

Feb. 18, 1947.

R. S. OHL

2,415,841

CONDUCTING MATERIALS AND DEVICE AND METHOD OF MAKING THEM

Filed Dec. 14, 1944

2 Sheets-Sheet 1

FIG. 1

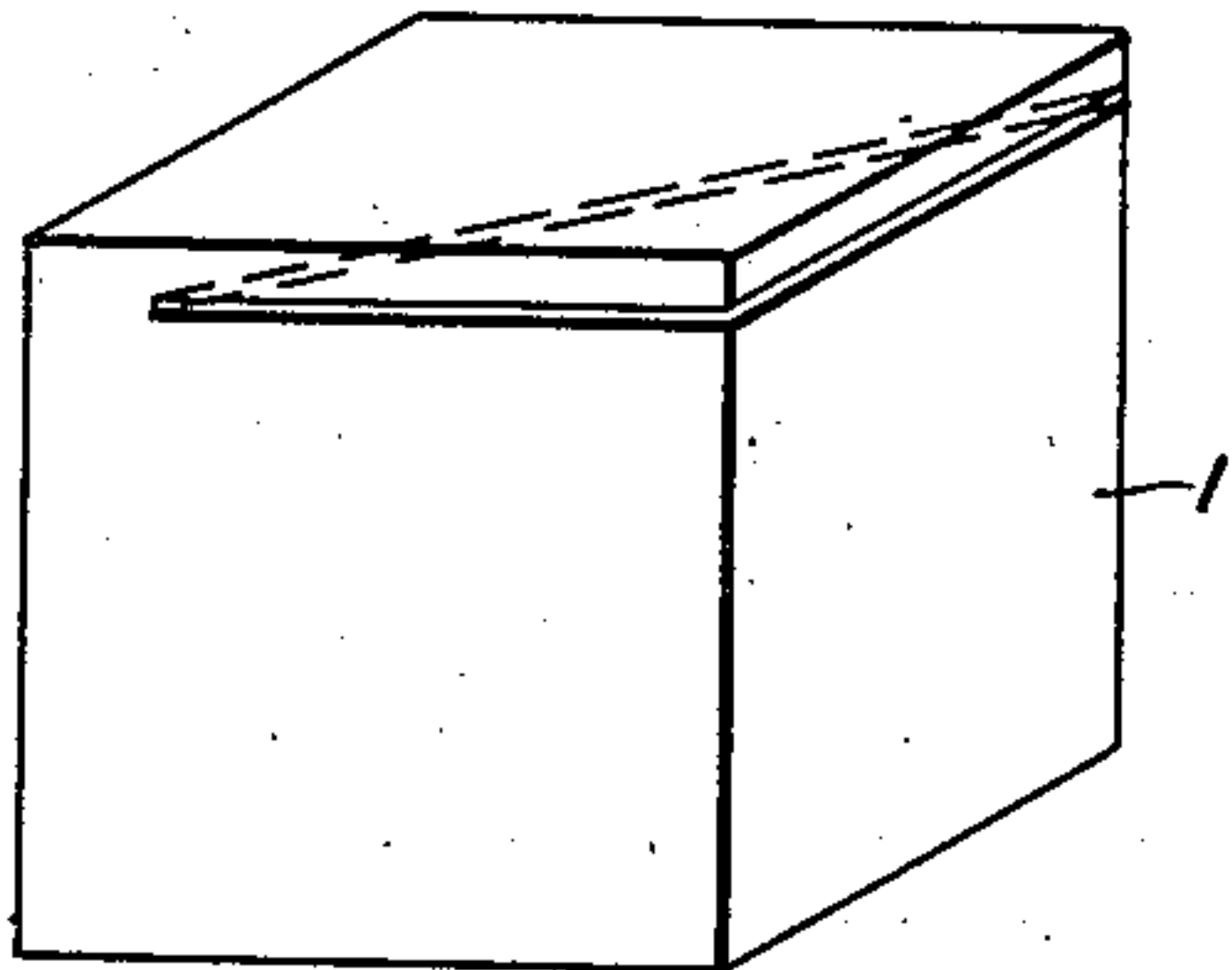


FIG. 2

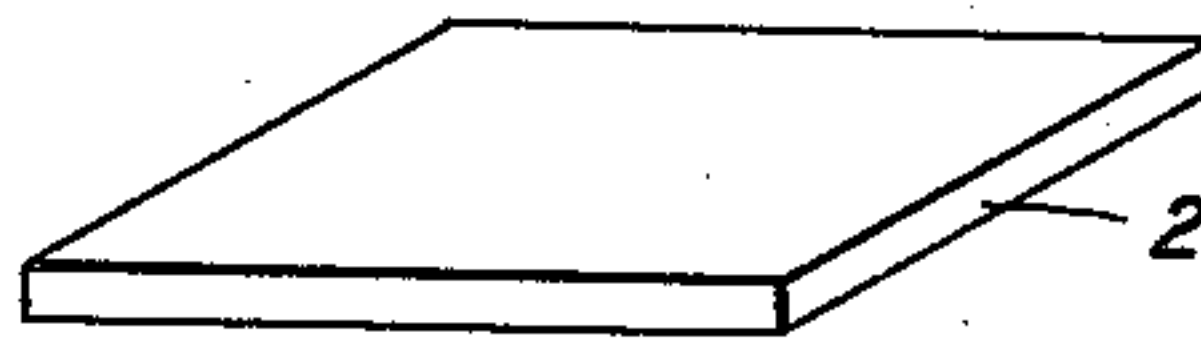
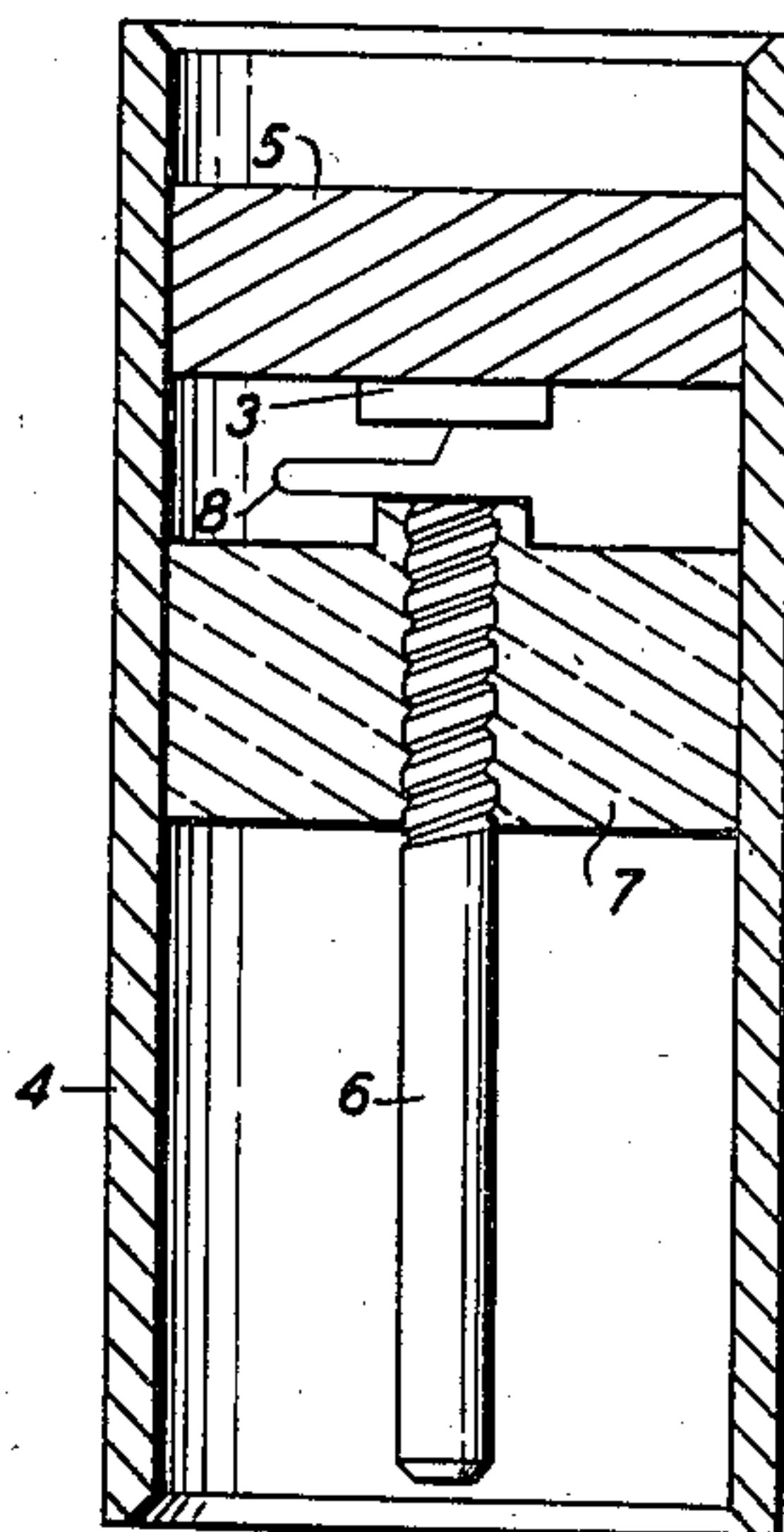


FIG. 3



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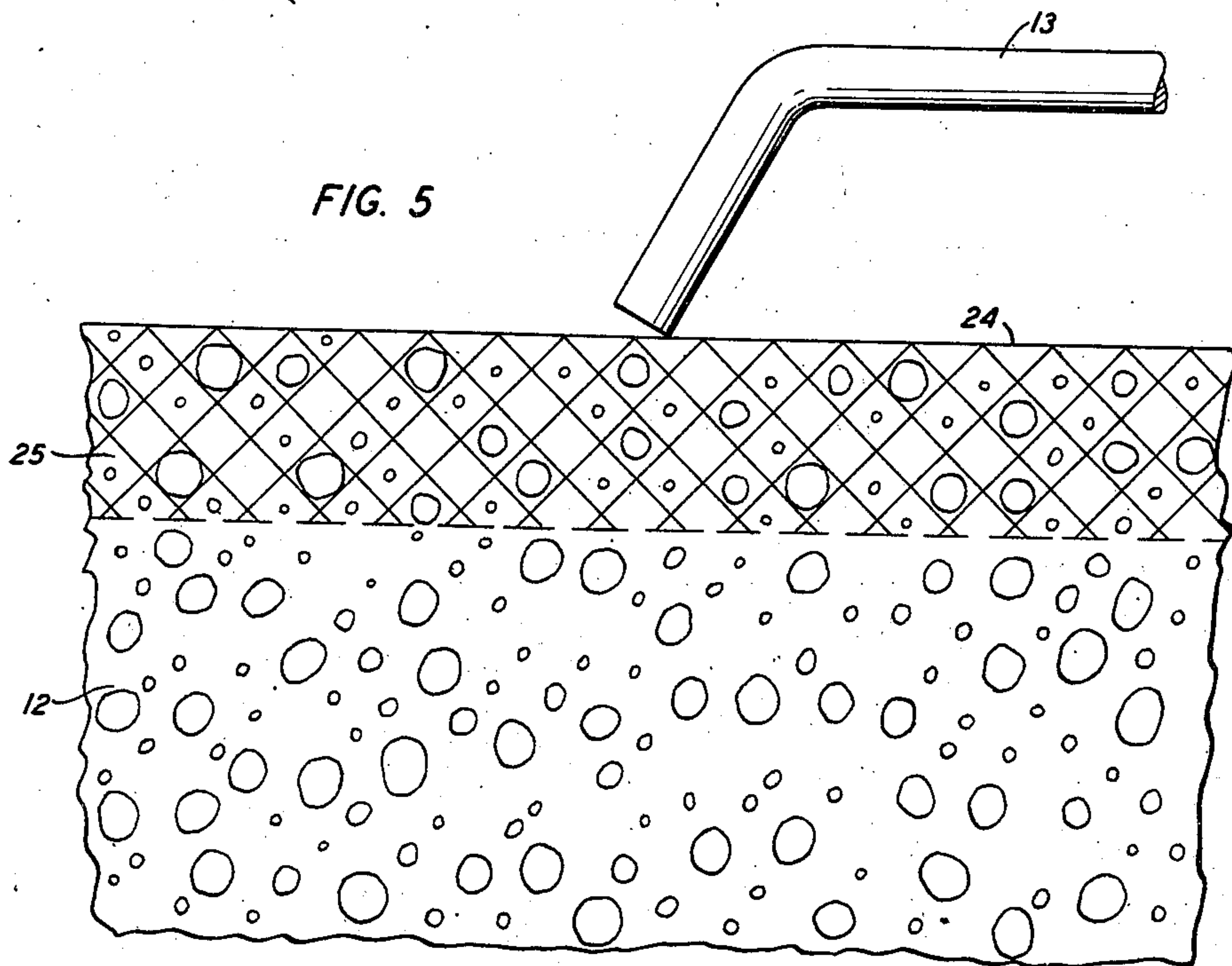
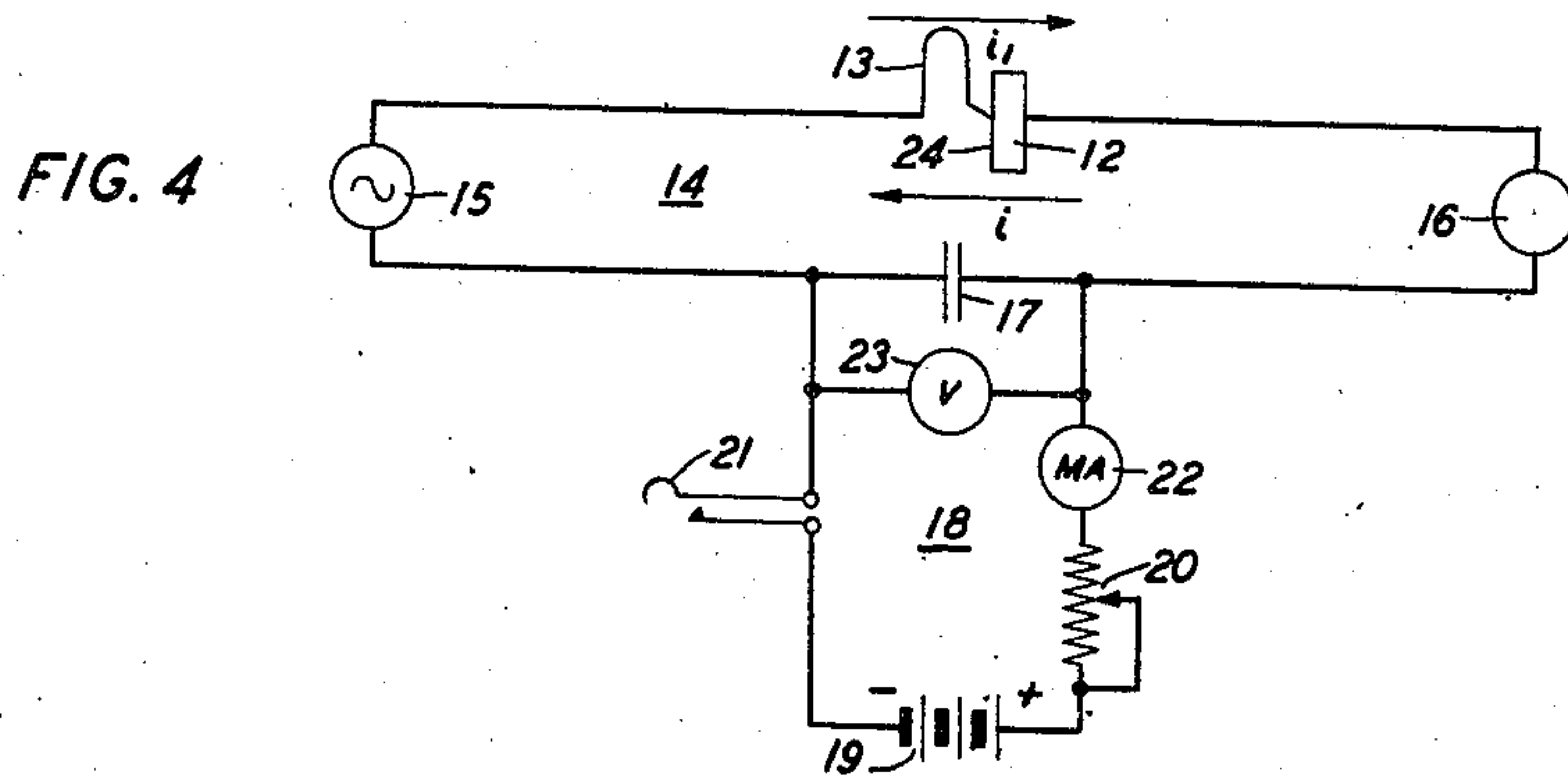
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2 Sheets-Sheet 2



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CONDUCTING MATERIAL AND DEVICE AND
METHOD OF MAKING THEM

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7 Claims. (Cl. 250—31)

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

The objects of the invention are to increase the stability of conducting and translating devices; to improve their operating characteristics, including their electrical efficiency; and in other respects to realize improvements in these devices and in the methods of preparing the materials of which they are made.

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 a method has been devised in which the crystal rectifier elements taken from the fused ingot are subjected to an oxidizing heat treatment for the purpose of forming on the rectification surface of the element a thin high-impedance layer which improves the power-handling capacity of the rectifier. When rectifiers prepared in this manner are used in harmonic generators or for other purposes where they are subjected to alternating fields of relatively high intensity, it is noted that there is a substantial reduction in efficiency with time. In other words they do not possess the desired degree of stability, and their initial efficiency is likely to diminish rather rapidly after they are put into use.

This decrease in the efficiency of the rectifier is believed to be due to a migration, away from the surface layer and into the body of the crystal element, of the positive ions of the metallic impurities that remain in the surface layer following the heat treatment. These ions are urged in a direction away from the crystal surface by the continuous self-biasing voltage developed across the rectifier contact by the applied alternating voltage. While the size of the ions, relative to the interstices in the molecular lattice of the silicon, may be such that the steady bias voltage does not cause them to migrate appreciably, the superposed alternating voltage agitates them and permits them to filter through the lattice toward the interior of the body. With this migrational effect in mind, applicant has discovered that he can exercise a selective control over the movement of the ions with respect to the surface layer of silicon and obtain an ultimate disposition thereof in which desired ions are fixed within the surface layer and undesired ions are excluded therefrom.

In accordance with the present invention, therefore, this desirable effect is achieved by first preparing the rectifier element of silicon to which is added a small per cent of some metal, such as aluminum, capable of producing ions of

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the desired characteristics, and then subjecting the rectifier to a succession of alternate applications of its self-biasing voltage and a reverse biasing voltage supplied from a direct current source, the source of superposed alternating voltage being continuously applied to the rectifier during the process. More specifically, with each application of the self-biasing voltage the ions that are small relative to the openings in the crystal lattice, notably the ions of the unwanted impurities, are urged out of the surface layer and into the body of the crystal. The ions of the desired impurities, however, such as the added aluminum, are sufficiently large in size to lodge within the lattice structure and remain permanently in the surface layer. With each application of the conditioning bias voltage the direction of migration reverses, and both wanted and unwanted ions move from the crystal body into the available openings in the surface layer. Because of their smaller sizes the unwanted ions readily reenter the surface layer, provided there is available space. At the same time by selecting the proper value of the reverse bias voltage some of the larger wanted ions are forced into the lattice of the surface silicon layer where they are locked and held indefinitely. As successive reversals occur fewer and fewer of the undesired ions find room to reenter the surface layer, whereas more and more of the larger wanted ions enter and become locked, until finally they occupy all available space therein.

One of the advantages of the rectifier material prepared in accordance with the present invention is an increase in rectification efficiency. The presence of the fixed metallic ions in the surface layer of the crystal increases the conductivity of the rectifier in the forward direction without impairing its resistivity in the reverse direction; in fact the resistance to flow of current in the reverse direction is somewhat greater.

Another advantage is a marked improvement in the stability of the rectifier after being subjected to the foregoing treatment.

Other features and advantages of the invention will be understood from the following detailed description.

In the drawings accompanying the specification:

Fig. 1 illustrates a block taken from an ingot of fused silicon;

Fig. 2 shows a slab cut from the block of Fig. 1;

Fig. 3 discloses an assembled rectifier unit;

Fig. 4 illustrates diagrammatically a work circuit including one of the rectifier units together with circuit means for treating the rectification surface of the unit; and

Fig. 5 is a view greatly enlarged of the crystal and contact elements of the rectifier unit.

Usually the purpose for which this rectification

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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. It is, therefore, desirable, as a preliminary step in the process, to calculate the exact amount of additional material that is to be combined with the high-purity silicon before casting the ingot. Also it is desirable, as alluded to above, to choose an addition material which is capable of producing ions having characteristics, particularly as to size, bearing a definite relation to the physical structure of crystalline silicon. One such substance is the element aluminum. Any suitable procedure may be employed for determining the desired amount of aluminum to add to the silicon material prior to casting. One suitable method is described in the copending application of Scaff and Theuerer, Serial No. 545,854, filed July 20, 1944. In any event, the amount of addition material is very small and may correspond roughly to the percentage of some of the inherent impurities present in the high-purity silicon material, all of which together do not exceed .2 per cent. However, it should be understood that the present invention is not limited to any particular percentage of addition material nor to any particular material, although, as mentioned, it has been found that aluminum gives good results.

Having determined the desired amount of addition material, it is thoroughly mixed with the selected quantity of high-purity silicon, and the mixture is cast in a furnace to produce an ingot of substantial size. One suitable method of effecting the fusing and casting steps is described in detail in the application of H. C. Theuerer, Serial No. 517,060, filed January 5, 1944.

Following the casting of the ingot, a block 1 is cut therefrom, and from the block 1 a thin slab 2 is cut, of suitable thickness, for example, for use as rectifier elements. Diamond saws are usually employed for this purpose, best results being 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 2 for use in rectifier units is to polish one of its large faces to a high finish. Any suitable method may be used for polishing the slab, one such method being described in detail in the application of Scaff and Theuerer, Serial No. 545,854, filed July 20, 1944.

If desired, the next step that may be taken in the preparation of the slab 2 is to oxidize the polished surface thereof. To this end the slab is placed in a heat chamber where it is subjected to a temperature of about 1050° C., for a period of two hours. For further details of the heat treatment process reference is made to the application of R. S. Ohl, Serial No. 530,419, filed April 10, 1944. The effect of the heat treatment is to form a thin coating of vitreous oxide material over the polished surface of the slab 2 and to produce thereunder a thin layer of crystallized silicon material which is characterized by its high impedance and good rectification properties.

Following the heat treatment the back or unpolished side of the slab 2 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 3 thus prepared is now ready for

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assembly in a rectifier unit, one type of which is illustrated in Fig. 3. This rectifier comprises a cylindrical metallic shell or housing 4, a crystal assembly, and a contact assembly. The metallic cylinder 4, which also serves as an electrical shield, may be made either of steel or beryllium copper and may be given a thin coating of tin. The crystal assembly comprises a solid cylinder 5 of brass, plated with tin, if desired, to which the polished silicon wafer 3 is affixed. The wafer 3 is prepared in the manner above described and is then soldered with its nickeled surface to the brass cylinder 5. The oxidized layer covering the polished rectifier surface of the crystal is now removed by etching, for example, in a bath of hydrofluoric acid and water. The spring contact wire assembly of the rectifier comprises a metallic pin 6, preferably of nickel, an insulating cylinder 7, and a short length of tungsten contact wire 8. A section of the pin 6 is threaded or corrugated, and the insulating cylinder 7 is then molded around this section of the pin. Good results are obtained by the use of a molding material composed of a mixture of quartz powder and a highly pure phenolic resin. The contact wire 8 is about .002 of an inch in diameter, and the contact end thereof is ground to a plane circular surface normal to the axis of the wire. The opposite end of the wire 8 is spot-welded to the end of the pin 6, and the wire is shaped in a single loop with the free end bent at such an angle that only a portion of the circumference of the tip of the wire engages the surface of the silicon crystal 3. The crystal supporting cylinder 5 and the contact wire assembly, including the insulating cylinder 7, are driven into opposite ends of the housing tube 4 where they are held by a force-fit securely in their required positions.

The assembled rectifier unit is now connected in a work circuit, such as the one illustrated in Fig. 4, where it is subjected to the final step in the process, namely, the step of conditioning the surface of the crystal for improved efficiency and stability. Only the essential elements of the rectifier, the silicon wafer 12 and the contact wire 13 (magnified in size), are illustrated in Fig. 4. These same elements are again illustrated in Fig. 5 with still greater magnification.

It may be assumed, for example, that the circuit 14 is designed to generate a desired harmonic of the fundamental wave developed in the source 15. If the third harmonic is desired, the source 15 is preferably arranged to offer a very small impedance to the harmonic wave, and the load circuit or device 16 is designed to offer substantially no impedance to the fundamental wave. The condenser 17 connected in the generator circuit serves as a by-pass for both the fundamental and harmonic waves.

The circuit 18 is employed in the final step of the process of preparing the rectifier unit, namely for conditioning the rectification surface. This circuit includes a source of direct current 19, an adjustable resistor 20, a circuit-closing key 21, a milliammeter 22 and a voltmeter 23.

When the rectifier unit, which has just been prepared and assembled as above described, is connected in the generator circuit 14, it produces waves of the desired harmonic frequency and also acts to rectify both the fundamental and harmonic waves flowing in the circuit 14. If it is assumed that the silicon element 12 is electropositive, the rectifying action of the unit will permit current to flow from the element 12 to the con-

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tact wire 13. During the portion of each cycle that positive potential is applied to the element 12 and negative potential to the contact wire 13, rectified current flows in a counter-clockwise direction around the circuit 14 and through the silicon element 12 in the direction indicated by the arrow *i*. Because of the rectification properties of the unit substantially no current is permitted to flow in the opposite direction in the circuit 14 nor through the element 12. Therefore, a continuous voltage is developed across the rectifier the value of which is the resultant of the successive half-cycle alternating potentials applied to the rectifier in the non-conducting direction. Although this continuous voltage does not cause the flow of current in the circuit 14, it does apply a force to the ions within the silicon element 12 which urges them to move in the direction indicated by the arrow *i*, that is, in the direction from the rectification surface 24 of the crystal 12 toward the interior thereof.

The presence of ions in the surface layer of crystallized silicon 25 is illustrated in Fig. 5. It is believed that the heat treatment to which the silicon element 12 is subjected produces on the surface of the element a thin layer 25 of crystallized silicon of extremely high purity. However, the ions of those metallic impurities remaining in the surface layer 25 are subjected to the force of the continuous voltage developed across the rectifier in the circuit 14 urging them to move downward out of the surface layer 25 and into the body of the element 12. In generating circuits, such as the one of Fig. 4, this developed voltage is relatively large, and the result is that the ions, which are constantly agitated by the superimposed alternating voltage, are forced through the interstices of the crystal lattice and into the interior parts of the element 12. This migrational effect is particularly true with respect to those elements which form ions relatively small with respect to the openings in the crystal lattice. In Fig. 5 both the smaller and the larger ions are illustrated, the smaller ions representing those impurities which inherently exist in the high purity material from which the element is cast and the larger ions representing the addition material, such as aluminum, purposely added to the silicon before casting.

It will be seen, therefore, from this explanation that the continued use of the rectifier element in the circuit 14 will result in the migration from the surface layer 25 into the body of the element of substantially all of the impurity elements which form the small ions. This migration of ions out of the rectification surface has a decided effect upon the efficiency and performance of the unit, and it is, therefore, very desirable to prevent such a change in performance after the unit is installed for use. Furthermore, it is known to be desirable to have a substantial percentage of the proper material, such as aluminum, permanently located in the surface layer of the element, particularly for certain uses. To avoid this change of stability and efficiency and to fix the rectification surface 25, the final step of the process is performed upon the rectifier unit by means of the circuit 18.

It will be noted that the polarity of the battery 19 is such that positive potential will be applied to the silicon element 12 and a negative potential to the contact wire 13 when the key 21 is closed. Thus a direct biasing voltage is applied across the rectifier which is opposite in polarity to the voltage of self-bias which is developed across the

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rectifier from the source 15. The voltage applied by the battery 19 is relatively large and serves to urge the ions in a direction toward the surface layer 25. Each time, therefore, the key 21 is closed the conditioning bias from the battery 19 causes relatively large numbers of the small ions to move readily in the lattice structure of the surface layer 25 together with substantial numbers of the larger ions, these larger ions being aided in their migration by the constant agitation produced by the superimposed alternating voltage. After the key 21 has been closed for a sufficient interval it is again opened, whereupon the self-biasing voltage causes the smaller ions to move back out of the surface and into the interior of the element. The larger ions, however, which have been forced into the lattice with considerable effort resist the return movement and in effect become lodged or locked in the interstices of the lattice structure. On the next closure of the key 21 the same process is repeated, both the smaller ions together with additional larger ions being forced from the body of the element up into the available openings in the crystal lattice. Again, when the key 21 is opened, the smaller ions escape readily and return to the body of the element, whereas the larger ions remain behind and become lodged in the surface layer. By repeating this step a sufficient number of times it is possible to fill the interstices in the surface layer with the desired number of large size ions of the addition material and to exclude the unwanted smaller ions, forcing them to remain below in the body of the silicon element. Thus the silicon rectification element is prepared with a surface having characteristics of stability, high efficiency and excellent rectification properties particularly when used in circuits requiring a substantial flow of current.

While one type of assembled rectifier is illustrated herein, it will be understood that the conducting and translating material prepared in accordance with the method described may be incorporated in numerous types of assembled devices. 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 silicon before fusion a small percentage of a metal capable of producing ions which are comparable in size to the interstices in the lattice structure of substantially pure crystalline silicon, shaping an element of the cast material from said ingot, heat-treating said element to produce on the surface thereof a thin layer of substantially pure crystalline silicon, applying an electrical stress to ionize the added metal present in said element and to cause said ions to lodge in the interstices in said surface layer.

2. 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 silicon before fusion a small percentage of a metal capable of producing ions which are comparable in size to the interstices in the lattice structure of substantially pure crystalline silicon, shaping an element of the cast material from said ingot, heat-treating said element to produce on the surface thereof a thin layer of substantially pure crystalline silicon, subjecting said element to a potential which causes the ions of said added metal to migrate into the said surface layer of silicon and to lodge

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therein, and impressing on said element an alternating potential which agitates said ions and facilitates their migration.

3. 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 silicon before fusion a small percentage of aluminum, shaping an element of the cast material from said ingot, heat-treating said element to produce on the surface thereof a layer of substantially pure crystalline silicon, subjecting said element to a potential which causes the aluminum ions to migrate into said surface layer of silicon and to lodge therein, and impressing on said element an alternating potential which agitates said ions and facilitates their migration.

4. The method of making a conducting device for electric waves which comprises forming a body by fusing a quantity of high-purity silicon containing a small percentage of inherent metallic impurities, adding to said silicon before fusion a small percentage of aluminum, shaping an element from said silicon body, heat-treating said element to produce on the surface thereof a thin layer of substantially pure silicon having a crystalline structure with interstices comparable in size with ions of aluminum and substantially larger in size than the ions of said inherent metallic impurities, subjecting said element to a potential for ionizing the metals present in said element, alternately reversing the direction of said potential first to cause the migration of said ions into said surface layer where the larger ions of the added aluminum are trapped and held and second to cause the migration of the smaller unwanted ions out of said surface layer and into the body of said element.

5. The method of making a conducting device for electric waves which comprises forming a body by fusing a quantity of high-purity silicon containing a small percentage of inherent metallic impurities, adding to said silicon before fusion a small percentage of aluminum, shaping an element from said silicon body, heat-treating said element to produce on the surface thereof a thin layer of substantially pure silicon having a crystalline structure with interstices comparable in size with ions of aluminum and substantially larger in size than the ions of said inherent metallic impurities, subjecting said element to a potential for ionizing the added aluminum and the inherent metallic impurities present in said element, applying said potential in one direction

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to cause the migration of said ions into the surface layer of silicon where the larger ions of the added aluminum are lodged, reversing the direction of the applied potential to cause the migration of the smaller ions of the unwanted impurities out of said surface layer and into the body of said element, and repeating the reversals of said applied potential until a desired number of aluminum ions have become lodged in said surface layer and the unwanted ions have been excluded therefrom.

6. 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 silicon before fusion a small percentage of a metal capable of producing ions which are comparable in size to the interstices in the lattice structure of substantially pure crystalline silicon, shaping an element of the cast material from said ingot, heat treating said element to produce on the surface thereof a thin layer of substantially pure crystalline silicon, ionizing the added metal present in said element, and fixing said ions in the interstices in said surface layer.

7. The method of making a conductive device for electric waves that comprises forming a body by fusing a quantity of high purity silicon containing a small percentage of inherent metallic impurities, adding to said silicon before fusion a small percentage of metal, shaping an element from said body, heat treating said element to produce on the surface thereof a thin layer of substantially pure silicon having a crystalline structure with interstices comparable in size with ions of the added metal and substantially larger in size than the ions of said inherent metallic impurities, subjecting said element to electrical stress for ionizing the metals present in said element, and selectively controlling said stress to cause the migration of ions into and out of said surface layer, whereby ions of the added metal are fixed within the surface layer and other ions are excluded therefrom.

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REFERENCES CITED

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

FOREIGN PATENTS

Number	Country	Date
551,209	British	Feb. 12, 1943