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GERMANIUM ELEMENTS AND METHODS OF PREPARING SAME

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This invention relates to germanium elements for use in signal translating devices and to methods of preparing such elements.

Germanium when produced in purities of the order of 99.9 per cent containing limited quantities of certain impurities is an extrinsic semiconductor, that is conduction occurs as a result of the impurities present which cause electrical-charge carriers to exist in the material in the unbound state. Thus it has been found that elements lying in the third column of the periodic table having three valence electrons and of about the same atomic dimensions as germanium substitute for a germanium atom in the crystal lattice and accept an electron from the filled energy band in order to complete the tetrahedral bond in the germanium lattice. A "hole," the equivalent of a positive charge carrier is thus left in the filled band and under the proper conditions is freely transferred through the lattice thereby permitting a flow of positive charges. Materials which have this effect are identified as "acceptor significant impurities" or "acceptors" and the germanium in which conduction by holes normally occurs is identified as a P-type, it also being characterized by the greater conductivity which occurs between it and a metallic electrode when the body is positive relative to the electrode than when negative. Similarly, negative charge carriers, "electrons," may be created in the lattice by adding materials whose atoms have five valence electrons (appearing in the fifth column of the periodic table) which as a result of the tetrahedral bond add an electron which may be free to the conduction band. Such materials are known as "donor significant impurities" or "donors" and germanium in which the normal conduction occurs by electrons is known as N-type.

Semiconductive translators are known which rely principally on the injection of charge carriers of the type opposite those normally present in the semiconductive body for their method of operation. These injected carriers change the conductivity of the material in the vicinity in which they are injected and also add current carriers which flow to an electrode, identified generally as a "collector," biased in the reverse or low conductivity direction. Semiconductive triodes wherein the carriers of the type opposite those ordinarily present in the body are injected from one electrode known as an "emitter" to modify the current flowing in a "collector" circuit are shown in several applications including that of J. Bardeen and W. H. Brattain, Serial No. 33,466, filed June 17, 1948, now Patent 2,524,035 issued October 3, 1950, that of W. Shockley, Serial No. 35,423, filed June 26, 1948, now patent 2,569,347 issued September 25, 1951, and that of G. L. Pearson, Serial No. 50,896, filed September 24, 1948, now Patent 2,560,594 issued July 17, 1951. Another form which these units may take wherein the absorption of light by germanium results in the production of free electron-hole pairs and the charge is separated and collected as a result of an electric field created by a collector, is disclosed in the application of J. N. Shive,

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Serial No. 85,788, filed April 6, 1949, now Patent 2,560,606 issued July 17, 1951.

In the above and related types of devices, the structure and operating characteristics are limited to a large extent by the tendency of the injected carriers to recombine with the carriers of opposite type thereby effectively removing them from the material. Thus, in a unit employing an N-type semiconductive body wherein the normal carriers are electrons the injected holes may combine or be filled with the electrons present before they reach the collector. The rate at which these injected charge carriers recombine is known as the "recombination rate" the reciprocal of which is the "lifetime" of the carrier.

This tendency toward recombination is present in two forms, volume recombination, and surface recombination, which as the names imply occur within the volume of the material and at the surface thereof respectively, and may be represented by the formula $S = S_v + S_s$ where S is the over-all recombination rate, S_v is the volume recombination rate and S_s is the surface recombination rate.

One general object of this invention is to improve the electrical characteristics of germanium bodies.

Another object is to reduce surface recombination of charge carriers in germanium.

A further object is to facilitate the treatment of the surface of germanium whereby the lifetime of the charge carriers is increased.

One feature of this invention resides in applying thin films of insoluble hydrolysis products formed by the reaction of metallic halides with water to germanium surfaces.

Another feature of this invention resides in preparing a germanium surface to obtain a high polish, and applying thereto an electrophoretic treatment with the surface positive, in sols of insoluble hydrolysis products formed by reacting metallic halides with water.

Referring now to the detailed treatment of germanium bodies to obtain long charge carrier lifetimes by the reduction of the surface recombination rate, it is apparent from the formula for the over-all recombination rate ($S = S_v + S_s$) that if the material employed has a high volume recombination rate the over-all rate will be high even with a low surface recombination rate; therefore it is desirable to employ germanium with a low volume recombination rate. One such material having long volume lifetimes is prepared in the form of single crystal according to the process disclosed in the application of J. B. Little and G. K. Teal, Serial No. 138,354, filed January 13, 1950, now Patent No. 2,683,676, which comprises drawing crystals from molten germanium in the form of rods by partly immersing a seed crystal of germanium in the melt and slowly withdrawing it vertically therefrom through an annular jet of hydrogen, hydrogen and water vapor, or an inert gas such as helium or helium with suitable additions of water vapor.

Since surface recombination depends upon the amount of surface present in the element, it is desirable to first reduce the amount of surface as much as possible. This may be done by highly polishing the faces of the element at which surface recombination would be important. The following polishing technique has been found to give a mirror finish to germanium and to remove all cracks and surface strains which occur in cutting the element. After the material is cut from the ingot or crystal, usually being in the form of slices, wafers, rods or filaments, it is ground on a plate glass surface with 600 mesh Carborundum mixed with water to a wet paste, then washed and ground with a paste of the same material on twill jean cloth laps followed by a wash. The final mechanical polish is effected with levigated alumina on felt laps after which the surface is subjected to a chemical etch or polish.

One particularly satisfactory chemical polish is dis-

closed in the application of R. D. Heidenreich, Serial No. 164,303, filed May 25, 1950, now Patent No. 2,619,414, comprising 15 parts by volume of glacial acetic acid, 25 parts of concentrated nitric acid (specific gravity 1.42), 15 parts of 48 per cent hydrofluoric acid and 1 part liquid bromine. This etch may be applied at room temperature for about two minutes after which the surface is washed in high purity distilled water or alcohol.

The rate of recombination of carriers at the surface can be reduced in accordance with this invention by applying a thin film of insoluble hydrolysis products formed by reacting a metallic halide or a combination of metallic halides with water to the surface. This film may be applied, for example, by an electrophoretic treatment in a sol of the material.

One such process which is effective on both N and P-type germanium surfaces involves the application of antimony oxychloride (SbOCl) from a fresh sol prepared by adding a small amount of antimony trichloride (SbCl_3) to distilled water. For example, a suitable sol may be prepared by adding 0.2 gram antimony trichloride to 100 cubic centimeters of distilled water. The reaction $\text{SbCl}_3 + \text{H}_2\text{O} \rightarrow \text{SbOCl} + 2\text{HCl}$ takes place to produce a white precipitate of SbOCl . In addition to the large precipitated particles which settle out, there is produced a colloidal solution of very fine SbOCl particles bearing a negative charge.

These negatively charged particles may be applied to the germanium surface by plating them from the sol at room temperature onto germanium as an anode by cathaphoresis. This may be done by making the germanium 1.5 volts positive with respect to a cathode which may be nickel or some other metal. The measured lifetime of injected carriers increases with the time of plating up to at least 5 minutes, the length of treatment determining the amount of SbOCl deposited. Suitable treatments have been effected by depositing films having thicknesses of from a few atomic layers to a few hundred angstroms. After the film has been deposited it can be rinsed in either high purity distilled water or in alcohol prior to associating the germanium body with its cooperative elements in the unit in which it is to be used.

Germanium single crystal surfaces of N-type material treated in accordance with the above procedure have exhibited hole lifetimes as long as 400 microseconds while similar surfaces treated by a two-minute immersion in SbOCl sol with no voltage applied had lifetimes of the order of 40 microseconds as compared with 6 microseconds for a mechanically worked surface and 18 microseconds for a surface treated as above through the chemical polish and alcohol rinse step. A shorter cathaphoric treatment of one minute at 1.5 volts in SbOCl sol gave a surface with a lifetime of 83 microseconds. These treatments produce similar results for electron lifetimes in P-type germanium.

The treatment to produce long hole and electron lifetimes is not limited to antimony oxychloride. It has been found that sols of other insoluble hydrolysis products formed by the reaction of metallic halides with water when applied to germanium surfaces by a cathaphoretic treatment in which the surface is an anode also markedly increase the lifetimes by decreasing the rate of surface recombination. The sols of bismuth oxychloride (BiOCl), stannous oxchloride ($\text{SnCl}_2 \cdot \text{SnO}_2 \cdot 3\text{H}_2\text{O}$) as well as sols of the oxybromides, oxyiodides, and oxyfluorides of tin, bismuth and antimony have all exhibited improved measured lifetimes. As adverse effects may result from the presence of certain materials on the surface of the germanium it has been found advantageous to employ materials of chemical purity in preparing these sols.

It is to be noted that the above treatments are surface treatments and are not intended to alter the bulk characteristics of the germanium to which they are applied. While the underlying reason for the long surface lifetime

phenomenon has not been established with full certainty, the following theory has been suggested and is presented here as an aid to an understanding of the invention. In order for a hole and an electron to combine they must be able to give up their energy to the crystal lattice. One region in which this energy can quite readily be transferred to the lattice is at the surface of the germanium. However, in order that recombination can take place, both holes and electrons must be present in the surface region. It has been theorized that the surface layer of this treatment provides some means of reducing the number of one of the types of carriers in the vicinity of the surface thereby reducing the rate of recombination. This result might be effected by the creation of an electric field on the surface which attracts carriers of one sign to the region of the surface and repels carriers of the opposite sign. Thus, considering that the layer creates a negative field, for N-type germanium having electron charge carriers normally and injected holes, the electrons will be repelled from the surface region while the holes will be attracted and the separation of the two will reduce the opportunity for their recombination. In the case of P-type germanium the same treatment is employed to reduce recombination; here the injected electrons are prevented from reaching the region of the surface while the holes normally present in such material are attracted to that region. Although holes are present to some degree throughout P-type material their presence with the injected electrons in the bulk is not such a condition as lends itself readily to recombination since there is only a limited means available to absorb the energy which would be given up by such combinations. This explanation will also fit the situation occasioned by a positive surface field where the electrons would be drawn to the surface and the holes repelled from that region, and such may be the case.

What is claimed is:

1. A germanium body having an adherent surface layer consisting essentially of at least one of the oxyhalides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.
2. A germanium body having a surface bearing an adherent layer consisting essentially of colloidal particles of at least one of the oxyhalides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.
3. A germanium body having a surface bearing an adherent layer consisting essentially of colloidal particles of at least one of the oxychlorides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.
4. A germanium body having an adherent surface layer consisting essentially of at least one of the insoluble oxychlorides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.
5. A germanium body having a surface bearing an adherent layer consisting essentially of colloidal particles of at least one of the oxybromides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.
6. A germanium body having an adherent surface layer consisting essentially of at least one of the insoluble oxybromides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.
7. A germanium body having a surface bearing an adherent layer consisting essentially of colloidal particles of at least one of the oxyiodides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.
8. A germanium body having an adherent surface layer consisting essentially of at least one of the insoluble oxyiodides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.
9. A germanium body having a surface bearing an

adherent layer consisting essentially of colloidal particles of at least one of the oxyfluorides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.

10. A germanium body having an adheret surface layer consisting essentially of at least one of the insoluble oxyfluorides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.

11. A germanium body having an adherent surface layer consisting essentially of antimony oxychloride.

12. A germanium body having a surface bearing an adherent layer consisting essentially of colloidal particles of antimony oxychloride.

13. A germanium body having an adherent surface layer consisting essentially of bismuth oxychloride.

14. A germanium body having a surface bearing an adherent layer consisting essentially of colloidal particles of bismuth oxychloride.

15. A germanium body having an adherent surface layer consisting essentially of antimony oxyiodide.

16. A germanium body having a surface bearing an adherent layer consisting essentially of colloidal particles of antimony oxyiodide.

17. A germanium body having an adherent surface layer consisting essentially of antimony oxybromide.

18. A germanium body having a surface bearing an adherent layer consisting essentially of colloidal particles of antimony oxybromide.

19. A germanium body having an adherent surface layer consisting essentially of bismuth oxyfluoride.

20. A germanium body having a surface bearing an adherent layer consisting essentially of colloidal particles of bismuth oxyfluoride.

21. The method of treating the surface of a germanium body to reduce the rate of electron-hole combination which comprises coating the surface with an adherent layer consisting essentially of at least one of the oxyhalides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.

22. The method of treating the surface of a germanium body to reduce the rate of electron-hole combination which comprises coating the surface with an adherent layer consisting essentially of colloidal particles of at least one of the oxyhalides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.

23. The method of treating the surface of a germanium body to reduce the rate of electron-hole combination which comprises immersing the surface in a colloidal suspension consisting essentially of at least one of the oxyhalides of the metals selected from the group consisting of antimony, bismuth, and stannous tin.

24. The method of treating the surface of a germanium body to reduce the rate of electron-hole combination which comprises cataphorically depositing a layer consisting essentially of the insoluble hydrolysis products of the reaction of at least one of the halides of the metals selected from the group consisting of antimony, bismuth, and stannous tin with water.

25. The method of treating the surface of a germanium body to reduce the rate of electron-hole combination which comprises immersing the surface in a sol consisting essentially of the insoluble hydrolysis products of the reaction of at least one of the halides of the metals selected from the group consisting of antimony, bismuth, and stannous tin with water, and applying a positive potential to said surface relative to an electrode in said sol.

26. The method of treating the surface of a germanium body to reduce the rate of electron-hole combination which comprises polishing the surface, and coating the surface with a layer consisting essentially of the insoluble hydrolysis products of the reaction of at least one of the halides of the metals selected from the group consisting of antimony, bismuth, and stannous tin with water.

27. The method of treating the surface of a germanium body to reduce the rate of electron-hole combination which comprises polishing the surface of germanium, immersing the surface in a sol consisting essentially of the hydrolysis products of the reaction of at least one of the halides of the metals selected from the group consisting of antimony, bismuth, and stannous tin with water, and applying a positive potential to the surface relative to an electrode in said sol.

28. The method of treating the surface of a germanium body to reduce the rate of electron-hole combination which comprises mechanically polishing the surface, chemically polishing the surface with an etchant consisting essentially of acetic acid, nitric acid, hydrofluoric acid and bromine, rinsing the surface, immersing the surface in a sol consisting essentially of the hydrolysis product of the reaction of at least one of the halides of the metals selected from the group consisting of antimony, bismuth, and stannous tin with water, applying a potential of about one and one-half volts, germanium positive, to the surface and continuing the cataphoretic deposition process for from 0.5 to 5 minutes.

29. A germanium body having an adherent surface layer consisting essentially of at least one of the oxyhalides of antimony.

30. A germanium body having an adherent surface layer consisting essentially of at least one of the oxyhalides of bismuth.

31. A germanium body having an adherent surface layer consisting essentially of at least one of the oxyhalides of stannous tin.

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