammatically at **16** is provided for control of the temperature of the lid. The entire asesmbly of quartz container **4**, platinum cylinder **8**, high frequency heating coil **10** and cooling coil **14** is enclosed within a chamber **18** adapted to be evacuated as by a connection, diagrammatically indicated at **20**, to a vacuum system. The chamber **18** is maintained at a pressure of about 10^{-6} mm. and the temperature of the starting material raised by radio frequency induction heating to about 900° C. As the coil surrounds the lower portion only of the platinum cylinder and as the lid **6** is maintained at a lower temperature by means of the cooling coil **14** there will be a temperature differential maintained between the starting material in the bottom of the quartz container and the metal lid **6**. Heating is maintained for about thirty minutes after which time the inside surface of the lid **6** will be found covered with a coating of crystals which sticks to the metal lid and may, after cooling, be removed mechanically. With a quartz cylinder of about ½" diameter and a height of 1" one run will form sufficient deposit from which up to fifty small photosensitive cells can be made.

The metal lid **6**, instead of being oxidized, may be coated with a thin layer of barium peroxide or with a thin layer containing an activator other than oxygen.

The following gives an indication of the results obtainable by practice of the invention and of the importance of the condition of the metal plate upon which the crystals are deposited. Crystals of commercial grade cadmium selenide were deposited on a molybdenum plate or lid that had ben hydrogen fired to remove all occluded oxygen and to clean the surface and also on a plate of oxidized molybdenum. The deposits on the plates were then removed and the increase in current with equal illumination and equal voltage applied across equally spaced silver paste electrodes on the crystals from each deposit was measured. The dark currents of both deposits were of the same order of magnitude but the currents of illuminated crystals removed from the oxidized molybdenum plate were over one hundred times as large as the currents of illuminated crystals removed from the cleaned plate. When commercial cadmium selenide was deposited on a molybdenum plate coated with barium peroxide, photocurrents over one thousand times greater than those of the deposit on cleaned molybdenum were obtained. The dark currents of the deposit from the barium peroxide coated molybdenum were however substantially larger than the dark currents of the deposits on either the oxidized or cleaned molybdenum plates. Photosensitivity of crystals of cadmium selenide deposited on oxidized molybdenum with 22.5 volts across an electrode spacing of about 1 mm. and illumination of 270 microwatts per square centimeter in the region of maximum spectral response ($\lambda=.750\mu$) averaged over 100 amperes per watt for four samples.

The above described results obtained when commercial cadmium selenide was deposited under vacuum on oxide coated molybdenum plates are typical of those obtainable by the process of the invention irrespective of the particular starting material and of the particular metal and activator employed. Suitable starting materials have heretofore been indicated. Metals suitable for use as the plate upon which the vaporized starting material deposits are molybdenum, tantalum and platinum.

The following is claimed:

1. The method of enhancing photoconductivity in crystalline material which comprises vaporizing the material under vacuum and depositing the vaporized material on

a metal plate carrying oxygen as an activator, said material being selected from the group consisting of sulfides, selenides and tellurides of cadmium, indium, thallium, tin, silver, lead, antimony and bismuth and combinations thereof.

2. The method according to claim 1 wherein the vaporized material is deposited on a metal plate carrying oxygen in the form of an oxide.

3. The method according to claim 1 wherein the plate is of a metal of the group consisting of molybdenum, tantalum and platinum.

4. The method according to claim 1 wherein the activator is oxygen occluded in the metal plate.

5. The further step in the process of claim 1 which comprises mechanically removing from the plate the photoconductive crystals deposited thereon.

6. The method according to claim 2 wherein the oxide is an oxide of the metal comprising the plate.

7. The method according to claim 2 wherein the oxide is barium peroxide and the plate is of a metal of the group consisting of molybednum, tantalum and platinum.

8. The method of enhancing the photoconductivity of cadmium selenide which comprises vaporizing crystals of cadmium selenide under vacuum and depositing the vaporized cadmium selenide on an oxide coated plate of molybdenum.

9. The method of enhancing the photoconductivity of cadmium selenide which comprises vaporizing crystals of cadmium selenide under vacuum and depositing the vaporized cadmium selenide on an oxide coated plate of tantalum.

10. The method of enhancing photoconductivity of cadmium selenide which comprises vaporizing crystals of cadmium selenide under vacuum and depositing the vaporized cadmium selenide on a plate of molybdenum carrying occluded oxygen.

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