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SEMICONDUCTING MATERIALS AND DEVICES MADE THEREFROM

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FIG. 1

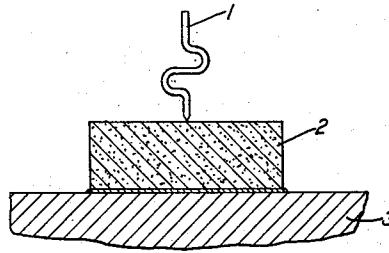


FIG. 2

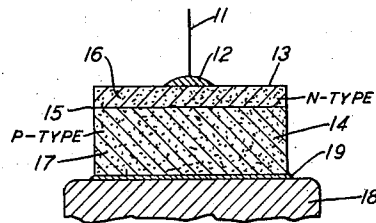
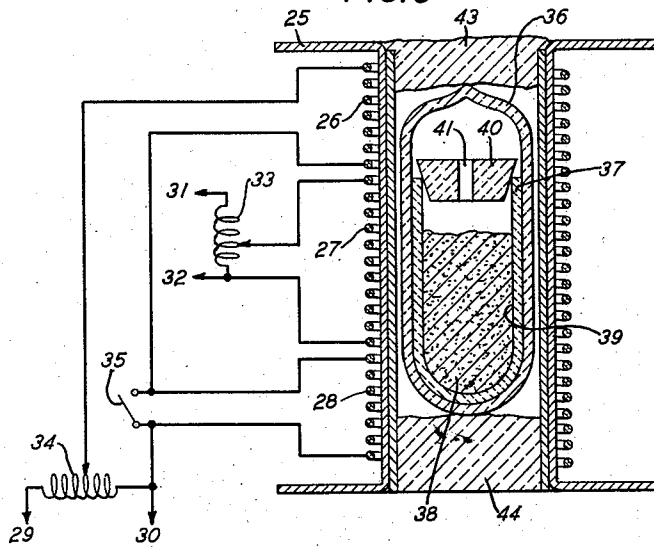


FIG. 3



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## SEMICONDUCTING MATERIALS AND DEVICES MADE THEREFROM

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This invention relates to ternary semiconductive compounds and to semiconductive devices containing such compounds.

In accordance with this invention there has been discovered a new series of semiconducting compounds of the general composition  $AgXSe_2$  in which X is antimony, bismuth or arsenic. These new materials have intrinsic energy gaps between 0.6 and 1.0 electron volts, a range making them useful in the construction of common semiconductor devices such, for example, as rectifiers and transistors and also in photo devices such as infrared detectors. All of these materials in addition to being intrinsic semiconductors evidence extrinsic semiconductive properties so that they are useful both in point-type and in junction-type devices.

These new compounds are discussed herein in terms of their electrical and physical properties and their use in two typical semiconductor transducing devices; one point-type and one junction-type. Since none of the materials which is the subject of this invention is known to occur in nature, a method by which each of them has been synthesized is described.

The invention may be more easily understood by reference to the following figures in which:

Fig. 1 is a schematic front elevational view in section of a point-type diode utilizing one of the compounds herein;

Fig. 2 is a schematic front elevational view in section of a junction-type diode utilizing one of the compounds herein; and

Fig. 3 is a schematic cross-sectional view of apparatus used in the preparation of each of the compounds of this invention.

Referring again to Fig. 1, point-electrode 1 makes rectifying contact with semiconductor block 2 which may contain any one or more of the compounds of this invention, silver antimony selenide, silver bismuth selenide or silver arsenic selenide, so modified by the incorporation of one or more significant impurities or other means as to exhibit extrinsic conductivity. Semiconductor block 2 makes ohmic contact with base 3 which may be made, for example, of copper. As is well known to those skilled in the art, such ohmic connection may be made, for example, by use of a solder containing a material having an excess of electrons where the material of semiconductor block 2 is n-type and a deficiency of electrons where the material of semiconductor block 2 is p-type. Methods of making satisfactory point contact are well known and are not discussed. For suitable materials for the construction of a point-type electrode such as electrode 1 and for suitable methods of pointing such electrodes and bringing them to bear on the surface of block 2, attention is directed to 81 Physical Review 882 (1951) and 175 Transactions of the A.I.M.E. 606 (1948). A point-type diode such as that depicted in Fig. 1 is an asymmetrical element conducting more readily in the one direction than in the other. Where the material of semiconductor block

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2 is n-type, ready conduction occurs with electrode 1 biased positive with respect to base 3. Where the material of block 2 is p-type ready conduction occurs with electrode 1 biased negative with respect to base 3.

The device of Fig. 2 is a junction-type diode consisting of electrode 11 making ohmic connection 12 with surface 13 of block 14 which may, for example, be  $AgSbSe_2$  and which block contains p-n junction 15 between region 16 which is of one conductivity type and region 17 of the opposite conductivity type. Semiconductor block 14 makes ohmic contact with electrode 18 by means, for example, of a solder joint at 19. As will be discussed, where block 14 is silver antimony selenide which is of p-type conductivity as made, region 17 may constitute the unconverted material and, therefore, be of p-type conductivity, while region 16 of n-type conductivity may be produced, for example, by doping with a significant impurity such as iodine from group VII of the periodic table according to Mendelyev.

In the description of the device of Fig. 2 as in the description of the device of Fig. 1, it is not considered to be within the scope of this description to set forth contacting means and other design criteria well known to those familiar with the fabrication of semiconductive devices.

Fig. 3 depicts one type of apparatus found suitable for the preparation of each of the three semiconductive compounds herein. Reference will be made to this figure in the examples relating to the actual preparation of these compounds. The apparatus of this figure consists of a resistance wire furnace 25 containing three individual windings 26, 27 and 28 as indicated schematically, these windings comprising turns of platinum-20 percent rhodium resistance wire. In operation, an electrical potential is applied across terminals 29 and 30 and also across terminals 31 and 32 by means not shown. The amount of current passing through resistance winding 27 is controlled by means of an autotransformer 33 while the amount of current supplied to windings 26 and 28 is controlled by autotransformer 34, so that the temperature of the furnace within winding 27 may be controlled independently of the temperature in the furnace within windings 26 and 28. Switch 35 makes possible the shunting of winding 28 while permitting current to pass through winding 26. The functions served by autotransformers 33 and 34 and switch 35 are explained in conjunction with the general description of the method of synthesis.

Within furnace 25 there is contained sealed container 36 which may be made of silica and may, for example, be of an inside diameter of the order of 19 millimeters within which there is sealed a second silica crucible 37 containing the component materials 38 used in the synthesis of a compound of this invention. Coating 39 on the inner surface of crucible 37 may be of a material such as carbon and has the effect of reducing adhesion between surface 39 and the final compound. Inner crucible 37 is closed at its upper end with graphite cap 40 having hole 41 so as to prevent possible boiling over into container 36 and to minimize heating of charge during sealing off of container 36. In the synthesis of the materials herein thermal losses are reduced and temperature control gained by use of insulation layers 43 and 44 which may, for example be Sil-o-cell refractory.

The following is a general outline of a method of preparation used in synthesis of the compounds of this invention. Reference will be had to this general outline in Examples 1 through 3 each of which sets forth the specific starting materials and conditions of processing utilized in the preparation of a compound herein.

In the preparation of the selenides of this invention, it was found necessary to coat the inner surface of the inner crucible 37 to prevent reaction between the crucible and

the materials therein contained. It was found that a suitable coating was produced by exposure of the crucible to a mixture of four parts of nitrogen and one part of methane for a period of 15 minutes, a flow rate of approximately 250 cubic centimeters per minute with a crucible at a temperature of about 1000° C. After coating the charge was placed in crucible 37 which was then stoppered with cap 40 and placed within container 36. Outer container 36 was then evacuated, filled with tank nitrogen at a pressure of two-thirds of an atmosphere and was sealed and placed within furnace 25. With switch 35 open, an electrical potential was then applied across terminals 29 and 30 and also terminals 31 and 32 and autotransformers 33 and 34 were adjusted so as to result in a temperature in the central portion of the furnace of from about 950° C. to about 1050° C. and preferably about 100° C. and so as to result in furnace temperatures within windings 26 and 28 of from about 75° C. to about 100° C. higher than that of the central portion of the furnace. The upper and lower portions of the furnace were maintained at the higher temperature to prevent dynamic loss by vaporization and condensation of vaporizable constituents.

The furnace was maintained at the temperatures and gradients indicated in the paragraph preceding for a period of about two hours after which power to terminals 31 and 32 was terminated and switch 35 was closed so as to shunt winding 28 thus creating a temperature gradient with the high end of the gradient at the top of the furnace and the low end of the gradient at the bottom of the furnace as the melt cooled. Under the conditions indicated the temperature gradient was from a high of about 1100° C. to a low of about 900° C. This gradient was maintained for a period of about one hour after which the current was turned off and the melt permitted to return to room temperature.

Heating of the furnace was gradual, taking about four hours from room temperature to the high temperature of about 1100° C., so that the major portion of the alloying was carried out over a range of temperature at which the vapor pressure of selenide is relatively low, thereby minimizing loss of this vaporizable material. The average weight of the resultant ingots was about 60 grams. Microscopic examination and thermal analysis showed that the compounds were single phase. Melting points and energy gaps are reported in the examples which follow:

#### Example 1

AgSbSe<sub>2</sub> was prepared in accordance with the above outline using a mixture of 20.22 grams of silver, 22.85 grams of antimony and 29.6 grams of selenium. These materials were thoroughly mixed with a spatula before being placed in crucible 37. The final ingot was single phase, had a melting point of 610° C., an energy gap of about 0.6 electron volt, a resistivity of about 0.002 ohm-centimeters and was of p-type conductivity. The ingot was zone-refined by the passage of 20 zones resulting in an increase in resistivity to a value of about 0.02 ohm-centimeters. The rectification ratio was about 2:1.

#### Example 2

AgBiSe<sub>2</sub> was prepared as above using a starting charge of 13.49 grams of silver, 26.13 grams of bismuth, and 19.74 grams of selenium. The final material was single phase, of a melting point of 780° C. and evidenced n-type conductivity.

#### Example 3

AgAsSe<sub>2</sub> was prepared as above using 20.22 grams of silver, 14.05 grams of arsenic and 29.6 grams of selenium. The final ingot was single phase, had a melting point of 390° C. and an energy gap of about 0.9 electron volt.

In all of the examples above, it was found that particle size of the starting constituents was not critical. Actual particle sizes varied from about 0.1" to about 0.5".

Each of the compounds of this invention manifests either hole or electron conductivity and is, therefore, an extrinsic semiconductor as made. That the conductivity type of these compounds is an extrinsic characteristic probably due to incorporation of significant impurities as in the well-known germanium and silicon systems, is further evidenced by the resistivity gradient which results upon zone-refining and also by changes in resistivity and in conductivity type by doping. As is indicated in Example 1 above, zone-refining of silver antimony selenide by passage of 20 zones through the ingot as prepared above resulted in a tenfold increase in resistivity.

The conductivity type of the compounds of this invention has been successfully converted by the use of small amounts of doping elements. In accordance with conventional doping theory the conductivity type of any one of the ternary compounds herein may be caused to approach n-type material by substitution of any one of the elements of the compound by any element having a larger number of electrons in its outer ring and may be caused to approach p-type by such substitution with one element having a smaller number of such electrons. The determination of practical significant impurities additionally depends upon physical and chemical characteristics which will permit such substitution without appreciably affecting the crystallography and the chemical composition of the compound. A substantial amount of study has been given these considerations in the field of doping of semiconductive materials in general and criteria upon which an accurate prediction may be premised are available in the literature, see for example, L. Pincherle and J. M. Radcliffe, *Advances in Physics*, volume 5, No. 19, July 1956, page 271. In general, it has been found that if the extrinsic element so chosen is chemically compatible with both the compound and the atmosphere to which the compound is exposed during high temperature processing, this element, if it has an atomic radius which is fairly close to that of one of the elements of the ternary compound, will seek out a vacancy in the lattice and will occupy a site corresponding with that of that element of the compound. Doping may be effected also by introduction of small atoms which appear to occupy interstitial positions as, for example, lithium in germanium and hydrogen in zinc oxide.

In accordance with the above, it has been found that iodine from group VII of the periodic table having a radius of 1.33 Å will readily occupy a selenium site in any one of the compounds of this invention and thereby act as a significant impurity inducing n-type conductivity. Selenium is an element from the sixth group of the periodic table and has a radius of 1.17 Å. Other elements from the seventh group of the periodic table have a similar effect. It has been found that chlorine, for example, having a radius of 0.99 Å, also substitutes for selenium and induces n-type conductivity although it is not generally considered to be a desirable significant impurity since it is extremely reactive with moisture and precautions must be taken to keep the atmosphere dry during its introduction. Starting with a compound herein which exhibits p-type conductivity as made, p-n junctions have been produced by diffusing iodine into the solid material. Such p-n junctions have exhibited rectification properties. Manganese having an atom radius of 1.17 Å is also effective as a donor.

Whereas the group VII elements act as significant impurities probably by substitution for selenium, which hypothesis is premised primarily on the range of atomic radii involved, conductivity type has also been affected by use of elements which in accordance with the present theory must, upon incorporation, occupy the site of the silver atom. For example, it has been found that cadmium and zinc from group II and antimony from group V all have the effect of inducing n-type conductivity in AgSbSe<sub>2</sub>. Assuming that doping proceeds by the substitution methods which is fairly well established, in the in-

stance of the common semiconductor systems it is hypothesized that since each of these materials produces n-type conductivity and must, therefore, introduce an excess of electrons, and since the only element in the compound having fewer electrons is silver that, therefore, substitution must be for that element. That such substitution in fact takes place is further to be expected in view of the range of atomic radii involved, the atomic radius of cadmium, zinc, antimony and silver being in that order 1.41 Å., 1.25 Å., 1.41 Å. and 1.34 Å.

That the conductivity effect of the presence of an excess of antimony is due not merely to the excess but rather to a substitution for the group I element contained in the compound is premised primarily on the conclusions reached on crystal structure studies made on  $\text{AgSbSe}_2$  and on other semiconductor systems. See, for example, L. Pincherle and J. M. Radcliffe, *Advances in Physics*, volume 5, No. 19, July 1956, page 271.

In common with experience gained from studies conducted on other semiconductor systems, it is found that addition of impurities in amounts of over about 1 percent by weight may result in degenerate behavior. Amounts of significant impurity which may be tolerated are generally somewhat lower and are of the order of 0.01 atomic percent. However, it is not to be inferred from this observation that semiconductor devices of this invention must necessarily contain 99 percent or more of a particular semiconductive compound disclosed herein. It is well established that desirable semiconductive properties may be gained by the combination of two or more semiconductive materials, for example, for the purpose of obtaining a particular energy gap value. For this reason, any one of the compounds herein may be alloyed with any other such compound or with any other semiconductive material without departing from the scope of this invention.

This invention is limited to semiconductor systems utilizing one or more of the compounds of the formula  $\text{AgXSe}_2$  where X is antimony, bismuth or arsenic and to devices utilizing such systems.

Although the invention has been described primarily in terms of specific doping elements and specific devices, it is to be expected that the wealth of information gained through studies conducted on other semiconductor systems may be used to advantage in conjunction with this invention. Refining and processing methods, as also diffusion and alloying procedures and other treatment known to those skilled in the art, may be used in the preparation of materials and devices utilizing the compounds herein, without departing from the scope of this invention. Other device uses for the compounds herein are also known.

What is claimed is:

1. A semiconductor system containing a compound in accordance with the composition  $\text{AgXSe}_2$  in which X is

an element selected from the group consisting of Sb, Bi and As.

2. A semiconducting material consisting essentially of at least 99 percent by weight of a compound of the composition  $\text{AgXSe}_2$  in which X is an element selected from the group consisting of Sb, Bi and As.

3. A semiconducting material in accordance with the composition of claim 2 containing up to 0.01 atomic percent of a significant impurity.

4. A semiconducting material in accordance with claim 3 in which the significant impurity is an element of group VII of the periodic table in accordance with Mendelyev.

5. A semiconducting material in accordance with claim 4 in which the significant impurity is iodine.

6. A semiconducting material in accordance with claim 4 in which the significant impurity is manganese.

7. A semiconducting material in accordance with claim 3 in which the significant impurity is an element of group II of the periodic table in accordance with Mendelyev.

8. A semiconducting material in accordance with claim 7 in which the significant impurity is zinc.

9. A semiconducting material in accordance with claim 7 in which the significant impurity is cadmium.

10. The semiconductor system of claim 1 in which 99 percent by weight of other material therein contained exhibits semiconducting properties.

11. A semiconductor device consisting essentially of a body of material of the system of claim 1 and having at least one rectifying contact made thereto.

12. The device of claim 11 in which rectification is by means of a point-type electrode making contact with the said body.

13. The device of claim 11 in which the rectifying contact is made by means of a p-n junction.

14. A semiconductor transducing device comprising a body of material of the composition of the system of claim 1, said body containing at least one p-n junction.

15. A semiconductor transducing device comprising a body of material of the composition of the system of claim 2, said body containing at least one p-n junction.

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