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METHOD FOR MAKING DIODES AND PRODUCTS RESULTING THEREFROM

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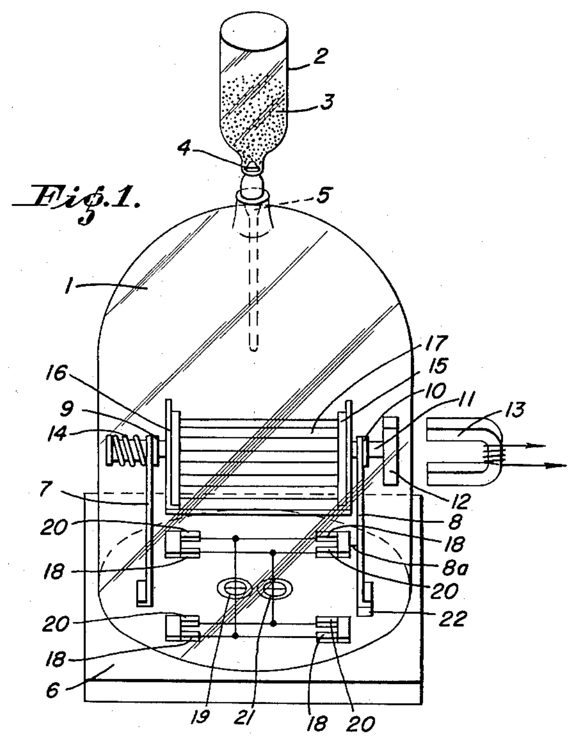
Fig. 1.



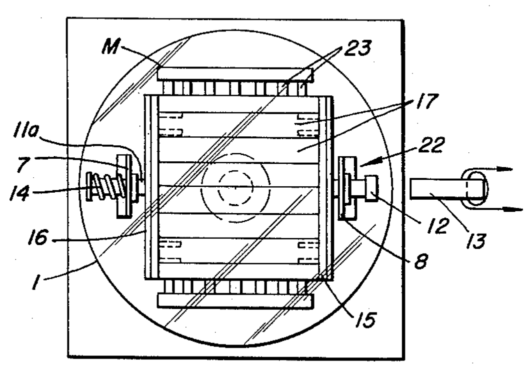


Fig. 2.

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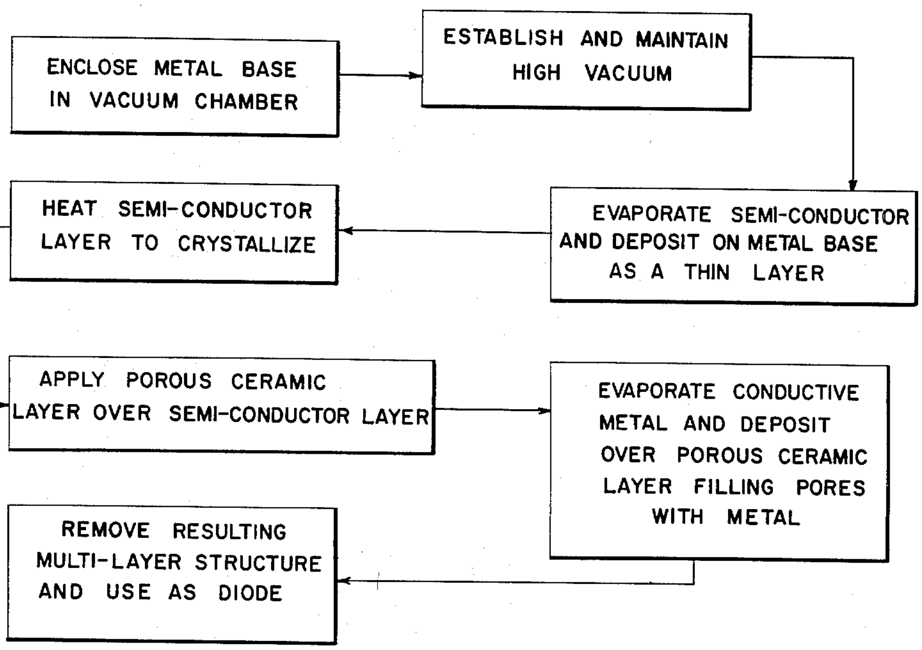

FIG 3

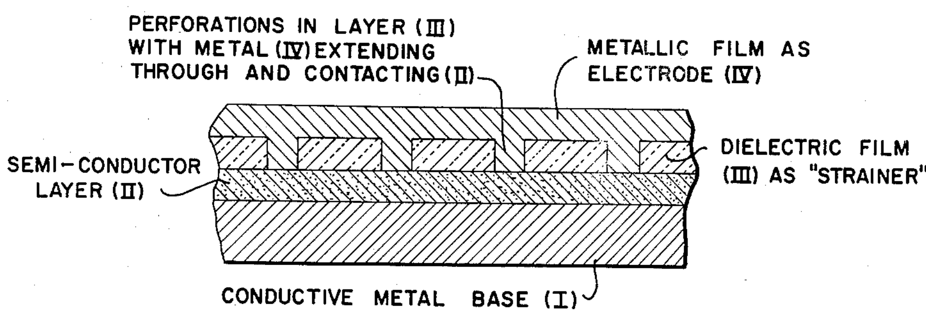

FIG 4

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METHOD FOR MAKING DIODES AND PRODUCTS RESULTING THEREFROM

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13 Claims. (Cl. 117—200)

The present invention has for its object a process for making diodes and similar elements using the current-rectifying properties of semi-conductive crystals and particularly those of the semi-conductors of group IV of the classification of elements, such as germanium and silicon.

A further object is the production of such diodes which, though made in a rapid and economical fashion, nevertheless offer intrinsically improved electrical performance when employed in circuits for currents of very high frequencies, such for example as commutation or switching circuits having great speed of operation.

Still another object is the production of a diode structure comprising a semi-conductor obtained by the instant process, and which includes a thin semi-conductive crystalline layer placed upon a polycrystalline conductive base, said semi-conducting layer being covered with a dielectric film forming a "strainer" or perforated layer, and a metallic film of counter-electrode applied over this dielectric layer and contacting the semi-conductive layer at a plurality of points of contact completed through the openings in the strainer layer. In such a structure the rectifying effect is naturally obtained by the phenomenon of injection of charge carriers into the semi-conductive crystal by said plurality of points of contact.

In order to facilitate the disclosure of the invention reference is made to annexed Figs. 1 and 2, which show an apparatus which may be used for putting into practice the process of making diodes according to the invention, Fig. 1 being a view in elevation as seen from a point located at one side of the apparatus and above it, while Fig. 2 is a view of the apparatus from above.

The invention is further illustrated by Figs. 3 and 4. Fig. 3 is a flow diagram which diagrammatically illustrates the order of steps involved in forming the new diode materials of the invention. Fig. 4 is a diagrammatic enlarged cross-sectional view of articles prepared in accordance with the invention, the plurality of layers involved with the new articles being designated by legends which indicate the materials involved.

A vacuum jar 1, having conventional pumping equipment not shown, is equipped at its upper part with a receptacle 2 containing enamel granules 3 and connected hermetically to the jar by a coupling tube 5, a valve 4 being interposed in the connection. The jar 1 is seated upon and hermetically sealed to the base 6.

Mounted upon the base 6 within the jar 1 is a support formed of two vertical brackets 7 and 8 carrying aligned bearings 9 and 10 at their upper ends. A shaft 11 extends through bearing 10 and carries on its outer end a magnetic pole piece 12 arranged opposite an electromagnet 13 which is mounted outside of the jar for turning about the axis of the bearings 9 and 10, the pole piece 12 being within the field of the magnet 13 so that turning of the magnet about its axis effects turning of the shaft 10 about its axis. Another short shaft 11*a* is mounted in bearings 9, and a return spring 14 surrounds the end of this shaft and tends normally to urge the shaft 11*a* to the left, and it also acts upon shaft 11 through a jig or holder which is supported between the two shafts 11 and 11*a*. Thus, when magnet 13 is energized by alternating current, the two shafts and the jig connecting them are subjected to vibratory movement along the axis of the shafts.

This jig or holder is made up of a frame having two lateral uprights 15 and 16 between which are stretched metal conductor ribbons 17 which are to serve as supports and eventually as bases for the diodes. Four crucibles 18 are mounted below this frame and supported on base 6 at the four corners of the orthogonal projection of the frame on the plane of the crucibles. A second set of crucibles 20 is associated with the set of crucibles 18, for example off-set laterally from the set 18, as shown in Figure 2, where these sets are indicated in dotted lines. Each set of crucibles can be heated by passage of an electric current supplied through conductor 19 for crucibles 18, and through conductor 21 for crucibles 20. The upright bracket 8 is insulated from the base 6 at 22, and bracket 7 is grounded to the base. A current for heating the frame and the ribbons which it supports is supplied by connection 8*a* leading to the insulated upright 8.

The ribbons 17 intended to form the base of the diodes are made of an alloy of iron and nickel, the coefficient of expansion of which is strictly identical with that of germanium which will be used as the semi-conductor. Preferably, the surface of these ribbons has been preliminarily treated to cover it with a layer of alloy of gold and bismuth of several molecules in thickness, which alloy layer has been thermically treated on the ribbons. The system of crystallization of the nickel-iron alloy belongs to the same spatial group as that of germanium and the ratio of meshes is a whole number. The gold-bismuth alloy also has a crystal form comparable with that of the preceding but allows, further, at the time of the formation of the germanium crystalline layer, the attainment of an automatic alignment of the crystallographic axis 110 of the germanium with the crystallographic axis alignment 100 of the alloy Au_2Bi, serving as an epitaxic reference which leads to a distribution of net like planes on the iron-nickel base which contains the axes 100 and 110 from whence a better ordered state of the crystallography of the diodes is obtained.

The ribbons can have an individual width of 3 mm. and a length of 100 mm., for example. A grouping of 33 ribbons in the frame then forms a plane surface area of about 100 mm. on the side. A mask M shown in Fig. 2, but omitted from Fig. 1 so as not to obscure the drawing, can be placed over the ribbons and held by the frame so as to delimit or outline the areas of the diodes. This mask M may consist of parallel ribbons 23 stretched transversely to the ribbons 17 and the area of each diode can, for example, be reduced to 4 $mm.^2$ by having ribbons 23 of a width of about 1 mm. and spaced apart about 1⅓ mm. With the above arrangement, one can, for example, make simultaneously 1300 to 1400 diodes, with substantially uniform dispersion characteristics, since they will be formed together and by a common treatment, thus assuring them of the same characteristics of dimensions and crystallography.

As a specific example of the instant process, 300 milligrams of doped germanium is placed in each of the four crucibles 18. An equal charge of an alloy of tin and cadmium is placed in crucibles 20. A vacuum of about 10^{-6} mm. of mercury is then drawn on the jar 1.

The distance of the crucibles 18 from the ribbons 17 is set so that at the residual gas pressure in the jar, it does not exceed 5 percent of the mean free path of the molecules. The occurrence of oxidation during the evaporation of germanium is thus held to a negligible amount. The crucibles **18** are heated to 1400° C. until the germanium has substantially evaporated and deposited on the ribbons **17** which are maintained at a temperature close to the eutectic point, that is, about 325° C., by supplying heating current to lead *8a*. The alloys do not diffuse and their crystalline structure is not modified. The germanium coating is applied to a thickness of about 5 microns, and the coating is quite uniform because of the uniform disposition of the crucibles with respect to the ribbon assembly and the uniform temperature conditions. During the evaporation operation the electromagnet **13** is not energized.

Without interrupting the vaccum at this time and keeping the heating reduced on the ribbons **17**, the frame is turned through 180° so that the face covered with germanium may be turned up. This is done by turning the electro-magnet **13** which is being fed by alternating current to assure a lateral periodic vibration of the frame carrying the ribbons **17**. Then the valve **4** is opened to cause to fall upon the exposed area of ribbons **17** a "rain" of granules of enamel **3**. The receptacle **2** may contain an atmosphere of helium, for example. The granules of enamel have been screened so as to present grains of a diameter between 20 and 40 microns at most. The material of the granules can be of the following composition (by way of illustration):

$$Na_2O—CaO—MgO—SiO_2—B_2O_3$$

The granules, because of the vibration of the frame, are distributed over the ribbons in a layer which is very uniform. The enamel softens at the low temperature of strips **17** and is formed on the germanium as a coarse porous layer of a thickness of 10 to 25 microns.

The frame is then reversed to its first position, whereupon the excess granules fall, leaving the germanium-covered surfaces of the ribbons covered with a veritable "strainer" of enamel, the holes or pores of which, after heating, scarcely exceed 5 to 7 microns in diameter at the maximum. Further spreading of the granules and consequent reduction of the hole size can, if desired, be made by continued heating.

With the frame held stationary in its original position, the crucibles **20** are heated to a temperature in the neighborhood of 850° C. to evaporate the alloy of tin and cadmium which deposits upon the strainer layer, and this alloy deposit fills the holes of the porous layer and forms a counter-electrode layer. Each filled hole or pore in the porous layer leading to the germanium-covered portions provides a filamentary connection between the germanium and the counter-electrode. The electro-magnet **13** is not energized during formation of the counter-electrode.

The ribbons **17** may now be removed from the vacuum jar. If the diode elements are to be used separately, they are separated from each other by severing the ribbons **17** along the transverse areas which were shielded by the shielding strips **23**. Upon providing the individual elements with conventional terminal connections, the diodes are finished.

The intrinsic characteristics of the diodes depend fundamentally on the thickness of the layer of germanium and the number of points of contact per unit area of surface. It is very evident that this thickness is adjusted by the evaporated charge and that the number of points of contact and their dimensions are regulated by the size of the granules of the enamel and the heating temperature imparted to the ribbons after they have received said granules. In the semi-conductor there is formed a barrier at each location of injection of bearers of charge at a point of contact, and the approximate diameter of this barrier is substantially double that of the resistance contact point. The thickness of the barrier is about 300 angstrom units. The small thickness of the semi-conductor between the barrier and the resistance contact practically makes the storage capacity of the holes negligible. The thinner the layer of germanium the more the series resistance diminishes and it is entirely possible to make it of a value of some hundredths of an ohm. By reducing the diameter of the points of contact the capacity of the barrier is reduced and, consequently, the diodes obtained permit efficient rectification of very high frequency currents. Further, the effect of temperature upon the inverse voltage is particularly reduced since the radiating surface of the counter-electrode is large as compared with that of the points of contact. Finally, the fact that the operative process is carried on entirely in a controlled vacuum assures the production of diodes with a surface entirely free of absorbed gas, thus increasing the quality of these products.

I claim:

1. A process for making multiple diodes on a common base, each diode comprising a metallic base having formed thereon a first layer of semi-conductor material selected from the group consisting of silicon and germanium, a second layer of porous ceramic dielectric material, and a third layer of conductive metal, said process comprising enclosing a metallic ribbon in a vacuum chamber maintained at a pressure of the order of 10^{-6} mm. of mercury, heating a semi-conductor material within said chamber to produce thermal radiation of said material, subjecting said ribbon to said radiation through a shield to deposit a layer of said semi-conductor only upon spaced linear portions of said ribbon, heating said semi-conductor layer to effect crystallization thereof, applying a porous ceramic layer over said layer of semi-conductor material, and subjecting said ribbon to radiation from a source of vaporized metal transmitted through said shield to form separate conductive layers over the linear sections of said ribbons which are covered by said semi-conductor layer.

2. A process according to claim 1 wherein the porous dielectric layer is formed by flowing granules of enamel over the surface of said ribbon, then heating the ribbon to melt the granules.

3. A process according to claim 2, in which the dielectric granules have a grain size between 20 and 40 microns, the porous ceramic layer finally obtained having a thickness of the order of 25 microns.

4. A process according to claim 1, in which the said ribbon is initially coated with an alloy of gold-bismuth.

5. A process according to claim 4, in which the ribbon is of metal selected from the group consisting of iron and nickel.

6. A process according to claim 1, in which the conductive layer is made of an alloy of cadmium-tin.

7. A process according to claim 1, in which a plurality of metallic ribbons are enclosed within said vacuum chamber and supported in a common plane upon a frame which can be inverted, and said shield comprises a plurality of spaced parallel ribbons arranged transversely of said metallic ribbons.

8. A process according to claim 7, wherein said dielectric layer is formed by flowing granules of enamel over the surface of said metallic ribbons supported upon said frame, and including the step of vibrating said frame to effect uniform distribution of the granules over the surfaces of said ribbons.

9. A process according to claim 2 wherein said granules of enamel are heated by passing electric current through said ribbon.

10. A process as claimed in claim 1 wherein the porous dielectric layer is formed by flowing granules of enamel over the surface of said ribbon, and the enamel is heated to melt the granules, said heating being continued to spread the granules and reduce the hole size of the resulting porous layer to less than about 7 microns in diameter.

11. A process as claimed in claim 1 wherein the porous dielectric layer is formed by flowing granules of enamel

over the surface of said metallic ribbon, said ribbon is vibrated to obtain uniform distribution of the granules over the ribbon and the distributed granules are heated to melt them and form a porous dielectric layer.

12. A diode comprising a metallic base of conductive metal having formed thereon a plurality of separate thin layers, the first layer being substantially continuous and formed of semi-conductor material selected from the group consisting of silicon and germanium, the second layer being porous and formed of ceramic dielectric material and the third layer being substantially continuous and formed of conductive metal, the pores of said second layer being filled with the metal of said third layer, the metal filling said pores being in electrical contact with the top surface of said first layer, said metal filling said pores further being integral with the metal of said third layer.

13. A diode comprising a metallic base of conductive metal, a layer of gold-bismuth alloy several molecules in thickness formed upon said base, a layer of semi-conductive material selected from the group consisting of silicon and germanium formed upon the gold-bismuth alloy coated base surface, said semi-conductive layer being substantially continuous and of a thickness of about 5 microns, said conductive metal of said base being an iron-nickel alloy having a coefficient of expansion identical to the coefficient of expansion of said semi-conductive material, a porous layer of ceramic dielectric material formed upon said semi-conductive material layer, said porous layer having a thickness of about 10 to 25 microns with the pores thereof being less than about 7 microns in diameter, and a substantially continuous top layer formed upon said porous layer of cadmium-tin alloy, the pores of the porous layer being filled with the alloy of said top layer, the alloy filling said pores being in electrical contact with the top surface of said semi-conductive material layer, said alloy filling said pores further being integral with the alloy of said top layer.

References Cited in the file of this patent

UNITED STATES PATENTS

2,702,259	Sommer	Feb. 15, 1955
2,766,144	Lidow	Oct. 9, 1956
2,768,098	Hoppe	Oct. 23, 1956
2,789,062	Cusano et al.	Apr. 16, 1957
2,818,831	Vine	Jan. 7, 1958