ALTERNATING CURRENT RECTIFIER

Filed March 1, 1941

2 Sheets-Sheet 1

F/G. /

99% SI IN SILICA CRUCIBLE IN ELECTRIC FURNACE IN VACUUM OR HELIUM ATMOSPHERE

HEAT SLOWLY TO SOME POINT(e.g. 1600 C) ABOVE THE FUSION POINT WHICH IS APPROXIMATELY 1400 C.

COOL TO PERMIT SOLIDIFICATION AT ABOUT 1410 C° AND DOWN TO 1100 -1200°C AT 60 C° PER MIN.

COOL TO ROOM TEMPERATURE AT 120'- 130 C° PER MINUTE

CUT FROM INGOT A SLAB CONTAINING COLUMNAR AND NON COLUMNAR ZONES WITH AN INTERVENING BOUNDARY SURFACE BISECTING THE SLAB

GRIND TWO SURFACES OF SLAB PARALLEL TO THE BOUNDARY" USING 600 MESH DIAMOND WHEEL, AND WATER LUBRICANT

ETCH THE SURFACES IN HOT SODIUM HYDROXIDE

WASH SURFACES WITH DISTILLED WATER

ELECTROPLATE SURFACES PARALLEL TO BOUNDARY
WITH RHODIUM FROM A HOT SOLUTION OF RHODIUM TRIPHOSPHATE
SLIGHTLY ACIDIFIED WITH PHOSPHORIC ACID OR SULPHURIC ACID

WASH AND DRY THE RHODIUM PLATING

TIN RHODIUM PLATING (AT LOW TEMPERATURE) WITH ORDINARY LEAD TIN SOLDER USING AN ACIDIFIED ZINC CHLORIDE FLUX

PLACE"TINNED"ELECTRIC TERMINAL ELEMENTS WITH FLAT SURFACES IN CONTACT WITH TINNED RHODIUM SURFACES AND HEAT JOINT UNTIL SOLDER FLOWS

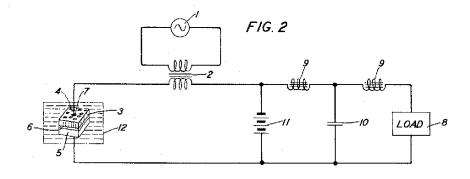
BY R.S. OHL

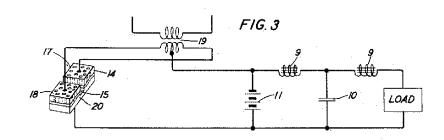
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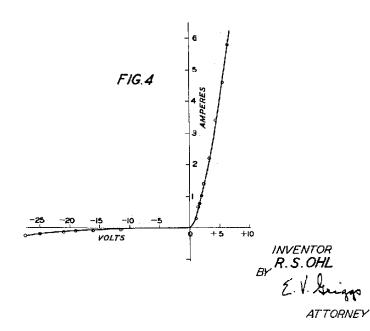
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2 Sheets-Sheet 2







UNITED STATES PATENT OFFICE

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ALTERNATING CURRENT RECTIFIER

Russell S. Ohl, Little Silver, N. J., assignor to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

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8 Claims. (Cl. 175-366)

1

This invention relates to rectifiers for alternating currents.

An object of the invention is to provide alternating current rectifiers suitable for production of large currents at low impressed voltages and 5 with a high degree of stability.

In accordance with the invention, silicon of a high degree of purity, say at least 99 per cent, is fused under non-oxidizing conditions and cooled slowly to form an ingot. The material 10 first to cool exhibits certain very different properties from that last to cool, the two zones of material being separated by a so-called "barrier surface." If a slab of material be cut so as to include a portion at each side of the barrier sur- 15 face and a terminal be connected to each portion, the device will function efficiently as a rec-.tifier.

Fig. 1 is an operational diagram of one form of the method employed for producing rectifying 20 substances in accordance with this invention:

Fig. 2 illustrates diagrammatically a circuit of a half-wave rectifier embodying the invention;

Fig. 3 is a corresponding diagram of the circuit of a full-wave rectifier; and

Fig. 4, a graph of the rectifying performance characteristic of the rectifying element of Fig. 2.

It has long been known that bodies of the class of materials sometimes known as semiconductors including silicon may be employed in point contact detectors such as are utilized for detectors in radio receivers.

Examples of such contact rectifier structures are those of U.S. Patents to G.W. Pickard, 836,531, November 20, 1906, and 888,191, May 19, 1908. In an article at page 1003 of the Electrical World, November 24, 1906, Pickard states that after a trial of a large number of elements and compounds pure silicon was found very satisfactory as a rectifying contact detector, As a matter of fact, the commercial "pure silicon' available to Pickard was a substance of about 98 per cent purity at most with at least 2 per cent of impurities. More recently, there has become available on the market silicon of a much higher purity of the order of 99.5 per cent. This material is in granular form but is not available in chunks of sufficient size to serve for contact. detectors. In a study made by applicant it was discovered that with silicon of this very high 50 per minute. purity, that is, of the order of 99.5 per cent, a very superior contact detector which exhibits a loss of the order of 15 decibels less than that of the Pickard detector is attainable. Coupled with this enormous gain in rectifying effectiveness is a 55 tion of the cooled ingot it is found that a portion

reduction of rectifier current noise of the order of 35 to 40 decibels. This improved contact detector is disclosed and claimed in U.S. application Serial No. 385,425, filed March 27, 1941.

2

In the course of studies of the characteristics of purified silicon, structures have been discovered which possess very desirable rectifying properties for lower frequency currents. To produce such structures a process, one example of which is illustrated in Fig. 1, may be employed. Silicon of a purity in excess of 99 per cent obtainable in granular form is placed in a silica crucible in an electric furnace in vacuum or helium atmosphere. Because of a tendency to evolution of gas with violent turbulence of the material, it is desirable to raise the temperature to the melting point by heating the charge slowly. Silicon will be found to fuse at a temperature of the order of 1400 to 1410° C.

In order to facilitate the heating process the silica crucible containing silicon may be placed within a graphite crucible which lends itself to development of heat under the influence of the high frequency field of the electric furnace to 25 a much greater degree than does the silica crucible or its charge of silicon. Care must be taken, however, to avoid exposure of the melted silicon to graphite, oxygen or other materials with which it reacts vigorously. In this manner, 30 the melt may be brought to a temperature of the order of 200° C. above melting point. In an example of this process "high form" crucibles of 50 cubic centimeter capacity obtainable from Thermal Syndicate Inc. were employed. A fur-35 nace power input of 7.5 to 10 kilowatts was employed, the required time for melting being of the order of ten to twenty minutes, depending upon the power. The power was then reduced in steps and the temperature of the melted silicon 40 dropped rapidly to the freezing point approximately six or seven minutes being required for the melt to solidify. The solid metal was then permitted to cool towards room temperature at the rate of 60 degrees per minute, this being 45 effected by decreasing the power input at the rate of about 1/2 kilowatt per minute. When the temperature had been reduced to the order of 1150 to 1200° C., the power was shut off and the temperature then fell at the rate of about 130 degrees

In cooling there is a tendency after the upper surface has solidified for extrusion of metal to occur through this surface during the solidification of the remaining material. Upon examina-

of the grain structure is columnar. This is, in general, the upper portion of the ingot or the first material to solidify and the columnar grains, which may be of the order of 1/2 millimeter in width, extend down into the structure to a distance of 5 to 10 millimeters. In the area last to solidify and beyond the columnar grains a noncolumnar structure occurs. Between the zone first to cool and that last to cool there is found to be some sort of a boundary or "barrier" which 10 occurs in a plane normal to the columns and this barrier has extremely important rectification properties. The barrier ordinarily occurs a short distance above where the columnar and noncolumnar zones merge so that it extends across 15 the columns near their lower ends. The region above the barrier develops a positive thermal potential with respect to an attached copper electrode and may, therefore, be designated as the P zone. The region below the barrier develops 20 a negative thermal potential with respect to an attached copper electrode. It will be designated as the N zone. In use as a rectifier the silicon unit permits electrons to flow freely into the N zone, from the N zone to the P zone, and out of 25 the P zone so that the P zone terminal of the rectifier will be connected to the more positive potential point of the charging source and the N terminal to the more negative point of the charging circuit.

To prepare a rectifier, a slab of material is cut from the ingot in such a manner as to be bisected by the rectifying boundary. The surfaces of the slab parallel to the boundary may be ground flat using a 600 mesh diamond wheel 35 and water lubrication. Thereafter the surfaces may be etched in a hot sodium hydroxide solution and washed in distilled water. The surfaces parallel to the boundary may thereupon be electroplated with rhodium from a hot solution of 40 rhodium triphosphate slightly acidified with phosphoric acid or sulphuric acid. Upon drying and washing the rhodium plating these surfaces may be tinned with ordinary lead tin solder using an acidified zinc chloride flux. The solder must not be heated much above its melting point or there is danger of the rhodium being completely dissolved. A flat freely tinned surface of a metal element which constitutes a terminal of the rectifier is then placed in contact with 50 each tinned rhodium surface and the joint is heated until the solder flows and the excess solder is squeezed from the joint. A strong bond results.

will operate satisfactorily if the temperature does not exceed about 90° C. A parallelepiped having a rectifying boundary cross-section of 1.5 square centimeters with solder connections such as have been described has been utilized as a half-wave 60 rectifier with an applied alternating current of 12 volts to supply rectified direct current of .9 ampere at 8 volts to a load. The peak reverse current was found to be about 3 per cent of the forward current. These characteristics were ob- 65 tained operating the unit without cooling. The same unit immersed in distilled water and with an alternating current supply voltage of 14 volts supplied 2.5 amperes at 5 volts to its load circuit. The currents and voltages specified are effective 70 values as measured by an electrodynamometer.

Fig. 2 illustrates in schematic diagram a rectifying system in which a source I of alternating current which may be of the ordinary 60 cycle

cuit by a transformer 2. The rectifier consists of a slab of material 3 having an upper columnar portion 4, a lower non-columnar portion 5 and a rectifying boundary surface 8. Terminals 7 are soldered to the upper and lower surfaces of the slab 3 and serve to connect the rectifier in circuit in series with the secondary winding of transformer 2 and a load 8 to which the rectified current is to be supplied. Between the rectifying system and the load \$ is a smoothing filter of well-known type comprising series inductance 9 and a shunt condenser 19. There may also be connected across the circuit in advance of the smoothing filter a storage battery II or electrolytic cell to serve as a floating stabilizer in wellknown manner. Under circumstances in which considerable heat may be evolved in the rectifler the unit may be submerged in a bath of distilled water in a container 12, preferably of, although not necessarily of, electrically non-conducting material. The container 12 may be provided with heat dissipating means of any well-known type as, for example, cooling fins, recirculating pipes or a fan for blowing air upon the container. In lieu of the distilled water a bath of any inert liquid such as oil may be used as a cooling agent.

4

Such a rectifying unit operates satisfactorily up to several kilocycles. It is suitable for rectifying speech currents in systems where relays are to be operated by speech currents.

In the system of Fig. 3, full wave rectification is effected. A slab 14 of material prepared in the same manner as slab 3 of Fig. 1 is slotted through the P zone and the barrier surface 15 as indicated at 15 to divide the P zone into two physically non-contiguous portions 17 and 18. Each of the portions 17 and 18 may serve as an individual half-wave rectifier. The mid-point of the secondary winding of the alternating current supply transformer 19 is connected to the undivided N zone 20 of the rectifier. The terminals of the secondary winding are connected respectively to the sections 17 and 18. In other respects, the rectifying system is identical with that of Fig. 2 45 and, accordingly, further description of its structure or operation is unnecessary. The slot 15 may be made through the N zone and the barrier surface with a corresponding modification of the circuit connections.

Fig. 4 is a graph showing the performance characteristic of a half-wave rectifier of the type illustrated in Fig. 2. It will be seen that the device performs very efficiently yielding a large current with a relatively low applied electro-A rectifier element constructed as described 55 motive force and that the reverse current is from a practical standpoint negligible in magnitude with respect to the forward current.

The nature of the boundary surface and the reasons for its electrical behavior are obscure. There is evidence to indicate that the phenomena observed are dependent not only upon high purity of the silicon but also upon the character of the extremely small amounts of impurities which remain. In the most satisfactory ingots the N zone portions have very tiny gas pockets and upon cutting through this zone a characteristic odor of acetylene is observed. Moreover, certain lots of highly pure silicon which have at first appeared to be defective in barrier-forming properties have been satisfactorily conditioned by the introduction of carbon or silicon carbide into the melt in amounts of the order of .1 per cent to .5 per cent and this should be done if a preliminary ample of a particular lot of material does 110 volt type is associated with the rectifier cir- 75 not 13rm the distinctive barrier structure.

5

The slow cooling is an important factor as is readily demonstrated upon microscopic examination of sectioned specimens of silicon ingots which have been etched and stained. The barrier is evident as one or more striations of a somewhat different appearing material in consequence of its different reaction to the etching acid. In the case of slow cooling the striation extends across the entire ingot, thus dividing it into discrete P and N zones. Where, however, the cooling is pre- 10 cipitate as in the case of shutting off the heating power suddenly as soon as fusion occurs and permitting the temperature to fall suddenly, the first spots to cool develop P zones and these are surrounded by N zone matrices in such irregular 15 fashion as to render the resulting ingot quite unsatisfactory for barrier rectification. The slow cooling rate is important in developing an orderly striation or barrier. This and other features of the method of preparing the most effective silicon 20 materials are described and claimed in the application of J. H. Scaff, Serial No. 386,835, filed April 4, 1941, for improvements in the Preparation of silicon materials.

It will be apparent that the device lends itself to a wide variety of circuit applications where very small units are desired and where permanence of all contacts is an important feature. It provides a low voltage current supply where high currents and good stability of operating characteristics are desirable.

What is claimed is:

- 1. An electrical transmission device comprising a body of silicon solidified in two zones of different formations with an integral interposed boundary surface, and an electrical terminal electrically connected to each zone, the boundary surface presenting an electrically asymmetrically conducting characteristic whereby an alternating electromotive force applied to the terminals gives rise to a substantially unidirectional current.
- 2. An electrical transmission element comprising a body of fused silicon having a zone of columnar structure and a second zone of non-columnar structure, an electrical terminal connected to the columnar zone and a second electrical terminal connected to the non-columnar zone.

6

- 3. An electrical transmission element comprising a body of silicon having a purity of the order of 99 per cent and so formed as to have a zone of columnar-like structure and a zone of non-columnar structure, an electrical terminal connected to the columnar zone and a second electrical terminal connected to the non-columnar zone.
- 4. A rectifier comprising a body of silicon having a purity in excess of 99 per cent and an internal structure comprising two zones of very different conformation separated by a barrier surface which exhibits electrical rectifying properties and an electrical terminal connected to each zone.
- 5. A rectifier comprising a body of silicon having a purity in excess of 99 per cent, the body having a pair of electrical terminal surfaces adjacent one of which the internal structure of the body is columnar and adjacent the other of which it is non-columnar.
- 6. An asymmetric electric conductor comprising an integral slab of silicon containing an electrical rectifying boundary surface which separates the slab into two portions, the slab having a cleft which divides one of the zones into noncontiguous portions and which extends to the other zone.
- 7. A rectifier comprising a slab of fused silicon 30 of a purity in excess of 99 per cent and having an interior structure comprising a columnar zone and a non-columnar zone, a cleft extending across one of the zones and into the other to divide the one zone into two separated portions, and an 35 electrode individual to the surface of the undivided zone and to each of the portions of the divided zone.
- 8. An electrical transmission device comprising a body of silicon including an interior inte40 gral rectifying barrier separating the body into two zones one of which yields a thermo-electric positive potential with respect to an attached copper electrode and the other of which yields a thermo-electric negative potential with respect to an attached copper electrode and an electrode conductively connected to each of said zones.

RUSSELL S, OHL.