April 25, 1950 R. M. WHALEY 2,505,633

ALLOYS OF GERMANIUM AND METHOD OF MAKING SAME

Filed March 18, 1946

Fig. 1.

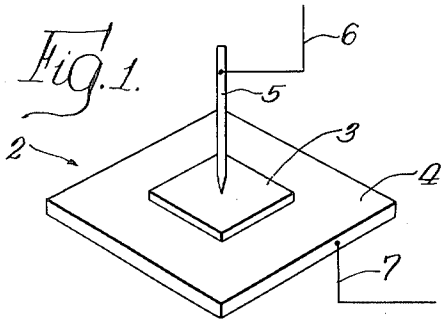


Fig. 3.

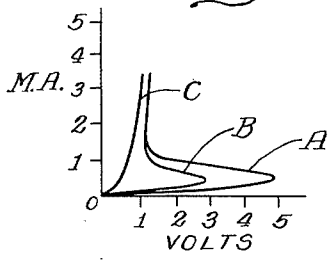


Fig. 2.

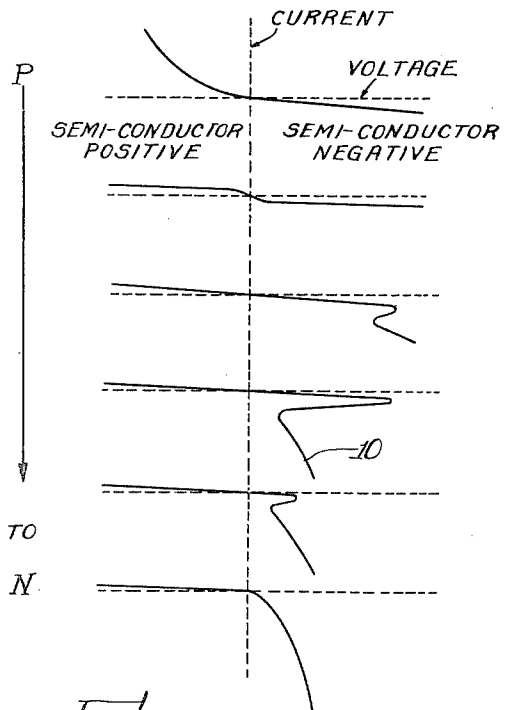


Fig. 4.

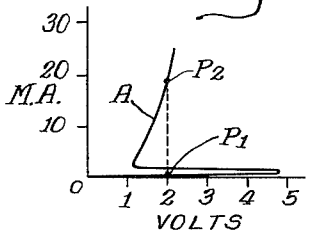


Fig. 6.

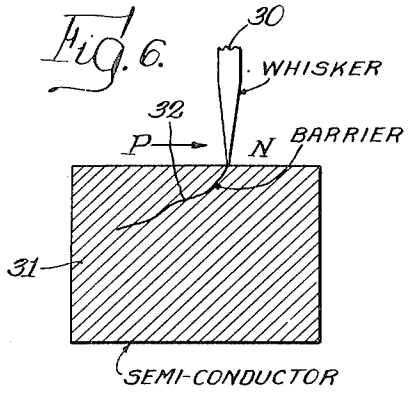
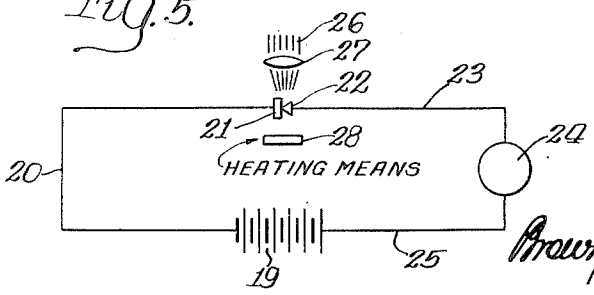


Fig. 5.



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UNITED STATES PATENT OFFICE

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ALLOYS OF GERMANIUM AND METHOD OF MAKING SAME

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Application March 18, 1946, Serial No. 655,225

9 Claims. (Cl. 148—13)

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My present invention relates to an improvement in alloys of germanium and method of making the same, which alloys have utility as semi-conductors in electrical devices sensitive to externally applied energy.

My present invention, as will appear in greater detail hereinafter, concerns the combining of the gas, nitrogen, with germanium so that the resultant material is not an alloy in the common meaning of that word. However, for purposes of the present disclosure, it will be understood that the word alloy means to include a union of germanium and nitrogen, the combination of which exhibits electrical properties such as are found in metals and semi-conductors.

As above indicated the alloys of my invention have use in electrical devices with one of such devices known to me being a device sensitive to externally applied energy, such as either light or heat, or combinations of light and heat. The device is constructed like a point contact type rectifier in which a whisker or electrode has contact with the surface of a semi-conductor, the latter in the present case being an alloy of my invention.

In the copending application of Karl Lark-Horovitz and myself, Serial No. 604,744, filed July 13, 1945, there is disclosed various alloys of which germanium comprises the principal constituent. As was disclosed in the mentioned application, the germanium was obtained from the Eagle-Picher Company of Joplin, Missouri, and had a purity of at least 99%. The various elements which were to be formed into the germanium alloy semi-conductor were then combined, mixed, or alloyed with the germanium so as to form the type of unit herein to be described. From these alloys rectifiers may be made which present high resistance to current flow in one direction therethrough, and a low resistance to current flow in the other direction. In that application, the semi-conductors disclosed are all of the type upon the surfaces of which points may be found which exhibit N-type characteristics, i. e., they present high resistance to current flow across a rectifying contact when the semi-conductor is positive and the contacting metal electrode or whisker is negative, and a lower resistance when the polarity of the applied voltage on the semi-conductor and electrode is reversed. My invention

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proceeds upon the further development of certain of the alloys of the aforesaid application so that they are deliberately caused to have many regions thereon exhibiting P-type electrical characteristics, i. e., regions that produce rectifying contacts of polarity opposite to that of the N-type region, in addition to the already present large number of N-type regions.

In the copending application of Seymour Benzer, Serial No. 651 271, filed March 1, 1946, there is disclosed and claimed a device constructed in the form of a point contact type rectifier and comprising a semi-conductor which may, if desired, be made of the alloys of my invention. In the latter application it is disclosed for germanium-alloy semi-conductors having both P-type and N-type regions, that point contacts made in the transitions regions between the P-type and N-type regions exhibit a change in current-voltage characteristics when subjected to externally applied energy in the form of light or heat, or both. The devices of that application exhibit the sensitive characteristics when the potential on the semi-conductor is negative and the potential upon whisker positive. It has been discovered, for such polarity of the semi-conductor and electrode, that selected points of contact in the transition region of the semi-conductor exhibit the following characteristics when exposed to light or at a temperature of predetermined values. As the current is progressively increased, the resistance to current flow in the low resistance direction is positive up to a certain point hereinafter referred to as the "trigger peak," after which the differential resistance becomes negative for a certain range of currents and then becomes positive again. Points may be found in the transition region of the semi-conductor where the trigger peak occurs at small currents of the order of 0.1 to 5 milliamperes and at voltages of 0.1 to 25 volts depending upon the selected point of contact on the surface of the semi-conductor. This range of values may be observed with the device in the dark and at a temperature of the order of 25° C.

This trigger peak is sensitive to externally applied energy in the form of light especially in the near infra red, and to heat and combinations of both light and heat. For a selected point of contact which has a trigger peak at

about 5 volts in the dark at ambient room temperature, and with that temperature being maintained substantially constant, it has been found that the trigger peak will be reduced to about 3 volts when white Mazda light of an intensity of about 0.5 lumen/cm.^{2} is projected on the selected point of contact. If stronger light of about 2 lumen/cm.^{2} white light is projected on the contact the differential negative resistance is entirely removed. The same effects may be observed with the device maintained in the dark upon progressively increasing the temperature of the rectifying contact. For the above selected illustrative point of contact the trigger peak at 5 volts occurs at a temperature of about 25° C. Upon increasing the temperature to about 50° C. the trigger peaks occur at about 3 volts. Further increase of the temperature to the order of 100° C. causes the complete removal of the negative resistance characteristic. This behavior of the device may be utilized to make a relay type of photosensitive or thermosensitive cell. The device may, for example, be biased to closely approach the trigger peak of a selected point of contact. Now when light or heat of a predetermined amount is applied to the selected point of contact the trigger peak disappears so that a trigger effect occurs with the current jumping to a much higher value. A jump in current by as much as a factor of 500 has been obtained with selected points of certain of the germanium crystals made of the alloys of my invention. Upon removal of the light or heat the electrical characteristics return to their original forms and values.

However, if a D. C. potential is applied to the semi-conductor and electrode it must be removed for an instant to effect restoration of the original current-voltage characteristics. When alternating current is used, however, the restoration is automatically achieved each cycle. The use of alternating current is possible since the current-voltage characteristic when the semi-conductor is positive and the contacting whisker or electrode is negative remains at a relatively high resistance even under changes of light and heat on the selected point of contact producing the aforesaid typical changes in the current-voltage characteristic on current flow in the other direction. Thus the current produced will automatically be rectified when the device is actuated by externally applied energy either in the form of light or heat.

It is an object of my invention to provide germanium-nitrogen alloys having P-type and N-type regions with transitions regions therebetween within which point contacts can be made which are sensitive to externally applied energy.

A further object of my invention is to provide a method of making germanium-nitrogen alloys having a large number of P-type and N-type regions with transition regions therebetween wherein point contacts can be made, the electrical characteristics of which are sensitive to externally applied energy.

A further object of my invention is to provide a method of making alloys of germanium-nitrogen having a large number of P-type and N-type regions.

The above and other objects and advantages of my invention will appear from the detail description.

Now, in order to acquaint those skilled in the art with the manner of practicing the method of my invention and producing the alloys thereof,

I shall describe a preferred embodiment of the method and resulting alloys of my invention.

In order to provide a clear understanding of my invention, I shall describe the use alloys have in constructing a device sensitive to externally applied energy shown in the accompanying drawings in which—

Figure 1 is a diagrammatic view of a device sensitive to externally applied energy in which the semi-conductor element thereof is made of an alloy of my present invention;

Figure 2 is a graphic illustration of the progressive changes in the electrical characteristics for point contacts made at different points in a transition region between P-type and N-type regions on the surface of a semi-conductor made of an alloy of my invention;

Figure 3 is a graph illustrating the effect of light or heat upon the electrical characteristics of the device of Figure 1 having the semi-conductor element thereof made of an alloy of my invention;

Figure 4 is a graph similar to Figure 3 with the current scale reduced and illustrating the trigger effect which may be obtained with the device of Figure 1;

Figure 5 is a typical simple circuit diagram in which the device of Figure 1 may be embodied; and

Figure 6 is a diagrammatic illustration of what is believed to be the physical structure of the semi-conductor of Figure 1 showing the whisker or electrode having contact with a barrier between the P and N-type regions in the semi-conductor element accounting for the external energy sensitive character of the device.

In a preferred embodiment of the method of my invention I propose to impregnate germanium with nitrogen at pressures ranging from about 2 mm. to 760 mm. mercury at temperatures in the neighborhood of 1000° C. to 1100° C. for about 5 to 15 minutes. This alloy and the method of preparing the same is disclosed in the above referred to copending application of Karl Lark-Horovitz and myself, to which reference may be had. As stated in the said copending application, Serial No. 604,744, the impregnation is carried out with the germanium being in the molten state. The melting point of germanium is known to be 958.5° C. As disclosed in that application, points of contact may be readily found on the surface of such an alloy which exhibit N-type rectification. Also as disclosed in that application, it is preferable in practice to grind a flat surface on the alloy and then etch the surface to facilitate finding of good points of contact. One suitable abrasive for grinding a surface of the alloy is 600 mesh alumina (Al_2O_3). Various etching solutions and techniques may be used and it has been found that an etch consisting of four parts of hydrofluoric acid (48% reagent), four parts distilled water, two parts concentrated nitric acid, and 200 milligrams $Cu(NO_3)_2$ to each 10 cc. of solution is satisfactory. This solution will produce a satisfactory etching of the ground alloy surface in about one to two minutes. The allow is then, in accordance with the novel step of my present invention, heat treated in vacuum at about 650° C. to 750° C. for about one-half hour to one hour. This latter step is additional to the steps in the method of preparation of the germanium-nitrogen alloys set forth in the above application of Lark-Horovitz and myself. I have found that this heat treatment is particularly effective in producing many P-type regions on

the surface of the alloy as distinguished from the appearance of mostly N-type regions thereon prior to the latter step. In the transition regions between the P and N-type regions thus created, a substantial number of sensitive points may be found, facilitating the construction therefrom of the devices sensitive to externally applied energy to be hereinafter referred to and forming the subject matter of the above referred to application of Seymour Benzer.

Referring now to the drawings, I have shown in Figure 1 an electrical device 2 comprising a semi-conductor 3 made of a germanium-nitrogen alloy in the manner above described. The semi-conductor 3 is preferably soldered to a conductor plate 4 of any metal or alloy having good electrical conductivity characteristics. An electrode or whisker 5 is formed with a pointed end which makes point contact with the surface of the semi-conductor 3. The electrode or whisker 5 may be made of metal or an alloy having good electrical conductivity and preferably of good mechanical strength. Several metals that have been found satisfactory for use in making the electrode or whisker are tungsten, platinum, copper, iron, gold, silver, manganese, tantalum, nickel, zinc, molybdenum, zirconium, lead, and platinum-iridium alloys. The electrode 5 preferably is provided with a sharp pointed end having a tip diameter of the order of 0.0001 to 0.001 inch. These electrodes may be readily made by forming suitable points on wires of about 0.005 inch in diameter. A lead 6 is suitably connected to the electrode 5 and a lead 7 has connection with the conductor plate 4 upon which the semi-conductor 3 is mounted.

As above mentioned, the points on the surface of the semi-conductor having properties sensitive to both light and heat may most often be found in the transition regions separating N and P-type areas or regions. Figure 2 of the drawing illustrates typical curves of the changes in the current-voltage characteristics of rectifying contacts made at points progressing from a P-type region to an N-type region. For purposes of constructing an electrical device sensitive to externally applied energy, the characteristic indicated by curve designated by the reference numeral 10 has been found to be the most suitable.

The effect of light with the temperature being held constant at about 25° C. is illustrated in Figures 3 and 4 of the drawing. In these graphs the current-voltage characteristic for a selected point of contact between the electrode 5 and the semi-conductor 3, while being maintained in the dark, is shown by the curve A. It will be observed that in Figure 4 the current ordinate is considerably reduced with respect to the current ordinate of Figure 3. Curve B illustrates the current-voltage characteristic when white light of about 0.5 lumen/cm.^{2} is projected on the point of contact between the whisker 5 and the selected point on the semi-conductor 3. Curve C illustrates the current-voltage characteristic when white light of about 2 lumens/cm.^{2} is projected on the selected point of contact of the whisker with the semi-conductor from which it will be seen that the trigger peak is completely removed. It will be observed from the curves A and B of Figure 3 and curve A of Figure 4 that as the current through the device is progressively raised, the resistance is positive up to a certain point, herein designated as the "trigger peak" after which the differential resistance becomes negative for a certain range of values and then

becomes positive again. This trigger peak occurs at small currents of the order of 0.1 to 5 milliamperes and points of contact may be found in the alloys of my invention at voltages in a range of about 0.1 to 25 volts. Also for such points the currents in the negative resistance region range from the order of 0.1 to 10 milliamperes at 0.1 to 25 volts, and the second positive resistance ranges from 50 to several hundred ohms.

Reference may now be had to Figure 4 which illustrates the trigger effect characteristic. Under a D. C. bias of about 2 volts there is for most practical purposes no passage of current of any appreciable amount. However, if white light of about 0.7 lumen/cm.^{2} is projected on the selected point of contact, the current immediately jumps to a value of about 20 milliamperes which is sufficient to effect operation of a relay or other electrical apparatus with which the device may be connected in circuit. The current jump is shown in Figure 4 with the point P_1 illustrating the current at a D. C. bias of 2 volts across the selected point of contact of the whisker 5 with the semi-conductor 3 and with the device in the dark. Now when light of about 0.7 lumen/cm.^{2} is projected on the selected point of contact, the current immediately jumps to the point P_2 on curve A providing for current flow of the order of 20 milliamperes. The above set of values, it will be understood, are only representative of one set of conditions obtainable on a selected point of contact between the electrode and semi-conductor, and it will be understood that other points of contact having characteristics lying within the above ranges may be found by probing of the transition region of the alloys of my invention. Of course, different D. C. bias voltage may be used within the range above set out for selected points on the semi-conductors.

As a general observation it may be stated that for a contact of relatively good sensitivity to light, the voltage of the trigger peak will fall to one-half of its dark value when it is illuminated with about one lumen per square inch of white light. This corresponds to the intensity of illumination produced by a 100 watt Mazda lamp at a distance of one foot. Only light which falls within the immediate neighborhood of the point contact is effective. Therefore, a much weaker source of illumination may be used provided the light is condensed to a small spot. As is usual in photosensitive devices, the sensitivity varies with the wave length of the light used. The device herein described shows maximum sensitivity in the neighborhood of 1.3 microns, which falls in the near infra-red region of wave length. It is of practical interest to know that the spectral intensity distribution of a Mazda lamp has its maximum in the same region of wave length.

The effect of temperature with the illumination held constant is also illustrated by curves A, B and C of Figures 3 and 4. With the device maintained in the dark at a temperature of about 25° C., points may be found on the alloys of my invention which will give the current-voltage characteristics shown by curve A of the values previously stated and shown in these figures. As the temperature is raised to the order of 50° C. for the selected point of contact, the current-voltage characteristics will be that of curve B. As the temperature is raised still further to that of the order of 100° C., the current-voltage characteristics will be that of curve C.

It is believed that from the above it will be clear that the device may also be caused to be

actuated by combinations of applied light and heat.

A typical circuit embodying the device of Figure 1 is shown in Figure 5 of the drawings. As shown in this figure, the circuit comprises a source of alternating current or direct current 19 from which a lead 20 extends to a germanium-nitrogen alloy semi-conductor 21 of the type above described having the properties previously referred to. An electrode 22 makes a rectifying contact with the semi-conductor 21. A lead 23 extends from the electrode 22 to a current responsive device 24 which in turn is connected by lead 25 to the source of current 19. A source of light 26 which may be concentrated by a lens 27 is directed upon the selected point of contact between the electrode 22 and the semi-conductor 21. The intensity of the light may be varied in any suitable manner to actuate the device, which in turn will alter the current flow through the current responsive device 24. The latter device may, for example, be a current indicator or a relay to be actuated by the current flow, for example, of the value P_2 of Figure 4. It is understood that a heat source or means 28 may be substituted for the light source 26, as above explained, to provide a thermosensitive device within the ranges above set forth to control the current responsive device 24 or, if desired, various combinations of both light and heat from sources 26 and 28 may be utilized to effect actuation of the device.

In Figure 6 I have shown diagrammatically an arrangement of an electrode 30 having contact with a selected point on the semi-conductor 31. It is thought that the germanium-nitrogen alloys of my invention have barriers, such as designated by numeral 32, extending between and separating P-type and N-type regions of the semi-conductor. It is believed, although at present not definitely ascertained, that the energy sensitive characteristics occur when the electrode has contact with the semi-conductor at the point where the barrier meets the surface of the semi-conductor. At any event, points may be found in the transition region between N-type and P-type regions in the alloys of my invention which possess the electrical effects above described and in the ranges stated.

Further, little is known of the effect impurities such as nitrogen have in the germanium. It is thought that the nitrogen is ionized and accounts in some manner for the conductivity of the alloy. However, it is quite feasible that the effect could be due to a change in lattice structure of the germanium due to the presence of the nitrogen impurity together with further changes due to the heat treatment which account for the results obtained.

I claim:

1. The method of making a semi-conductor having transition regions between N-type and P-type regions of the character described comprising alloying nitrogen with germanium having a purity of at least 99% at pressures ranging from 2 mm. to 760 mm. Hg at a temperature of 1000° C. to 1100° C. for 5 to about 15 minutes to form an alloy having an abundance of said N-type regions, and then heating the alloy thus formed in vacuum at a temperature of 650° C. to 750° C. for about one-half hour to one hour to produce a plurality of said P-type regions in said allow.

2. The method of making a semi-conductor having transition regions between N-type and P-type regions of the character described comprising alloying nitrogen with germanium having a purity of at least 99% at pressure ranging from 2 mm. to 760 mm. Hg at a temperature of 1000° C. to 1100° C. for 5 to about 15 minutes to form an alloy having an abundance of said N-type regions, etching a surface on the alloy thus formed, and then heating the alloy thus formed in vacuum at a temperature of 650° C. to 750° C. for about one-half hour to one hour to produce a plurality of said P-type regions in said alloy.

3. An alloy consisting of germanium having a purity of at least 99% and nitrogen characterized by nitrogen having been impregnated in the germanium at pressures ranging from 2 mm. to 760 mm. at a temperature of 1000° C. to 1100° C. for 5 to about 15 minutes and the alloy thus formed having then been subjected to heat treatment in vacuum at a temperature of 650° C. to 750° C. for about one-half hour to one hour to provide transition regions the resistance of which is sensitive to externally applied energy, such as heat or light, between P-type and N-type regions thereof of the character described.

4. An alloy consisting of germanium having a purity of at least 99% and nitrogen characterized by nitrogen having been impregnated in the germanium at pressures ranging from 2 mm. to 760 mm. at a temperature of 1000° C. to 1100° C. for 5 to about 15 minutes, with a surface of the alloy thus formed having been etched, and said alloy then having been subjected to heat treatment in vacuum at a temperature of the order of 650° C. to 750° C. for about one-half hour to one hour.

5. The method of making a semi-conductor having transition regions between N-type and P-type regions of the character described comprising alloying nitrogen with germanium having a purity of at least 99% at pressures ranging from 2 mm. to 760 mm. Hg at a temperature of 1000° C. to 1100° C. for 5 to about 15 minutes to form an alloy having said N-type regions, etching a surface on the alloy thus formed with an etch comprising four parts hydrofluoric acid (48% reagent), four parts distilled water, two parts concentrated nitric acid and 200 milligrams $Cu(NO_3)_2$ to each 10 cc. solution for about one to two minutes, and then heating the alloy thus formed in vacuum at a temperature of 650° C. to 750° C. for about one-half hour to one hour to produce said P-type regions in said alloy.

6. The method of making a semi-conductor having points thereon between N-type and P-type regions of the character described, the electrical resistance characteristics of which points change in response to externally applied energy, said method comprising alloying at pressures ranging from 2 mm. to 760 mm. Hg nitrogen with germanium having a purity of at least 99% by impregnation of said germanium, in the molten state, with said nitrogen to form an alloy having said N-type regions, grinding a surface of the alloy thus formed, etching said surface of said alloy, and then heat-treating the alloy thus formed in vacuum at temperatures in the range between 650° C. and 750° C. to produce therein said P-type regions.

7. The method of making a semi-conductor upon which point contacts may be made, the resistance of which is varied by varying the intensity of externally applied energy comprising, etching a surface of an alloy consisting of germanium having a purity of at least 99% and nitrogen, and then heat-treating the alloy in vacuum at a temperature in the range between

650° C. and 750° C. for one-half hour to one hour.

8. The method of making a semi-conductor upon which point contacts may be made, the resistance of which is varied by varying the intensity of externally applied energy comprising, grinding a surface of an alloy consisting of germanium having a purity of at least 99% and nitrogen, then etching said surface of said alloy, and then heat-treating said alloy in vacuum at a temperature in the range between 650° C. and 750° C. for one-half hour to one hour.

9. In a method of making a semi-conductor having transition regions between N-type and P-type regions of the character described, from an alloy consisting essentially of nitrogen and

of germanium having a purity of at least 99%, said alloy having only N-type regions therein, the step of heat treating said alloy in vacuum at a temperature of 650° to 750° C. for about one-half hour to one hour, whereby said P-type regions are formed.

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REFERENCES CITED

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

Journal of the American Chemical Society, vol. 52 (1930), pages 5160–5164.