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2,685,728

TRANSLATING MATERIAL AND METHOD OF MANUFACTURE

Filed Feb. 21, 1949

FIG. 1

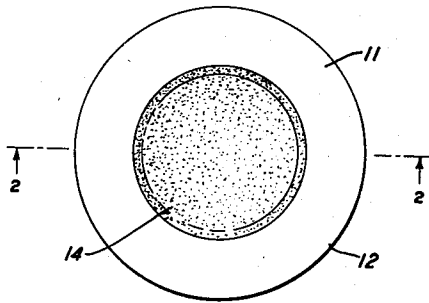


FIG. 4

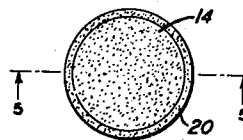


FIG. 2

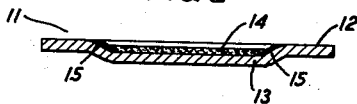


FIG. 5

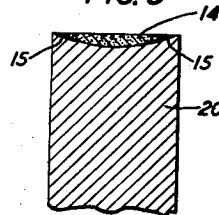


FIG. 3

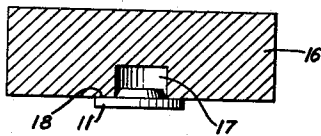


FIG. 6

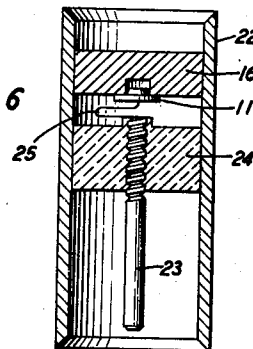
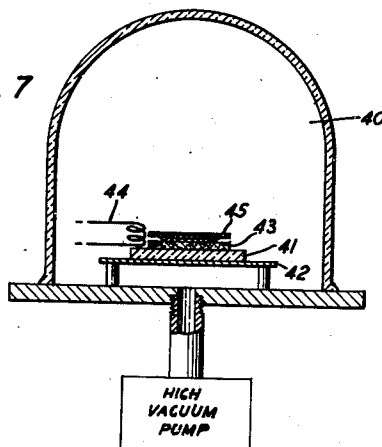


FIG. 7



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## UNITED STATES PATENT OFFICE

2,685,728

TRANSLATING MATERIAL AND METHOD  
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6 Claims. (Cl. 29—25.3)

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This invention relates to electrical translating materials and devices and to methods of making them.

More particularly, the invention relates to the manufacture of translating devices having silicon portions which exhibit rectifying properties when combined with limited area contacts.

The objects of this invention are to improve the electrical efficiency of translating devices employing silicon elements, to improve the mechanical connection of such elements to metallic backing pieces, to make practicable the formation of small silicon elements on a limited area of a backing member, and to simplify the techniques of manufacture of such silicon translating devices.

In the past few years, development of translating devices employing various semiconductor materials has been greatly accelerated by the extension of the signaling art into the ultra-high frequency range where waves of a few centimeters are employed. At the present stage of the development, these translating devices are usually of the point-contact type having one or more fine wires mounted so their free ends engage the surface of an element having suitable rectifying properties. Silicon crystals containing significant traces of other elements which modify their electrical characteristics exhibit these rectifying properties and provide a conveniently handled element when mounted upon a highly conductive backing piece.

Recent developments have indicated that best results are attained with high purity silicon containing in excess of 99.9 per cent of the pure material with traces of significant impurities in solution. Heretofore these metal mixtures have been cast into ingots in the manner set forth for example in R. S. Ohl Patent 2,402,839 issued June 25, 1946.

In producing rectifying elements from this type of material, the ingot is cut into slabs from which are cut wafers which in turn are secured to highly conductive backing members. These silicon elements are then secured to a terminal block by various bonds as exemplified in G. W. Pickard Patent 1,137,714 of April 27, 1915, wherein a metallic cup containing fusible metal is heated and the rectifying element placed therein and secured by the freezing of the fusible

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metal. Another commonly employed bond is formed by first electroplating the back of the element with a metal such as nickel or rhodium and then soldering the plated element to a suitable base by means of any desirable solder.

When the elements are formed by either of the above-mentioned methods it is necessary that the silicon be separated from its ingot. This can be done by crushing, or as previously described, by cutting and grinding pieces from the ingot. When rectification is to be accomplished at very high frequencies, it is desirable to use thin, small area silicon wafers. The fabrication of the bulk material into sufficiently small dimensions for these frequencies by the aforementioned methods is extremely difficult. There is no control of the size of the elements produced by crushing, and in the cutting and grinding operation the crystallites of which the bulk material is made up tend to chip out along the cutting edges. Thus the formation of silicon rectifying elements into dimensions of the order of less than one millimeter heretofore has been impractical.

Silicon has been deposited on tantalum chemically by heating a tantalum body in a controlled atmosphere of hydrogen and silicon tetrachloride. Such a process is disclosed in J. A. Becker Patent 2,438,892 of April 6, 1948. This process coats the entire exposed area of tantalum with silicon and cannot be conveniently limited to a particular portion of a tantalum body. Further, the gases remaining after the deposition of the silicon must be removed under controlled conditions to prevent its contamination.

The present method of forming silicon bodies for translating devices presents an advantage over the old processes in that it provides a means whereby very small silicon elements can be formed either on a small backing member or a limited area of a larger member. Further it produces no by-products which might contaminate the silicon and therefore the apparatus employed is considerably simplified over that of the silicon deposition processes of the prior art.

The method of forming silicon body portions on a limited area of a tantalum backing member in accordance with this invention produces a very active P-type silicon surface having extremely high peak-back voltage when employed with a

limited area contact as a rectifier, and both P and N-type silicon elements with up to 50 volts peak-back voltage, when combined with tungsten point contacts, have been produced. Briefly, this method comprises placing particles of high purity silicon on a prefabricated tantalum back member of any size and of various forms, and heating the tantalum to melt the silicon. The process is carried on a high vacuum of the order of  $10^{-5}$  millimeters or better. The tantalum is first heated sufficiently to start the fusing of the silicon, and on this initial fusing, which does not occur until the temperature of the tantalum is well above the fusing temperature of silicon, the tantalum is cooled to below the fusing temperature of silicon to stop any reaction between it and the silicon. The tantalum is then reheated slowly until the silicon fuses uniformly over its entire surface. Since the second melting does not require as high a temperature as was employed in the initial melting, no chemical reaction occurs between the silicon and the tantalum. Upon cooling, the silicon crystallizes and the surface is ready to be employed in a translating device.

It is to be understood the designation "P-type silicon" used throughout this specification refers to silicon which passes current readily only when it is positive, while "N-type silicon" passes current readily only when the silicon is negative.

Other features and advantages of the invention will be discussed more fully in the following detailed description which is more clearly and fully understood when read with reference to the accompanying drawings in which:

Fig. 1 is a plan view of one form which can be employed in the construction of a rectifying element in accordance with this invention;

Fig. 2 is a cross-section of the element of Fig. 1 taken along the line 2—2 of Fig. 1;

Fig. 3 is an elevation of a holder for an element such as that disclosed in Fig. 1 adapted for use in a translating device of the type disclosed in Fig. 6;

Fig. 4 is a plan view of another form in which the rectifying element of this invention can be made;

Fig. 5 is a cross-section of the element of Fig. 4 taken along the line 5—5;

Fig. 6 is an elevational view partially in cross-section of a translating device including one of the rectifier elements of this invention; and

Fig. 7 illustrates the apparatus used in applying the silicon to the metal backing.

Limited area rectifier elements constructed in accordance with this invention may assume various forms and sizes all of which include a high purity silicon body fused on a tantalum body which forms the back contact for the device. The structure of these devices can most readily be understood by reference to the process by which they are manufactured.

The tantalum back contact for the silicon rectifier element must be of extremely high purity since any impurities which might be present would contaminate the silicon by combining or going into solution with it during the manufacturing operation. The element shown in Figs. 1 and 2 employs a dished tantalum body formed from sheet tantalum and that of Figs. 4 and 5 employs a tantalum rod dished on its end. In the operation of forming these and other types of back contacts, the high purity tantalum is subject to contamination from handling and

from the tools employed. Therefore, it is necessary to clean the tantalum as a preliminary step in the forming of the rectifier element. As an example, where a steel punch and die are employed to form the tantalum body as in Fig. 1, it is first cleaned in chloroform to remove the grease, which might be deposited on it during handling, then dried and heated in diluted sulphuric acid to remove any traces of iron which might have adhered to the body from the die and punch.

Particles of high purity silicon are then placed in the clean tantalum cup. Most satisfactory results have been obtained by employing finely divided silicon supplied by E. I. duPont de Nemours and Company having a purity considerably in excess of 99.9 per cent produced by pyrolytic reduction of silicon tetrachloride on zinc at high temperatures. The elements in a typical sample of this material include:

|                 | Per cent |
|-----------------|----------|
| Silicon -----   | 99.95    |
| Iron -----      | .03      |
| Calcium -----   | .005     |
| Sodium -----    | .005     |
| Copper -----    | .001     |
| Manganese ----- | .001     |
| Magnesium ----- | .001     |

In some samples traces of zinc, silver and aluminum have been found, all of these in quantities less than .03 per cent.

The element is then placed in an apparatus such as that shown in Fig. 7 and the tantalum is heated to fuse the silicon. This apparatus comprises a high vacuum system including an evacuated chamber 40 containing a vacuum of the order of  $10^{-5}$  millimeters or better which is established and maintained by a high vacuum pump represented by the labeled block. A quartz plate 41 is mounted within this chamber on a platform 42 and supports a graphite disc 43 which in combination with a surrounding high frequency induction coil 44 (shown adjacent the disc for purposes of clarity) serves as an induction heater. The tantalum body 45 is placed on this graphite disc and heat is applied by the application of high frequency current to the induction coil.

In order to produce a satisfactory rectifying element the heating process must be carefully controlled. Under the application of excess heat the tantalum and silicon combine chemically to form a brittle non-rectifying compound which obviously is extremely undesirable for the purpose of this invention. In order to fuse the silicon particles it is necessary to raise the temperature of the tantalum backing to about 1600° C. which is well above the fusing temperature of silicon. When this fusing begins an absorption of heat is evident indicating an endothermic chemical reaction occurring between the silicon and tantalum. If this reaction were allowed to continue, it would destroy the element for rectifying purposes as pointed out above. Therefore, the power is removed from the heating coil as soon as the silicon begins to fuse thereby cooling the element and preventing more than a very limited reaction between the tantalum and silicon. When the temperature of the element is cooled sufficiently to stop the reaction, this has been found somewhat below the fusing temperature of silicon, heat is again applied to the tantalum body and it is slowly brought up to the fusing temperature of silicon, about 1420° C., and

held at that temperature until the remaining silicon particles are fused. When the silicon is completely fused it is slowly cooled to crystallize it into a very high purity body having a smooth surface which exhibits excellent rectifying properties.

The silicon point contact rectifiers of the prior art have been limited in their peak-back voltages to a range extending from about 2 to 15 volts. Rectifiers produced by this method exhibit much higher peak-back voltages with tungsten point contacts, 50 volts being not at all uncommon for both P and N-type silicon, and some P-type silicon elements having peak-back voltages of up to 200 volts with tungsten point contacts have been produced by employing selected particles from the lots of material supplied by E. I. duPont de Nemours and Company and fusing them to the tantalum back contact in the manner described above. These particles which can be formed into high peak-back voltage material are selected by their appearance which differs from the crystalline appearance of the remainder of particles in the lot as received from the supplier in that their surface appears sintered and appears to be coated with a dirty brown film.

Referring now to the drawing, the rectifying element of Figs. 1 and 2 which may be utilized in various forms of translating devices and particularly point contact rectifiers, comprises a tantalum body 11 having a peripheral flange 12 included for convenient mounting of the element and a dished portion 13 providing a receptacle for the silicon rectifying body 14. The small area in which the reaction between the silicon and tantalum occurs, referred to in the preceding description of the process, is represented by the shaded area 15 in the cross-section view of Fig. 2 (greatly exaggerated in size for purposes of clarity). This element can be conveniently employed in the conventional type of point contact rectifier disclosed in Fig. 6 by mounting it on the metallic contact holder 16 and securing it so that the dished portion 13 rests in the bore 17 by some convenient method such as spotwelding the flange 12 to the lip 18 on the end of the holder.

Fig. 4 shows a modified form of rectifier element which may conveniently be employed where it is desirable to have a silicon rectifier body 14 mounted on the end of a rod 20. This structure might be of particular advantage in the construction of a rectifier for use in wavelengths of a few millimeters since it avoids the necessity of fabricating the bulk materials into satisfactorily small dimensions or machining a chemically formed unit to reduce the area of the silicon rectifying body. Units for these frequencies must often have dimensions of the order of less than one millimeter and are therefore difficult to handle and to form by the processes known in the prior art while no such limitations are imposed on the silicon body of Figs. 4 and 5 and therefore they can quite conveniently be produced and mounted in the small spaces which are required for millimeter wave reception.

An assembled rectifier of the point contact type which might employ the rectifier element of this invention is illustrated in Fig. 6. This rectifier comprises a cylindrical metallic shell or housing 22, a crystal assembly, and a contact assembly. The metallic cylinder 22, which also serves as an electrical shield, may be made either of steel or beryllium copper and may be given a thin coating of tin. The crystal assembly is that

shown in Fig. 3 and comprises a silicon surface on the tantalum body 11 secured to the solid conductive cylinder 16. The spring contact wire assembly of the rectifier comprises a metallic pin 23, an insulating cylinder 24 molded around the pin 23 or otherwise permanently affixed thereto, and a short length of tungsten contact wire 25 secured in conductive relationship to one end of the pin 23. The crystal supporting cylinder 16 and the insulating cylinder 24 are inserted in opposite ends of the housing 22 and are advanced towards each other until the wire 25 engages the surface of the silicon element to form a limited area rectifying contact with the silicon. These elements are maintained in their proper relationship by a force fit between the cylinders 16 and 24 and the housing 22.

What is claimed is:

1. An element for use in rectifying devices exhibiting peak-back voltages of the order of 200 volts when employed in combination with a limited area tungsten contact, comprising a tantalum member, a layer of a compound of tantalum and silicon in intimate contact with said tantalum member, and a layer of high purity silicon in intimate contact with and superposed on said layer of tantalum and silicon, said silicon being fused and crystallized in a vacuum from particles having a purity in excess of 99.9 per cent and a brownish sintered appearance.

2. The method of making material for use in electrical translating devices which comprises mechanically placing solid particles of silicon having a purity in excess of 99.9 per cent on a tantalum surface, heating the tantalum in a vacuum to a temperature above that at which tantalum and silicon react until said silicon commences to fuse, cooling said tantalum to stop any chemical reaction between it and said silicon, reheating said tantalum to completely fuse said silicon, and cooling said tantalum to crystallize said silicon.

3. The method of making material for use in electrical translating devices which comprises shaping a tantalum base to form a cup surface on one side, mechanically placing solid particles of silicon having a purity in excess of 99.9 per cent in said cup portion, mounting the silicon and tantalum in a vacuum, heating the tantalum to a temperature above that at which tantalum and silicon react to cause an initial fusing of the silicon, cooling the silicon to stop any chemical reaction between it and the tantalum, slowing reheating the tantalum to a temperature sufficient to complete the fusion of the silicon, and thereafter slowly cooling the tantalum to crystallize the silicon.

4. The method of making an element for use in electrical translating devices which comprises, mechanically placing solid particles of silicon having a purity in excess of 99.9 per cent on a body having a tantalum surface, heating the body in a vacuum to about 1600° C., cooling the body to below the fusion temperature of silicon upon the initiation of an endothermic chemical reaction between the silicon and tantalum surface to stop said reaction, reheating said body to about 1420° C. to completely fuse the silicon, and cooling said body to crystallize the silicon.

5. An element for an electrical translator comprising a tantalum base member, a layer of a compound of tantalum and silicon in intimate contact with said base member, and a layer of high purity silicon in intimate contact with and superposed on said layer of tantalum and silicon.

6. The method of making an element for an electrical translator which comprises placing silicon on a tantalum surface, heating the tantalum in a vacuum until said silicon commences to fuse and form a compound of tantalum thereby establishing an intimate heat transfer relationship between said tantalum and the remaining unfused silicon, cooling said tantalum to stop any chemical reaction between it and said silicon, maintaining said tantalum above the fusion temperature of silicon and below the temperature at which tantalum and sili-

con react, and cooling said tantalum to crystallize said silicon.

## References Cited in the file of this patent

## UNITED STATES PATENTS

| Number    | Name            | Date          |
|-----------|-----------------|---------------|
| 1,826,955 | Ruben -----     | Oct. 13, 1931 |
| 2,235,051 | Thompson -----  | Mar. 18, 1941 |
| 2,438,892 | Becker -----    | Apr. 6, 1948  |
| 2,452,577 | Kotterman ----- | Nov. 2, 1948  |