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H. E. HARING
SEMICONDUCTIVE TRANSLATOR

2,816,850

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FIG. 1

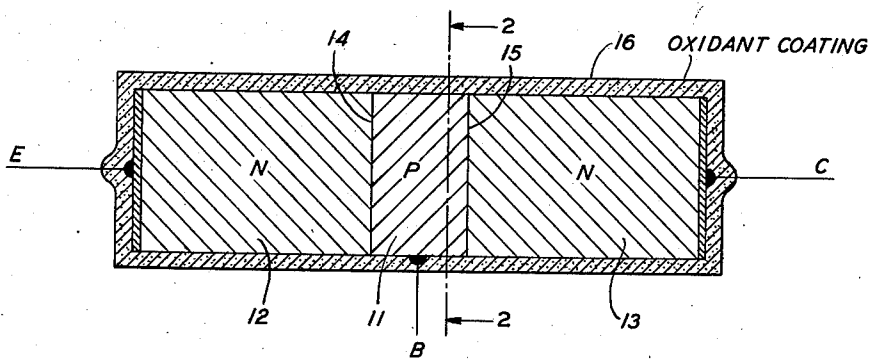


FIG. 2

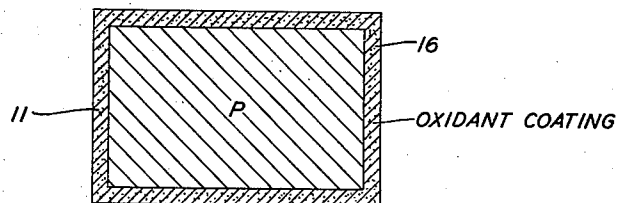
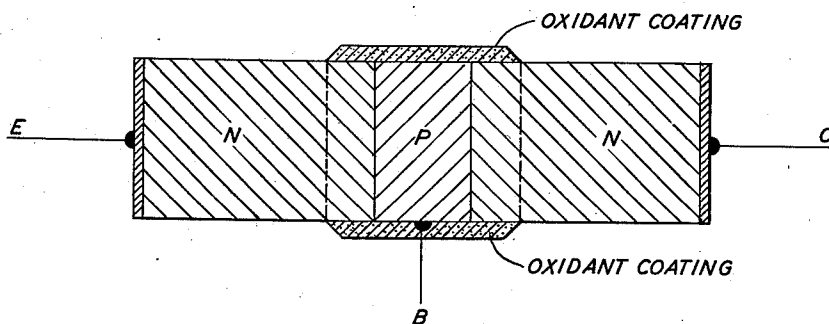


FIG. 3



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SEMICONDUCTIVE TRANSLATOR

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2 Claims. (Cl. 148—33)

This invention relates to semiconductor translating devices and to methods for controlling the surface potential of semiconductors to avoid undesired conducting paths and high reverse currents in devices employing semiconductors.

This invention involves the use on semiconductive devices of particular coatings containing ions of appropriate charge so as to render and maintain the semiconductive surface in the desired condition as to conductivity type.

There is recognition in the art of the degradation of the performance of semiconductor devices resulting from the existence of leakage paths on or near the surface of the semiconductive body. Generally, several schools of thought exist to explain the phenomena of these leakage paths. Material of a general nature relating to surface phenomena of semiconductors, specifically germanium, by W. H. Brattain and J. Bardeen is found in the Bell System Technical Journal, vol. 32, No. 1, January 1953, pages 1-41.

One of the several theories regarding surface phenomena is disclosed in a paper by W. L. Brown appearing in the Physical Review, vol. 91, No. 3, August 1, 1953, page 518. As set forth herein, the occurrence of an extra conducting path, termed a channel, in a crystal of semiconductive material appears to be a consequence of the existence of a charge on the surface of the material. A positive charge on the surface of a P-type crystal induces a net negative charge within the crystal adjacent to the surface. This negative space charge or net deficit of positive charges is provided in part by the loss of holes from the valence band near the surface of the crystal and in part by the presence of electrons in the conduction band. It is these electrons which form a layer of N-type conductivity at the semiconductor surface. Conversely the existence of a negative surface charge on N-type material may result in a layer of P-type conductivity. These conductivity layers then function as extra conducting paths or channels.

According to another widely held view regarding the mechanism controlled by the practice of this invention, the unwanted leakage paths are formed either by the electrons associated with adsorbed positive ions or by the positive holes associated with adsorbed negative ions. In this instance the term "bridges" has been applied to describe the nature of the conductivity. Thus, for example, in the presence of moisture, hydrogen ions are electrolytically discharged on the surface of germanium as a result of the reaction between germanium and water. It appears that the discharged hydrogen is present as positively charged hydrogen ions (H^+) and their associated conductivity electrons. Considering the effect of this increase in the surface concentration of positive ions and conductivity electrons in relation to the type of germanium involved indicates the nature of objectionable leakage paths. At the surface of P-type germanium, which is P-type because it contains a slight

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excess of negative ions, such an increase generally more than neutralizes the slight excess of negative ions which make it P-type thereby establishing an N-type layer on P-type germanium. Such a layer will constitute an extra conducting path or bridge.

Finally, there is some thought which holds that water vapor or moisture itself provides the unwanted surface leakage path. According to this view water vapor adsorbed at the surface provides a leakage path as a result of the conductivity of the moisture itself.

While there is divergence of opinion regarding the underlying theory therefor, the existence of such extra-conducting paths and indications that the environment contributes to their creation is recognized. However, there has been little success, so far as applicant is aware, in controlling or eliminating their deleterious effects. The expedient or hermetic sealing not only is not satisfactory but carries with it disadvantages both from the standpoint of manufacturing techniques, and a less rugged and reliable device structure. In semiconductor devices of the junction-type such as disclosed in Patents 2,569,347, granted September 25, 1951, to W. Shockley, and 2,567,970, granted September 18, 1951, to J. H. Scaff et al., it is apparent that an extra-conducting path will act as a shunt or unwanted leakage path. Thus, in transistors of the junction-type leakage paths across the base zone, such as may be caused by moisture, will render the device extremely unstable and in single junction devices will result in undesirably high reverse currents.

This invention involves a surface treatment of the semiconductive material which comprises the application of a surface coating containing an agent capable of transferring ions of the appropriate charge to the semiconductor surface thereby to control the surface potential and the surface conductivity type, and thus avoid the formation of extra-conducting paths regardless of the moisture content of the ambient atmosphere.

It is an object of this invention to produce semiconductor devices having improved performance characteristics and stability. Specifically, an object is to inhibit the formation of deleterious leakage paths in semiconductor devices of the junction-type.

It is a further object of this invention to facilitate the manufacture of semiconductor devices. More specifically, it is an object to simplify the production of semiconductor devices by eliminating the need for hermetic-sealing or encapsulation.

According to this invention, improved semiconductor devices are attained by applying to the clean external surfaces of the assembled devices a coating of an inhibiting primer. For example, a suitable material for coating junction transistors of the N-P-N type may comprise a mixture of red lead (Pb_3O_4) and a vehicle composed of polyethylene and polybutene. Similarly, zinc chromate or strontium chromate may be substituted for red lead with equally satisfactory results. Other oxidants may also be used. In certain applications it may be found advantageous to apply the coating only to the intermediate or base zone.

A remarkable feature of the structure attained by the practice of this invention is the permanence of the surface stabilization. Devices provided with the inhibitive coatings of this invention remain permanently free from "bridges" regardless of the moisture content of the ambient atmosphere.

A better understanding of the marked success attendant upon this invention may be obtained by a consideration of the best present theory supported by practical investigation regarding the phenomena associated therewith,

Without necessarily subscribing to any one of the aforementioned theories regarding surface mechanisms, it can be said that the existence of channels or leakage paths is attributable to a reversal of conductivity type at the surface, or edge of a layer of one conductivity type, for example an N-type surface layer, on the edge of the P-type layer of an N-P-N germanium junction transistor. Experimentation and theory indicates that this N-type layer is established on the exposed surface of the P-type layer by the adsorption of hydrogen ions (H^+) made available by the reaction between the germanium and moisture upon its surface. Instead of the relatively unsuccessful and costly techniques heretofore followed of attempting to completely exclude moisture, this invention involves the continuous inhibition of the hydrogen-forming reaction and the complete removal of hydrogen adsorbed during the cleaning process, by providing a surface coating of a material which will furnish oxygen for adsorption on the germanium surface. The surface is thereby converted from an unstable N-type to a stable P-type as a result of the replacement of hydrogen ions (H^+) by oxygen ions (O^-). In this way, the effective energy level of the surface is fixed so that the surface conductivity type is the same as that of the adjacent bulk material regardless of the moisture content of the ambient atmosphere. Under such circumstances the formation of the objectionable "bridge" or leakage path is impossible.

Having thus recognized the essentiality of the oxygenated surface condition as (1) an antidote for moisture and the effects of moisture and (2) a stabilizing influence in the absence of moisture, applicant has by his invention proceeded to the attainment of devices wherein this advantageous structure is realized.

A better understanding of this advantageous structure will be had from the following dissertation taken in connection with the drawing, in which:

Fig. 1 shows in section one embodiment of this invention;

Fig. 2 is another section of the embodiment of Fig. 1; and

Fig. 3 shows in section another embodiment of this invention.

Referring to Fig. 1, there is shown in longitudinal section a filamentary semiconductive device of the junction type such as is disclosed in the aforementioned patent to Shockley. The device comprises a layer or zone 11 of P-type material, such as germanium or silicon, interposed between two layers or zones 12 and 13 of N-type material of the same composition as that of the P-type zone, separated respectively by barriers 14 and 15. Connections are made to each layer by electrodes termed emitter (E), collector (C), and base (B). The entire body is encased in a coating 16 composed and applied as hereinafter set forth.

Fig. 2 is a section taken along the line 2-2 of Fig. 1 through the base region to show the adherence of the oxidant coating 16 to the entire periphery of the filament.

Fig. 3 is a longitudinal section of a semiconductive device identical to that of Fig. 1 to which the coating of this invention is applied only over the base region and a portion of the adjacent N-type regions 12 and 13 and including the barriers 14 and 15. Such a technique requires less coating material and leaves the filament ends free of coating for possible fabrication steps.

In preparing semiconductive translating devices in accordance with this invention certain attributes of the inhibiting coating should obtain. The inhibiting agent, such as for example red lead, should be non-conductive. Where a vehicle is used the agent should not react with the vehicle so as to deteriorate the film. In the presence of moisture, the water solubility of the agent should be sufficient to provide a uniform and continuous oxidizing environment at the interface between the semiconductor and the coating. The solubility must not be so great however, as to lead to leaching and consequent electrical leakage. This

is not to be interpreted to indicate that moisture is essential to a proper conditioning of the surface. Stable surfaces of the desired potential and conductivity type can be established and maintained by inhibiting agents such as red lead regardless of the moisture content of the ambient atmosphere. It is desirable even where the semiconductive material is confined within an atmosphere of a high degree of dryness to provide an environment of a definite character in order to firmly fix the surface in the desired condition and thus stabilize device characteristics.

In the coated devices of this invention, the above-mentioned oxidizing agents, namely red lead (Pb_3O_4), zinc chromate ($ZnCrO_4$), and strontium chromate ($SrCrO_4$) are generally employed in the form of powdered pigments. In order to place the inhibitor in contact with the semiconductive surface in as homogeneous a fashion as possible it is usually desirable to provide a vehicle which will enable and maintain such contact. For example, gel-type, hot-melt coatings of the class composed of low molecular weight polyethylene and polybutene mixtures may be used with the pigment type inhibitors heretofore mentioned. Mixture is readily accomplished by adding the polyethylene to the polybutene at a temperature of the order of $160^\circ C$. with thorough stirring. Likewise, the epoxide resins and other well-known paint vehicles may be employed.

In selecting a satisfactory vehicle certain properties should be considered. It should adhere well to the surface of the semiconductive material, hold the inhibiting agent in a finely dispersed condition, have a high electrical resistance and be reasonably impermeable to moisture. In addition, as was mentioned in connection with the inhibitors, reaction between the agent and vehicle is undesirable.

Generally, satisfactory oxidizing coatings containing pigment type oxidants, such as red lead may comprise about 25 percent by volume with the vehicle making up the balance of the finished coating. The percentage range of the oxidant may vary to the extent of fifteen or twenty above and below the above-determined figure.

The preparation of suitable coating material involves conventional practices for the grinding or powdering of pigment type oxidants which may then be mixed with a vehicle of the polyethylene-polybutene type by stirring at a temperature somewhat above the melting point, or by mixing on a paint mill at a temperature either above or below the melting point. The coating may then be applied to the device in any of a number of conventional ways such as dipping, brushing, or spraying at a temperature above the melting point. Generally, where vehicles of the polyethylene-polybutene type are used, elevated temperatures of the order of 100° to $160^\circ C$. are desirable to insure the proper fluidity for convenient mixing, application, surface wetting, adhesion and coverage. If the selected coating material is one of the many varieties usually referred to as paints, the oxidant may be dispersed throughout the vehicle with the aid of a suitable solvent such as toluene and then applied at room temperature to the surface to be coated. Any of the conventional methods of application may be employed. Among the paints which appear to be suitable for the purpose of this invention is one with a polymeric vehicle known as epoxide resin. This vehicle, readily obtainable commercially, is a product of the condensation reaction between bisphenol A and epichlorhydrin. It may be prepared for mixing with the oxidizing pigment by thinning with toluene. Immediately prior to application a curing agent such as triethylamine or diethylene triamine may be added to cross link the polymer and thus harden the film. Baking at 50° to $60^\circ C$. for several hours is recommended.

It will be understood that the semiconductive material should present a proper surface before coating. To this end the material may be subjected to any of the chemical or electrolytic etching techniques known to the

art followed by rinsing in high purity water and thorough drying.

In one specific example, an N-P-N junction-type transistor of germanium as disclosed in the aforementioned patent to Shockley was coated as described below. The coating mixture comprised one part by volume of commercial grade 97 percent red lead to three parts by volume of a mixture consisting of 7.5 percent by weight of low molecular weight polyethylene and 92.5 percent by weight of polybutene. Adequate dispersion of the oxidant was accomplished by thorough mixing at a temperature in the range of 125° to 160° C.

The N-P-N junction device was then dipped in the coating mixture at a temperature of 112° C. Several seconds of immersion was sufficient to bring the device to the temperature of the coating compound and assure thorough wetting. It was then withdrawn, allowed to cool and subjected to initial measurements.

Likewise, a similar procedure was followed, substituting however, zinc chromate (ZnCrO_4) for red lead as the oxidant with completely satisfactory results.

In another specific example, the procedure of the first example was followed using, however, a vehicle composed entirely of polybutene.

In still another specific example, P-type germanium coated with an epoxide resin paint containing red lead was found to maintain a P-type surface regardless of the moisture content of the ambient atmosphere, thus demonstrating that this kind of coating also will stabilize the surface and protect semiconductor devices against moisture and its effects. A repetition of this test, using zinc chromate as the oxidizing agent, yielded the same result.

In further tests it was found that the surface of P-type silicon could be maintained P-type in the presence of moisture by means of the oxidizing coatings of this invention.

It may be found desirable, although not essential, to treat the semiconductor device in an aqueous solution of chromic acid or of a dichromate immediately prior to the coating step. It appears that this pretreatment accelerates establishment of the desired surface condition in those cases where surface cleaning prior to coating has not been of the best quality.

It may be remarked that other combinations may be employed to provide the surface environment in accordance with this invention. Thus, where the semiconductor device is to be enclosed in an envelope such as a metal can, an oxidant such as red lead or a dichromate may be employed suspended or dissolved in dielectric oil.

What is claimed is:

1. A semiconductive body selected from the group consisting of germanium and silicon having two zones of N-type conductivity and an intermediate zone of P-type conductivity, and a surface coating on said zone of P-type conductivity comprising an oxidizing agent selected from the group consisting of red lead, zinc chromate, and strontium chromate, dispersed in a vehicle consisting of a mixture of 8 percent polyethylene and 92 percent polyisobutylene for producing a substantially continuous oxidizing environment at the interface between said layer and said body.
2. A semiconductive body selected from the group consisting of germanium and silicon having two zones of N-type conductivity and an intermediate zone of P-type conductivity, and a surface coating on said zone of P-type conductivity comprising red lead dispersed in a mixture of 8 percent polyethylene and 92 percent polyisobutylene for producing a substantially continuous oxidizing environment at the interface between said layer and said body.

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