

Oct. 18, 1949.

J. H. SCAFF ET AL

2,485,069

TRANSLATING MATERIAL OF SILICON BASE

Filed July 20, 1944

3 Sheets-Sheet 1

FIG. 1

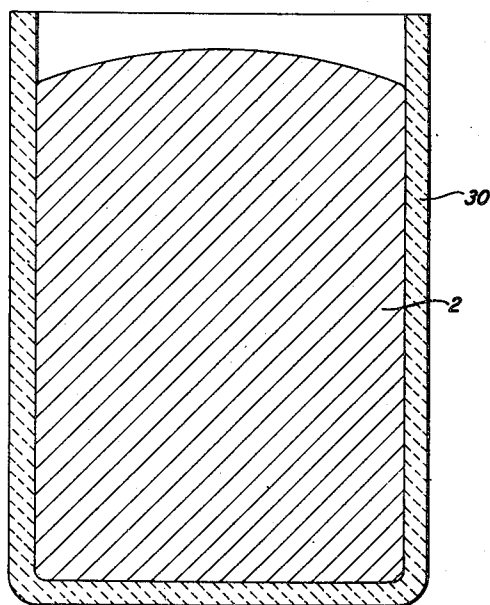
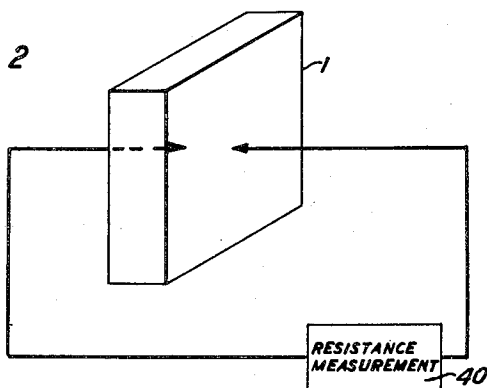


FIG. 2



INVENTORS J. H. SCAFF
H. C. THEUERER

BY

W. R. McHenry
ATTORNEY

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FIG. 3

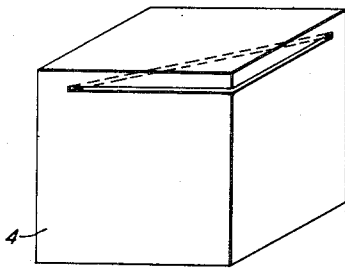


FIG. 4

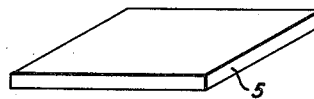


FIG. 5

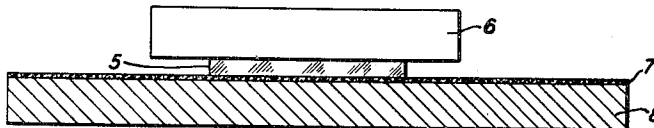
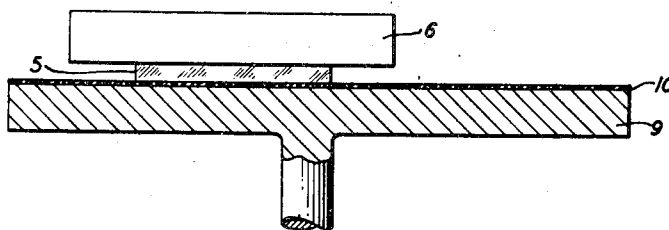


FIG. 6



INVENTORS J. H. SCAFF
H. C. THEUERER

BY *W. R. McManis*
ATTORNEY

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J. H. SCAFF ET AL

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FIG. 7

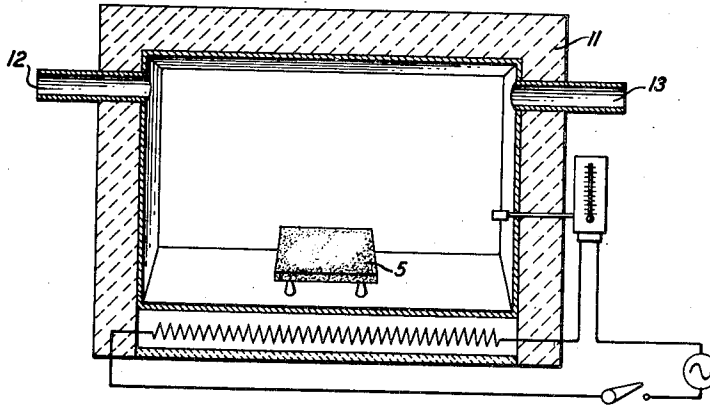


FIG. 8

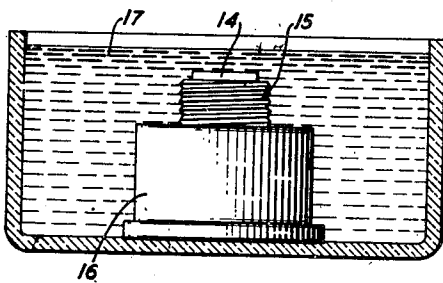
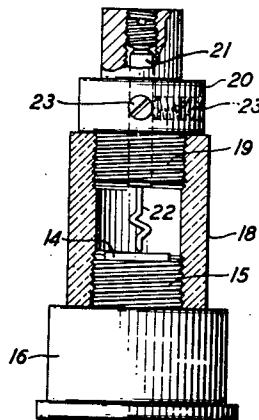


FIG. 9



INVENTORS J. H. SCAFF
H. C. THEUERER
BY *M. D. McFenney*
ATTORNEY

UNITED STATES PATENT OFFICE

2,485,069

TRANSLATING MATERIAL OF SILICON BASE

Jack H. Scaff, Summit, N. J., and Henry C. Theuerer, New York, N. Y., assignors to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

Application July 20, 1944, Serial No. 545,854

9 Claims. (Cl. 175-366)

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

The objects of the invention are to improve the electrical properties of conducting and translating materials; to improve the operating characteristics of translating devices; to increase the translating and conversion efficiency of these materials and devices; to improve their operation as electrical rectifiers by reducing their resistance to the flow of signal currents; to enlarge their field of application; to improve the methods of making them; and in other respects to obtain improvements in materials and devices of this character and in the methods of making them.

It has been the practice heretofore to make rectifier elements of fused high-purity silicon containing less than two-tenths of one per cent of impurities. This small residue consists of a substantial number of specific substances which are usually inherent in the high-purity material. Also it has been suggested heretofore to subject crystal rectifier elements made of the high-purity silicon material to an oxidizing heat treatment for the purpose of forming on the rectification surface of the element a thin high-impedance layer which makes it possible to achieve substantial gains in the power-transmitting capacity of the rectifier. Rectifiers using crystal elements prepared with this high-purity silicon material and subjected to the oxidation heat treatment have given good results in the high-frequency signaling field. In fact they have made possible the successful use in practical signaling systems of wavelengths in the centimeter range. And the superior rectification properties of elements that have had the benefit of the heat treatment enable the use of much higher voltages with the attendant result that the rectifiers are capable of operating at correspondingly higher power levels. Nevertheless there has remained the problem of attaining improved efficiency, particularly for signal conversion systems.

With this problem in mind, applicants have discovered that striking results may be obtained in the electrical performance of rectifier crystals made of the high-purity silicon by the addition of very small quantities of an element, such as boron, having certain specific characteristics, particularly as to atom size and valence. More specifically, the addition to the high-purity silicon prior to the fusion operation of a minute quantity of boron comparable in percentage to that of some of the impurities, which in total constitute the two-tenths of one per cent above mentioned,

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so alters the electrical character of the silicon element taken from the melt that a large gain is achieved in conversion efficiency. Although numerous elements have been added to silicon in amounts up to one per cent, none has been found which is as effective as boron in improving the conversion efficiency of crystal rectifiers.

A feature of the invention, therefore, is the method of making a translating material in which an element of crystallized silicon is prepared by fusing high-purity silicon to which a minute percentage of boron has been added and in which the crystal element thus prepared is subjected to an oxidation heat treatment to condition the rectification surface thereof. One of the important effects of the added boron is to cause a large reduction in the electrical resistance of the body of the silicon element which occurs in series with the impedance of the rectifying surface layer. Since the power dissipated in this series resistance decreases the conversion efficiency, the large reduction in resistance accomplished by the boron additions results in a correspondingly large gain in the conversion efficiency.

Another feature of the invention is the method of preparing crystallized silicon rectifier material in which silicon of high purity is fused and cast in ingots from which rectifying crystal elements are derived and in which a small percentage of an element, such as boron, is added to the silicon before fusion for the purpose of controlling the polarity and other electrical characteristics of the resultant material.

Another feature of the invention is a conducting and translating element for signaling systems comprising a body of silicon to which a definite small percentage of an element such as boron has been added for the purpose of reducing the electrical impedance of said silicon body.

Another feature is the method of making electrical conducting or translating material for use where hardness, durability, electrical or thermal stability, or the capability of developing high thermoelectric power is desired which comprises fusing ingots of high-purity silicon alloyed with small predetermined percentages of boron for the purpose of greatly reducing the electrical resistance of the material and bringing it within the required limits.

In addition to improving the conversion efficiency, applicants' discovery also facilitates the commercial production of crystal rectifiers. Thus, for the variety of units now produced, with different ranges of operating frequency and with rigid specification of the signal-to-noise perform-

ance, impedance, and power-handling ability, it is necessary that silicon materials of different specific resistances be used depending upon the application intended. In order that production may be carried out in an efficient manner it is necessary both that the specific resistance be controlled within definite, narrow limits and that it be uniform. Heretofore the desired degree of control could not be attained owing to inherent variations in the raw material. By applicants' process not only is the desired degree of control realized, but also for a given quantity of raw material processed the yield of material of the desired specific resistance is increased.

The foregoing and other features of the invention will be described in greater detail in the following specification.

In the drawings accompanying the specification:

Fig. 1 illustrates an ingot of fused silicon material;

Fig. 2 illustrates a circuit arrangement for testing the resistance of the material;

Fig. 3 illustrates a block of fused silicon taken from the ingot;

Fig. 4 shows a slab cut from the block of Fig. 3;

Figs. 5 and 6 disclose apparatus for polishing the surface of the silicon slab;

Fig. 7 illustrates a heat chamber for treating the silicon slabs;

Fig. 8 shows an etching bath; and

Fig. 9 discloses an assembled rectifier unit.

Since the purpose for which this material is to be used, whether in rectifier units for high-frequency systems or in electrical circuits and systems of other types, determines the optimum resistance value in each particular instance, one of the preliminary steps in the process is to calculate the exact amount of alloy material, such as boron, that will need to be added to the high-purity silicon to give a resultant material having the desired resistance characteristics. To this end a sample of the high-purity silicon is used to prepare a test ingot without the addition of the alloy material. From this preliminary ingot a test specimen 1 is cut, one-quarter inch from the top of the ingot, to predetermined dimensions, and the specific resistance is measured by standard measuring apparatus 40. While the values obtained will vary somewhat with variations in the material, it may be noted, by way of example, that the specific resistance will usually be between 0.1 and 0.2 ohm-centimeter, when the test specimen is made of silicon of a purity somewhat higher than 99.8 per cent. In certain cases where silicon of extreme purity is used a specific resistance as high as 2.0 ohm-centimeters may be found.

With this preliminary information concerning the resistance characteristics of the high-purity silicon, it is now possible to determine the exact amount of alloy material that should be added to effect the desired reduction in specific resistance. If the test specimen 1 of unalloyed silicon has a specific resistance of 0.15 ohm-centimeter, the specific resistance of a similar specimen can be reduced to 0.03 ohm-centimeter by adding about 0.003 per cent boron to the melt, or to 0.01 ohm-centimeter by adding about 0.01 per cent boron. In the case of extremely pure silicon the addition of 0.005 per cent boron will reduce the specific resistance of the test specimen to 0.03 ohm-centimeter. It will be noted that these boron percentages are very small compared with the effect they have on the resistance of the final

material. In fact, they are as small or smaller than the percentages of some of the component impurities which in total constitute the residue of .2 per cent in the high-purity material. With a purity substantially in excess of 99.8 per cent these boron additions may easily be made without reducing the purity below that percentage. If, therefore, it is desired to obtain material with a specific resistance of 0.03 ohm-centimeter, a master alloy is first prepared by fusing an ingot of high-purity silicon to which 1 per cent of boron powder has been added. This boro-silicon ingot is then crushed in a steel die and ground to a fine powder in a suitable mortar. Next the final ingot 2 is prepared by adding to the crucible 30 a mixture of the high-purity silicon powder and the powdered master alloy in such a ratio that the total contains, say, 0.003 per cent boron, or some other percentage depending upon the final specific resistance desired. The purpose of first preparing the master alloy is to increase the accuracy with which the measurements of the ratio are made. A suitable method for fusing the powdered material and forming the ingot 2 is described in detail in the Theuerer application Serial No. 517,060, filed January 5, 1944, now Patent No. 2,475,810, dated July 12, 1949.

Following the casting of the ingot 2, a block 4 is cut therefrom; and assuming the material is to be used for rectifiers, a thin slab 5 is cut therefrom. Diamond saws are usually employed for this purpose, and best results are obtained when the large surface of the slab is normal to the axis of the ingot.

The next step in the preparation of the slab 5 for use in rectifier units is to polish one of its large faces to a high finish. To accomplish this step the slab 5 is cemented to a flat steel block 6 with a suitable thermoplastic cement. The exposed surface of the slab 5 is then polished by rubbing it over the surface of an abrasive paper 7 secured to a flat plate 8, the paper 7 being changed from one degree of fineness to another as the process proceeds. If desired the polishing surface may be lubricated with a mixture of light oil and kerosene. The final step in the polishing operation is performed by applying the slab 5 to a rubbing lap 9, having its surface covered with polishing paper 10 of extreme fineness. During this operation the slab 5 is pressed against the polishing surface with a definite force and is moved in a circle eccentric to the lap 9 and in the direction opposite to the direction of rotation of the lap. During the wet stage of the polishing a scum of fine particles of silicon suspended in the lubricant forms over the surface of the slab. As the process proceeds the scum dries and distributes itself over the surface of the lap to form the final polishing medium. Once this surface is formed a very few seconds of additional polishing are necessary to produce a high finish on the slab 5. The slab is now removed from the block 6 and cleaned.

The next step in the preparation of the slab 5 is to oxidize the polished surface thereof. To this end the slab is placed in a heat chamber 11 where it is subjected to a temperature of about 1050° C., for a period of two hours. During this interval a normal atmosphere is maintained in the chamber by means of inlet and outlet pipes 12 and 13 and any suitable external controlling apparatus. The effect of this heat treatment is to form a thin coating of vitreous oxide material over the polished surface of the slab 5 and to produce thereunder a thin layer of silicon

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material which is characterized by its high impedance and exceptional rectification properties.

Following the heat treatment the back or unpolished side of the slab 5 is ground with an abrasive material to remove completely the vitreous oxide layer. The ground back of the slab is then plated with nickel, and the slab is cut into small wafers of dimensions suitable for use in the rectifier units.

The wafer 14 thus prepared is soldered with its nickered surface to the threaded stud 15 of the metallic base 16, Figs. 8 and 9. Following the soldering of the wafer to the threaded stud of the base member and before the rectifier unit is assembled, as seen in Fig. 9, the vitreous oxide layer covering the polished upper surface of the wafer 14 is removed by etching the entire base assembly in a bath 17 of hydrofluoric acid and water. After the vitreous layer has been removed the base member 16 is screwed into the ceramic cylinder 18. In a similar manner the stud 19, which is integral with the cap 20, is firmly screwed into the opposite end of the cylinder 18. The cap 20 contains a central bore for receiving the cylindrical contact holder 21. The holder 21 is adjusted until the tip end of the tungsten wire 22, the opposite end of which is soldered into the holder 21, makes contact with the polished surface of the wafer 14. When a desired degree of force has been applied to the contact engagement of the wire 22 with the silicon wafer 14, the stud screws 23 are tightened to seize the holder 21. The unit is then tapped lightly on its side until the desired characteristic is obtained.

As an alternative process the oxidation stage may be omitted, and in this case one surface of slab 5, as cut from the ingot, is prepared for electroplating by grinding with an abrasive such as 600-grit aluminum oxide in water, subsequently etching this ground face in a hot solution of 10 per cent sodium hydroxide, and then electroplating this etched surface with nickel. The slab is then cut into small wafers 14. The wafer thus prepared is soldered to the threaded member 15 of the metallic base 16 and its free surface lapped flat on dry 600-grit silicon carbide abrasive paper. The lapped face is then etched by applying thereto a drop of a solution of 20 per cent concentrated hydrofluoric acid in concentrated nitric acid. Subsequently the etchant is removed by rinsing, and the surface of the crystal dried. The base member 16 is now ready for assembly into the ceramic cylinder as described earlier.

It should be understood that the alloyed material described herein may be used for many purposes in the electrical arts. In particular it will be found useful as a conducting and translating material where hardness, durability, electrical or thermal stability, is required, where high values of thermo-electric power are involved, or where an easily controlled resistance characteristic is desirable. In such cases, elements of any desired size and shape may be taken from the ingot 2.

With this process of producing silicon material it is not only possible to control the resistance characteristics of the elements taken from the ingot 2, but the polarity properties of the material may also be controlled. In casting ingots from high-purity silicon it has been discovered that material of opposite polarities are found to occur in the same ingot. Usually the upper portion of the ingot is electropositive, an

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intermediate section is neutral, and the lower sections are electronegative. Within the electropositive portion of the ingot there is a systematic change in specific resistance with depth in the ingot. With applicants' process it is feasible to produce ingots which are entirely of electropositive material with a more uniform specific resistance with depth. This addition results in an increase in the yield of usable material derived from the ingot.

What is claimed is:

1. The method of making a translating device for electric waves which comprises casting an ingot from a quantity of silicon of high purity, adding to said quantity of silicon before casting, a definite percentage of boron for the purpose of controlling the electrical resistance of the cast material, shaping an element of the cast silicon-boron material from said ingot, and treating said element to produce on the surface thereof a thin integral layer of silicon of high electrical resistance.

2. The method of making a rectifying device which comprises fusing and casting an ingot from a quantity of silicon having therein a number of inherent impurities, the total of which constitutes a fraction of one per cent of the whole, adding to said quantity of silicon before the casting operation a quantity of boron, the percentage of which is substantially less than that of said impurities, for the purpose of controlling the electrical characteristics of the cast material, shaping an element of the cast silicon-boron material from said ingot, and heat-treating said element to produce on the surface thereof a thin layer of material of high electrical resistance.

3. The method of making rectifying elements for translating devices which comprises casting an ingot from a quantity of silicon of high purity, and adding to said quantity of silicon before the casting operation a definite percentage of boron for the purpose of controlling the electrical resistance of the cast material and shaping the rectifying element from the resulting silicon-boron ingot.

4. The method of making material for electrical translating devices which comprises casting an ingot from a quantity of silicon of high purity, adding to said quantity of silicon before the casting operation a definite percentage of boron, and controlling the casting operation to retain boron in the finished ingot for the purpose of reducing the electrical resistance and controlling the electrical polarity of the cast material.

5. An element for the translation of electric energy comprising a body of silicon to which a definite small percentage of boron has been added and retained for the purpose of reducing the electrical impedance of said body.

6. An element for the translation of electric energy comprising a body of silicon to which a definite small percentage of boron has been added and retained for the purpose of reducing the electrical impedance of said body, said body having on the surface thereof a thin layer of silicon of high impedance.

7. The method of making material for electrical conducting devices which comprises casting an ingot from a quantity of silicon of high purity, adding to said quantity of silicon before the casting operation a definite percentage of boron, and casting in a manner to retain boron in the finished ingot for the purpose of reducing the electrical resistance of the cast material.

8. The method of making a translating device

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for electric waves which comprises casting an ingot from a quantity of silicon of high purity under conditions tending to form zones of electropositive and of electronegative material in the ingot, adding to said quantity of silicon before the casting operation a definite percentage of boron for the purpose of controlling the relative volumes of said zones in the cast material, shaping a block of the cast silicon-boron material from said ingot and heat treating said block to produce on the surface thereof a thin integral layer of silicon of high electrical resistance.

9. In a method of making translating devices for electric waves, which comprises casting an ingot from a quantity of silicon of high purity, whereby zones of electropositive and of electronegative material are formed, and dividing the ingot into a plurality of translating devices; the steps of controlling the relative volumes of said zones that comprise adding to said quantity of

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silicon a definite percentage of boron before casting, and casting so as to retain the boron in the finished ingot.

JACK H. SCAFF.
HENRY C. THEUERER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
Re. 18,579	Ballantine et al.	Aug. 23, 1932
1,037,713	Allen	Sept. 3, 1912
2,419,561	Jones et al.	Apr. 29, 1947

FOREIGN PATENTS

Number	Country	Date
551,209	Great Britain	Feb. 12, 1943