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2,978,618

SEMICONDUCTOR DEVICES AND METHOD OF MAKING THE SAME

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Fig. 1.

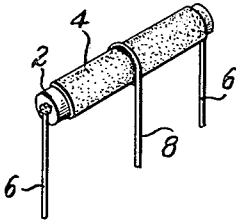


Fig. 2.

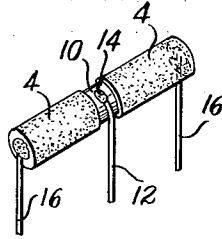


Fig. 3.

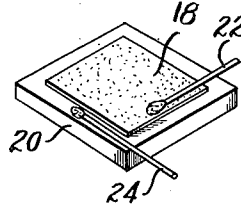


Fig. 4.

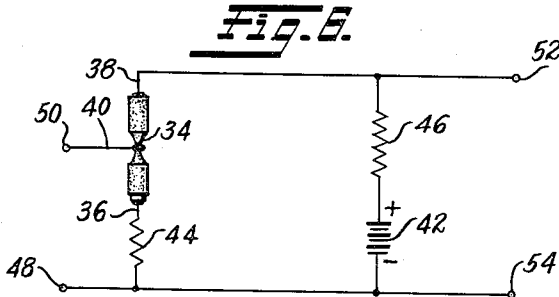
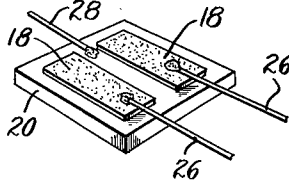


Fig. 6.

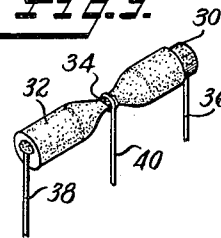


Fig. 7.

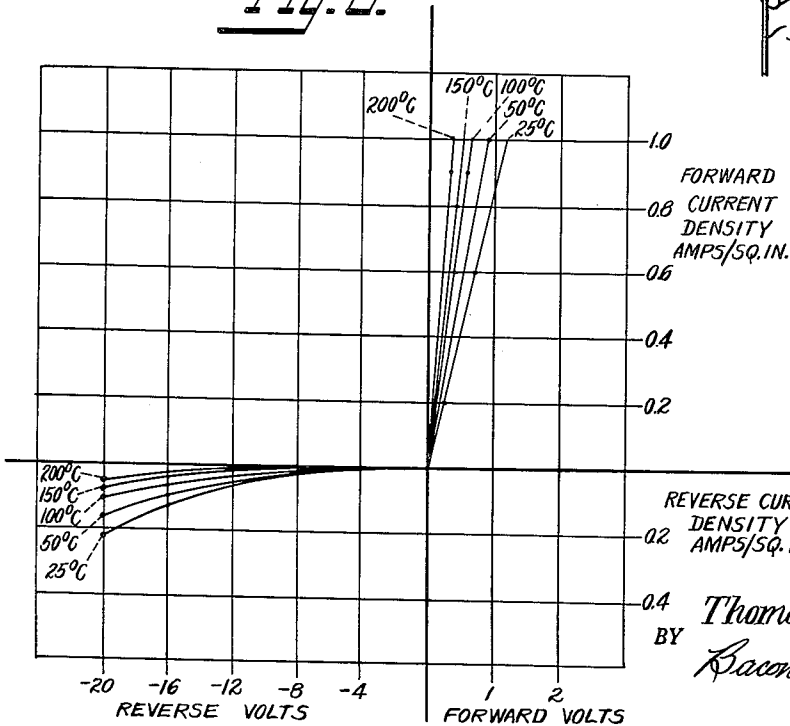
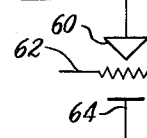


Fig. 8.



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SEMICONDUCTOR DEVICES AND METHOD OF MAKING THE SAME

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8 Claims. (Cl. 317—235)

This invention relates to semiconductor devices, which may be in the form of rectifiers or amplifiers.

The present invention concerns a new semiconductor material and method of making the same wherein a compound of titanium is formed as a surface on a titanium base, thus producing an ohmic junction employable as a rectifier and also providing a structure capable of being used as an amplifying device. In general the invention comprises a device of the type set forth wherein the titanium compound is produced by packing a body of titanium in a powdered material and heating the same to a sufficiently high temperature to produce the desired reaction at the surface. The powdered material may be powdered carbon, in which case a surface of titanium carbide is formed, or it may be a powdered manganese dioxide, in which case the semiconductive coating is titanium dioxide.

The carbide coating may be formed on the titanium by placing the titanium part of any shape in a covered solid carbon container with no loose carbon and then heating the combination to a sufficiently high temperature to produce the multi-crystalline coating on the titanium piece. Heating the titanium in the presence of carbons or hydrocarbons by many techniques will produce the same multicrystalline carbide surface.

After the coating is formed on the article a portion of the coating may be removed to expose the titanium base, and by making an electrical connection to the base and another to the coating, a rectifier is formed wherein the resistance to current flow in one direction is extremely high while resistance to current flow in the other direction is very low.

The invention further contemplates the production of an amplifying device functioning in the same manner as a conventional vacuum tube. A body of titanium having the carbide or oxide surface described may be connected in a circuit with a cathode connection at one end and an anode connection at the other end and wherein a control electrode is connected to the coating intermediate the cathode and anode connections. When the control electrode is biased negative relative to the cathode connection, the device is "cut off" and no current flows. As the control electrode is driven, more positive current begins to flow from the cathode connection to the anode connection in proportion to the change in bias on the control electrode. The cathode connection may be made either to the coating or to the titanium base, although better results accrue if the cathode connection is made to the titanium base.

It is therefore an object of this invention to provide semiconductor devices that are inexpensive to make and adaptable to manufacture in large quantities in a short time.

Another object of the invention is to provide a semiconductor device as set forth which is readily adapted for use as a rectifier or an amplifying device.

Still another object is to provide a semiconductor de-

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vice of the type set forth that is dependable and operative throughout an extremely wide range of temperatures.

A further object is to provide a rectifier and/or amplifier structure which can be easily and readily designed and constructed for any desired power and frequency conditions.

A still further object of the invention is to provide a novel method for producing the semiconductor device described.

10 An additional object is to provide a semiconductor device and method of making the same wherein the device may be produced repetitively with known and predictable characteristics.

Other objects and advantages will become apparent to those skilled in the art as the description proceeds in connection with the accompanying drawings, wherein:

Figs. 1 through 4 illustrate different forms of rectifier device constructed in accordance with the present invention;

20 Fig. 5 is a perspective view of a semiconductor amplifying device embodying the present invention;

Fig. 6 is a circuit diagram illustrating a manner of employing the amplifying device of Fig. 5;

25 Fig. 7 illustrates the schematic symbol for the amplifying device of Fig. 5; and

Fig. 8 is a chart illustrating the flow of current in different directions through the rectifier of the present invention and shows how that flow is affected by temperature changes.

30 The semiconductor device is a body of titanium with a surface coating of either titanium carbide or titanium dioxide. The titanium employed need not be of extremely high purity since excellent results have been obtained with titanium having a purity no greater than 98.5%. The devices may be of any suitable geometric shape but it will be found to be more expedient to use sheet stock or round wire or rod.

When titanium is milled, rolled or otherwise handled, contamination of its surface occurs and this contamination must be removed and the titanium rendered absolutely clean before forming a coating thereon. A satisfactory method of cleaning the titanium surface is to etch it with a dilute hydrofluoric acid comprising 1 part of hydrofluoric acid to 20 parts of distilled water. The acid may be as strong as 1 part of acid to 5 of water or as weak as 1 part of acid to 50 parts of water, depending upon the particular surface and the speed desired.

45 After the surface has been completely etched in the dilute acid the titanium must be thoroughly rinsed in distilled water. There must be no trace of acid and rinsing should continue until all traces of acid have been completely washed away.

50 The cleaned titanium body is placed in a carbon container and packed tightly in a body of powdered carbon completely surrounding the titanium. The titanium parts may also be placed in a covered solid carbon container or in a hydrocarbon atmosphere. The container of titanium and powdered carbon are then placed in a furnace and brought to a temperature of 1000° C. and held at that temperature for the desired length of time. The length of the heating cycle depends largely on the size of the piece being treated and the thickness of the semiconductive coating desired. Obviously, if a large container with many pieces is being treated, the time in the furnace must be increased. After the articles have been brought to a temperature of 1000° C. they may be held at this temperature for 30 minutes, which produces a titanium carbide surface of substantial thickness.

70 Thereafter the containers with their contents are cooled to room temperature, then removed and all loose carbon is gently brushed from the surface of the article. The

particular form of carbon is not critical in that all forms of carbon thus far tried have produced titanium carbide surfaces exhibiting the characteristics herein described although the total resistance in the forward direction varies with different forms of carbon and the form of carbon may be so chosen that the forward resistance of a rectifier, for example, may be of the order of 10 ohms/cm. up to 5,000 megohms/cm.

Exactly the same procedure is employed in forming a titanium dioxide semiconductor except that the materials are placed in a porcelain container rather than a carbon container and the titanium pieces are packed in powdered manganese dioxide instead of powdered carbon. The materials are brought to the same temperature and held for the same period of time and produce a titanium dioxide coating having semiconductor characteristics.

The surface of the titanium carbide articles was found to be materially improved when anodized, which improved surface homogeneity. The preferred method of anodizing the carbide surface is to connect the article to be anodized as the anode and use a pure carbon cathode in an electrolyte comprising sodium hydroxide and distilled water. This gives a very homogeneous surface. The anodizing is conducted for a period of time depending upon the type of carbon used to form the carbide and the size and area of the piece to be anodized. It has been found that by placing an ammeter in the anodizing circuit the attainment of the lowest stable reading of the meter indicates completion of the anodizing step. After anodizing the article is rinsed in distilled water and thereafter dried.

Other anodizing electrolytes were successfully used, comprising dilute sodium perborate or dilute sodium tetraborate. Anodizing with the sodium hydroxide, however, was found to be more rapid.

In some forms of the semiconductive device it is necessary that a portion of the semiconductive coating be removed to expose the titanium base for making electrical connections thereto. In those cases the coating is preferably ground from the article and an electrical conductor spot-welded to the titanium. Good contact has been made by spot-welding nickel to the clean titanium but conductors of other metals may also be so employed. Electrical connection to the semiconductive coating may be made in different ways. For example, Woods metal may be sprayed thereon and a conductor soldered to or clamped against the Woods metal to make good electrical contact. Rectifiers made in this way operate very satisfactorily at moderate temperatures but are, of course, limited in their application by the low melting point of the Woods metal. Bismuth was also used as a connector and has proven highly successful because of its higher melting point. The bismuth is applied to the surface by depositing the same thereon from the vapor state in a suitable vacuum chamber and the electrode thereafter clamped against the bismuth to make good electrical contact therewith. Also silver paste or other conductive paste may be employed to cement a conductor to the semiconductive surface to make electrical contact therewith.

A body of titanium provided with the semiconductive surface described and from which a portion of the carbide or oxide has been removed to expose the underlying titanium base was formed into a rectifier by making electrical connection to the titanium base with one electrode and to the coating with another electrode. The combined surface coating and the base metal exhibits rectifying characteristics that are quite stable over a wide temperature range.

Fig. 8 shows the characteristics of a titanium carbide semiconductor in a rectifier arrangement as described. As is evident from the figure, a voltage of approximately one volt will produce current flow in the forward direction as high as one amp. per sq. in. of junction at 25° C.

As the temperature increases current flow in the forward direction increases and current density of one amp. per sq. in. is attained at a forward voltage of less than one-half volt when operated at a temperature of about 200° C. In the reverse direction, on the other hand, a voltage of 20 volts must be applied to attain a current density of $\frac{1}{10}$ amp. per sq. in. at 25° C. Thus the device of this invention exhibits highly efficient and desirable rectifying characteristics. It will also be noted that the rectifying characteristics of the device are improved as the temperature increases.

In Fig. 1 a rectifier device is shown wherein a base body 2 of titanium is provided with the semiconductive surface layer herein described and identified by numeral 4. The surface layer is shown in the drawings in exaggerated thickness for ease of illustration. The layer 4 is ground away from the base metal 2 at the ends of the device and cathode electrodes 6 are shown spot-welded directly to the titanium base 2 at the bare ends thereof. An anode electrode 8 is electrically connected to the surface layer 4 at about the midpoint thereof by being at least partially wrapped around the surface of the body and electrically connected thereto in any of the manners heretofore described, that is, by conductive paste or by being crimped against the spattered or otherwise applied metal coatings referred to.

The rectifier device of Fig. 2 is formed from the same starting body as that of Fig. 1 but the layer 4 was removed from the central portion 10 to expose the base metal and to which a cathode electrode 12 is connected by spot-welding at 14. Anode electrodes 16 are connected to the layer 4 at the ends of the device.

The rectifier devices shown in Figs. 1 and 2 may be connected together in a bridge circuit to constitute a full wave rectifier, in a manner that will be obvious to those skilled in the art. The forward direction may be defined as the direction of maximum current flow when the anode surface is at a plus potential of a battery and the titanium base metal is at the negative potential of the battery. Under such conditions the rectifier conducts whereas it is substantially nonconductive when the polarity is reversed.

Obviously a rectifier may be constructed employing only a single anode and a single cathode connection.

Figs. 3 and 4 illustrate further forms of rectifier wherein the surface layer 18 is formed on a flat titanium plate or section of a flat bar 20. Fig. 3 shows a simple rectifier having a single anode electrode 22 and a single cathode connection 24. Fig. 4 illustrates a device similar to Fig. 3 wherein double anode connections 26 are provided and one cathode connection 28 is made to the base metal 20. In all of the forms of rectifiers shown herein and other forms that will be obvious to those skilled in the art, the total current flowing through the rectifier at any given voltage will be proportional to the total surface area of the semiconductor surface layer on the device. Thus rectifiers capable of handling large currents may be provided by merely increasing the size of the device and the total surface area thereof.

Fig. 5 shows a semiconductor device of the type described heretofore but so constructed that it functions as an amplifier in the same manner as a triode vacuum type. The amplifier of Fig. 5 comprises a main body portion 30 of titanium with a surface layer 32 of either titanium carbide or titanium dioxide, produced in exactly the same manner as described heretofore. In the embodiment shown, however, the body 30 was formed to provide a reduced neck portion 34 at substantially the middle of the body and the semiconductive surface layer 32 formed thereon. A cathode electrode 36 is spot-welded or otherwise electrically connected to the titanium body 30 while an anode or "plate" electrode 38 is electrically connected to the layer 32 at the other end of the device. The connection may be made in any of the manners heretofore described with reference to the rectifier struc-

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tures. A control or "grid" electrode 40 preferably comprises a wire having its end wrapped around the reduced neck 34 and secured thereto in any suitable manner in electrically conductive relation to the surface layer 34.

Fig. 6 shows the amplifier device of Fig. 5 connected in a conventional circuit to serve as an amplifier. In the circuit shown a battery 42 applies a potential difference between the cathode electrode 36 and the anode 38 with the negative terminal of the battery connected to the cathode 36 through a biasing resistor 44. A load resistor 46 is connected in series with the battery 42 and the anode 38. The resistor 44 provides for self-bias of the amplifier in a well-known manner. When current flows through resistor 44, the terminal 48 becomes more negative than the cathode 36. Thus, when terminal 50 of the control element 40 is at the same potential as terminal 48, the control element 40 is more negative than the cathode 36. When the control element 40 is more negative than the cathode 36, the device is biased toward "cut off" and if the bias is sufficiently high no current flows. However, as terminal 50 becomes more positive, a proportional amount of current is permitted to flow from the cathode to the anode 38. Thus a signal applied across the terminals 48-50 results in current flow through the amplifier in proportion to changes in the signal but of much greater intensity. A triode of the type described was found to amplify a signal, applied at 48-50, by several hundred times across output terminals 52-54.

It has also been found that the cathode electrode 36 need not be connected directly to the base titanium, but may be electrically connected to the coating material itself at the cathode end of the amplifier. Such connection and arrangement in the same circuit as shown in Fig. 6 results in signal amplification, although not as satisfactorily as where the cathode is connected directly to the titanium base.

The amplifier need not have the reduced neck portion 34, the control electrode 40 may be connected to a uniform diameter member. However, the transverse section of the device at the point of connection of the control element determines the frequency response of the amplifier. As the transverse sectional area is decreased, higher frequencies are amplified without undue distortion. On the other hand the total power output depends upon the total area of the semiconductive surface 32. Thus an amplifier constructed to handle a reasonably large current at suitably high frequencies would have to have a large surface area but small transverse section at the control electrode. The shape illustrated has those desirable characteristics.

The device may also be provided with a multiplicity of control elements identical to the electrode 40 and function in the same manner as a multigrid vacuum tube. Each of the control elements would be connected in circuit in the same manner as the different grids of a multigrid tube and produce substantially the same results in the circuit. The amplifier of this invention may therefore be readily constructed, in a manner obvious to those skilled in the art, to exhibit any of the characteristics of a conventional vacuum tube.

Fig. 7 shows a schematic symbol representing the triode amplifier described. The portion 60 of the symbol represents the anode, portion 62 represents the control element 40, and portion 64 represents the cathode.

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While a limited number of embodiments of the invention have been shown and described herein, it is to be understood that various modifications may be resorted to within the scope of the appended claims.

I claim:

1. A semiconductor device comprising, a body of titanium having at least a portion of its surface defined by a layer of titanium carbide, at least a portion of said titanium body being exposed for connection to an electrical conductor.
2. A semiconductor device as defined in claim 1 wherein said layer of material is anodized titanium carbide.
3. A semiconductor device comprising, a body of titanium having at least a portion of its surface defined by a layer of material from the class consisting of titanium carbide and titanium dioxide, at least a portion of said titanium body being exposed for connection to an electrical conductor, said body of titanium being elongated and formed with a reduced central neck portion, the entire surface of said body, except one end portion thereof, being said layer of material, a cathode electrode connected to said one end portion, an anode electrode connected to said layer at the other end of said body, and a control electrode connected to said layer at said reduced neck portion.
4. A semiconductor amplifying device comprising a body of titanium having end portions and an intermediate portion of reduced cross section, at least a part of the outer surface of said intermediate portion and one of said end portions comprising a surface layer of material from the class consisting of titanium carbide and titanium dioxide.
5. A semiconductor amplifying device as defined in claim 4 including electrode connections to said surface layer on said one end portion, on said intermediate portion, and to said titanium body at the other end portion.
6. A semiconductor amplifying device comprising, a generally elongate body of titanium, a substantial portion of the outer surface of said body being defined by a layer of material of the class consisting of titanium carbide and titanium dioxide, at least three electrodes connected to said device at the ends and central portion thereof, respectively, at least two of said electrodes, including the one at said central portion, being connected to said layer.
7. An amplifying device as defined in claim 6 wherein said central portion comprises a reduced neck portion of relatively small transverse dimensions.
8. An amplifying device as defined in claim 6 wherein the body of titanium is exposed at one of said ends, one of said electrodes being connected to said exposed titanium.

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