

June 15, 1948.

R. S. OHL

2,443,542

LIGHT-SENSITIVE ELECTRIC DEVICE INCLUDING SILICON

Original Filed May 27, 1941

4 Sheets-Sheet 1

FIG. 1

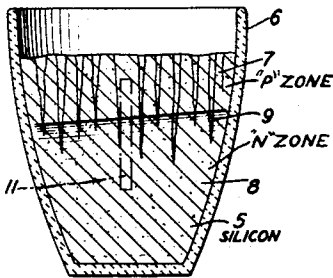
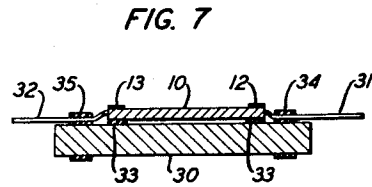
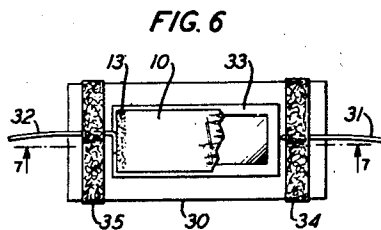
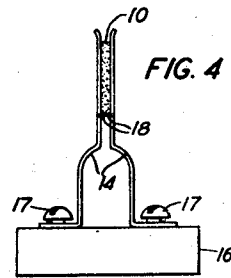
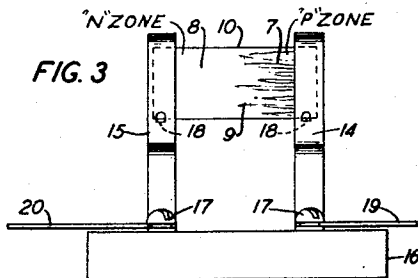
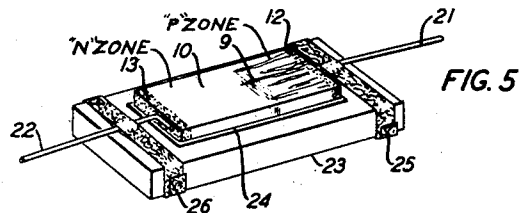
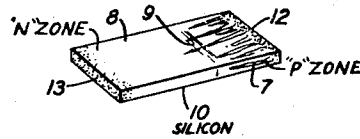


FIG. 2



INVENTOR
R. S. OHL

BY
Stanley B. Kent

ATTORNEY

June 15, 1948.

R. S. OHL

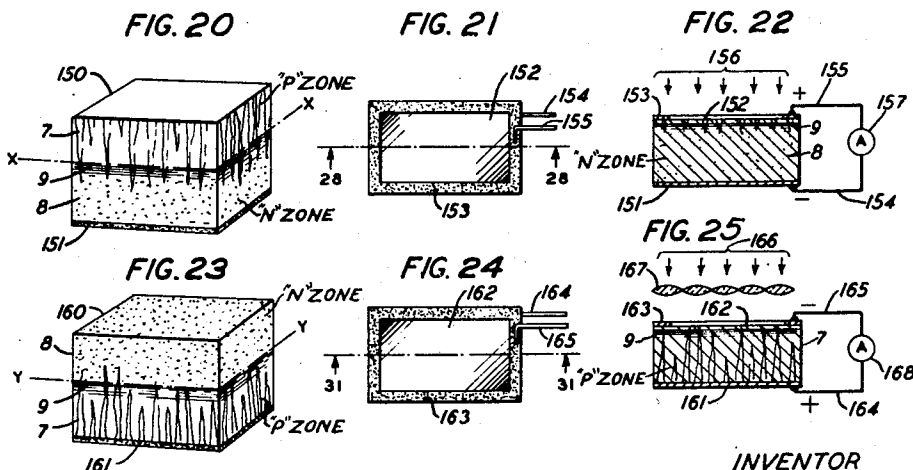
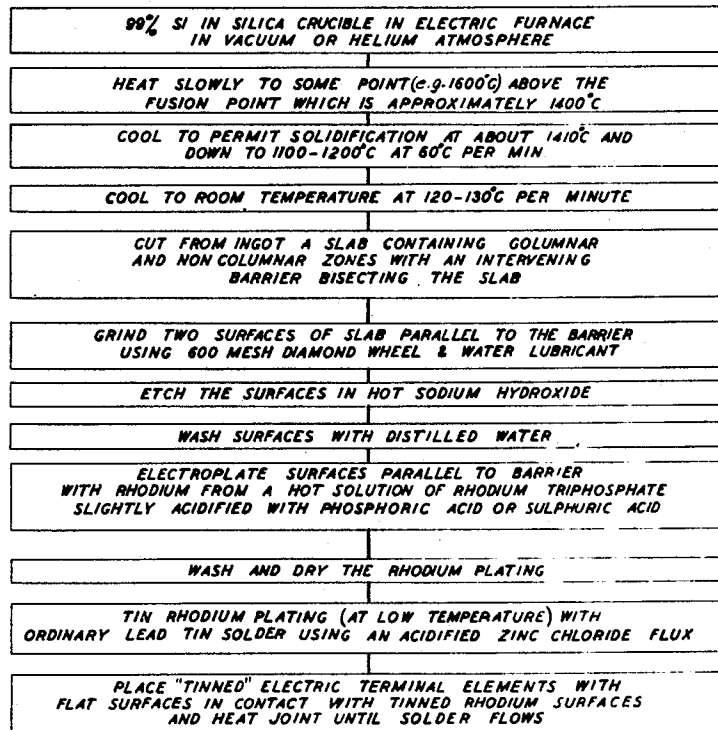
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LIGHT-SENSITIVE ELECTRIC DEVICE INCLUDING SILICON

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4 Sheets-Sheet 2

FIG. 8



INVENTOR
R. S. OHL

BY

Stanley B. Kent.
ATTORNEY

June 15, 1948.

R. S. OHL

2,443,542

LIGHT-SENSITIVE ELECTRIC DEVICE INCLUDING SILICON

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FIG. 9

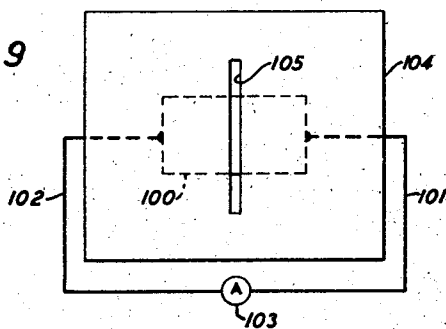


FIG. 11

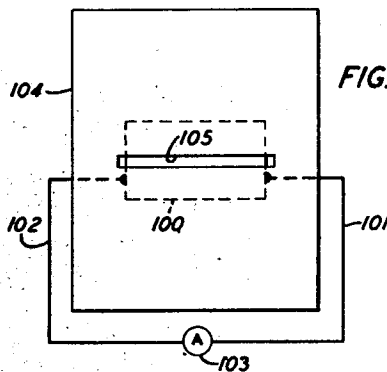


FIG. 10

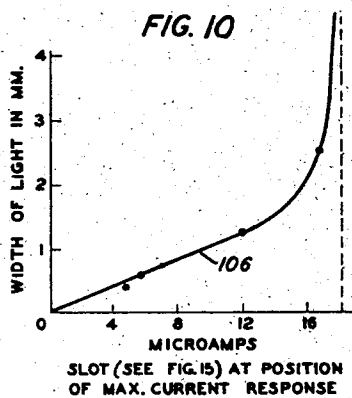


FIG. 12

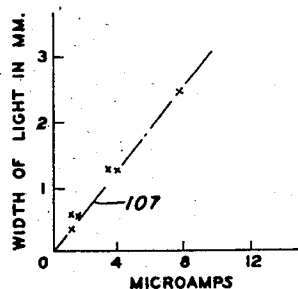


FIG. 14

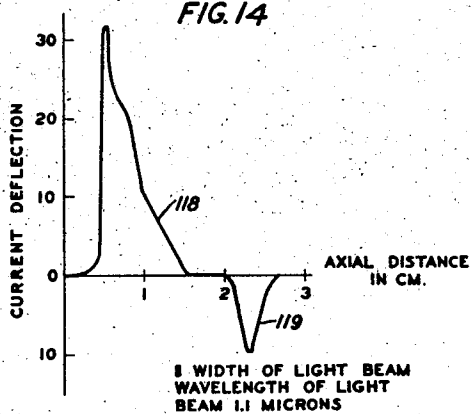
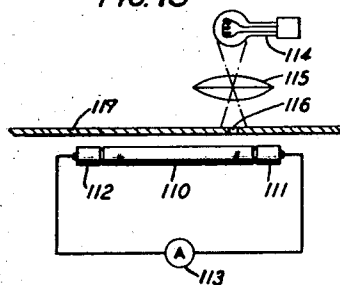


FIG. 13



INVENTOR
R. S. OHL

BY

Stanley B. Kent.
ATTORNEY

June 15, 1948.

R. S. OHL

2,443,542

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FIG. 15

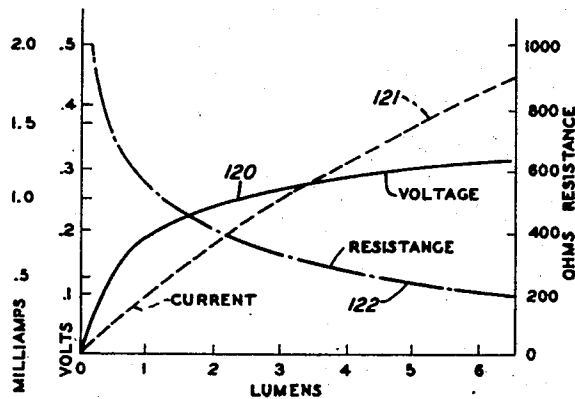
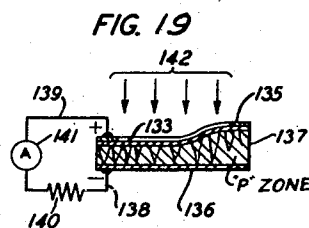
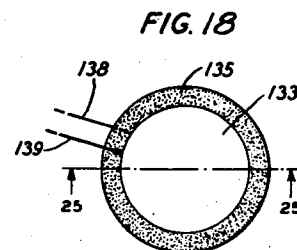
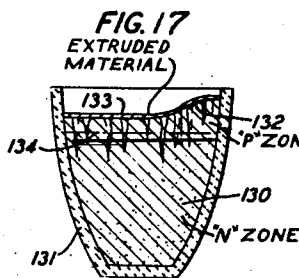
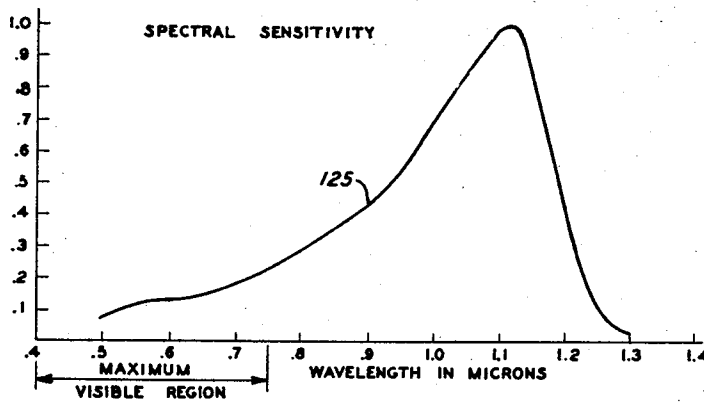


FIG. 16



INVENTOR
R. S. OHL
BY
Stanley B. Kent
ATTORNEY

UNITED STATES PATENT OFFICE

2,443,542

LIGHT-SENSITIVE ELECTRIC DEVICE
INCLUDING SILICON

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

Original application May 27, 1941, Serial No. 395,410, now Patent No. 2,402,662, dated June 25, 1946. Divided and this application September 17, 1942, Serial No. 458,709

9 Claims. (Cl. 136—89)

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This invention relates to light sensitive electric devices and more particularly to photo-E. M. F. cells comprising fused silicon of high purity.

This application is a division of application Serial No. 395,410, filed May 27, 1941, issued as U. S. Patent 2,402,662, June 25, 1946, for Light sensitive electric device.

An object of the invention is to provide an improved light sensitive electric device.

Another object of the invention is to provide an improved method of making light sensitive electric devices of fused silicon of high purity.

In an example of practice illustrative of this invention, a photo-E. M. F. cell is formed of a portion of a silicon ingot which is provided with conductive terminals. The ingot is produced by fusing metallic silicon in powdered form in a silica (SiO_2) crucible in an electric furnace and slowly cooling the fused material until it solidifies and for a period of time thereafter. The powdered metallic silicon used is of a high degree of purity, say 99 per cent or higher. Certain material which has proved very satisfactory has a purity of approximately 99.85 per cent. Ingots which are suitable for the production of photo-E. M. F. cells possess a characteristic structure which is visible when the surface is suitably prepared in vertical section. The upper portion of the ingot exhibits a columnar crystalline structure while the lower portion is non-columnar, and across the ingot in the lower section of the columnar portion is a striated zone, the striations extending across the ingot. This striated zone has the characteristics of a barrier zone or barrier layer and is conveniently designated simply a so-called "barrier." The portion of the ingot suitable for photo-E. M. F. cells includes this barrier.

A portion of silicon is cut from the ingot in such a way that the barrier forms an extended surface backed by a relatively large amount of metallic silicon which was adjacent to the unexposed surface of the barrier. A low resistance conductive terminal is secured to the metallic surface remote from the barrier by plating with rhodium. Another conductive terminal is secured to the exposed barrier surface remote from the metallic silicon in such a way as to permit illumination of an appreciable portion of the exposed barrier surface. Circuit connections may be soldered to these terminals. The silicon adjacent to the barrier may have either the columnar structure or the non-columnar structure.

In another example of practice illustrative of the invention a photo-E. M. F. cell is formed by

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slicing off the top of an ingot which has a hump of extruded material in the upper surface of the ingot, the whole upper surface being covered with an active layer so that the top surface has a pale yellow or greenish fluorescent appearance and attaching contact terminals such as a plating of rhodium on the metallic silicon surface remote from the active layer and a ring of sputtered platinum around the outer edge of the active layer. Circuit connections may also be soldered to these terminals.

The invention will now be described more in detail having reference to the accompanying drawing.

Fig. 1 shows in cross section an ingot of fused silicon within a silica crucible from which ingot material for photo-E. M. F. cells according to this invention may be cut;

Fig. 2 illustrates a photo-E. M. F. cell of another form cut from the ingot of Fig. 1;

Figs. 3 and 4 show the cell of Fig. 2 in one form of mounting;

Fig. 5 shows the cell of Fig. 2 in a modified form of mounting;

Figs. 6 and 7 illustrate another form of mounting of the cell of Fig. 2 wherein a reflecting surface is employed;

Fig. 8 is an operational diagram of one form of the method employed for producing photo-E. M. F. cells some of the steps of which are used in making photo-E. M. F. cells in accordance with this invention;

Fig. 9 is a diagrammatic showing of a test arrangement for determining the longitudinal distribution of the sensitivity of a photo-E. M. F. cell;

Fig. 10 is a plot of data obtained with the arrangement of Fig. 9;

Fig. 11 is an arrangement, similar to Fig. 9, for determining the transverse distribution of the sensitivity;

Fig. 12 is a plot of data obtained with the arrangement of Fig. 11;

Fig. 13 shows diagrammatically a test arrangement for determining the axial distribution of the sensitivity of a cylindrical section cut from an ingot having two barriers;

Fig. 14 is a plot of data obtained with the arrangement of Fig. 13;

Fig. 15 are plots of current, voltage and resistance, respectively, versus lumens of a typical photo-E. M. F. cell embodying this invention;

Fig. 16 is a plot of the spectral response of another typical photo-E. M. F. cell embodying this invention;

Fig. 17 shows in cross section an ingot of fused silicon within a silica crucible in which ingot the top surface is electrically light sensitive;

Figs. 18 and 19 illustrate a form of photo-E. M. F. cell cut from the upper portion of the ingot of Fig. 17 according to this invention;

Figs. 20, 21 and 22 illustrate a modified photo-E. M. F. cell according to this invention in the fabrication of which the columnar material above the barrier and a small amount of light sensitive barrier material is removed; and

Figs. 23, 24 and 25 illustrate still another modification according to this invention in the fabrication of which the material on the non-columnar side of the barrier and some of the barrier material is removed.

Like elements in the several figures of the drawing are indicated by identical reference characters.

During an investigation of the production of fused silicon of high purity and its use for point contact rectifiers applicant discovered that under certain conditions this material was sensitive to visible light, generating an electromotive force independently of any applied voltage. The light sensitive effects were of a magnitude comparable to the most effective photoelectric substances then known.

The manner of the discovery was briefly as follows:

A considerable number of melts of pure silicon had been made up in connection with the above-mentioned investigation. The material for some of these melts had been heated in a dry helium atmosphere. From each of a plurality of ingots resulting from some of these melts in helium a cylindrical rod had been cut for the purpose of making specific resistance measurements. These rods were about $\frac{3}{4}$ inch long and $\frac{1}{8}$ inch diameter. The rod from one of these melts had been equipped with metal end-pieces by a rhodium plating and lead-tin soldering process hereinafter to be described, to provide a good connection for the specific resistance measurements. Such a measurement was being made on this rod by applicant when he noticed, while viewing on an oscilloscope the wave shape of the 60-cycle current flowing through the rod, that the current in one direction was affected by light from an ordinary 40-watt desk lamp. A battery was then substituted for the 60-cycle current source and a rotating shutter was held between the rod and lamp to produce 20-cycle interruptions. A substantially square-top wave form was seen by applicant in the oscilloscope. Upon reduction and, finally, the elimination of battery voltage the square-top form persisted, although at a reduced amplitude.

This entirely unexpected phenomenon was recognized as of possibly great importance in the art of light sensitive electric devices and further study of this phenomenon was undertaken forthwith. The outcome of such study is that improved light sensitive electric devices and particularly photo-E. M. F. cells of high sensitivity and great stability have been made available. The present invention is a result of the above-mentioned discovery.

A form of ingot from which photo-E. M. F. cells can be cut is shown in Fig. 1. The ingot 5 is formed by the solidification of fused silicon in a silica crucible 6. Such an ingot made from certain kinds of highly purified silicon powder in a manner hereinafter to be described, comprises two zones of visibly different structure.

The upper zone 7 has a columnar structure, the columnar grains being of the order of one-half millimeter in width and extending down from the top of the ingot to a distance of 5 or 10 millimeters. The lower zone 8 has a non-columnar structure. The ingot fractures most easily in the lengthwise direction of the columns. The columnar portion of the fracture appears lustrous while the non-columnar portion has the appearance of a grayish mass of smaller crystals. Across the lower portion of the columnar zone 7 some sort of boundary or barrier 9 is found. In this region 9 the columnar portion tends to be striated, the striations extending across as well as between the columns. These striations appear, under a microscope, to have discontinuities at the columnar boundaries.

The above-mentioned barrier 9 is apparently the seat of the photo-E. M. F. effect. The upper zone 7 of the ingot 5 develops, on exposure to light, a positive potential with respect to the lower zone 8.

The photo-E. M. F. devices of Figs. 2 to 7, even though they are not being claimed in this application, will first be described to show the characteristics of the material used in the specific devices disclosed and claimed in this application. An understanding of these characteristics will facilitate an understanding of the invention of this application.

The photo-E. M. F. device of Fig. 2 comprises a silicon slab 10 cut from the ingot 5 of Fig. 1 at the position indicated by the dot and dash rectangle 11. This rectangle 11 outlines the section of the slab 10 midway between the edges and parallel thereto. In other words, the slab 10 is so cut from the ingot 5 that the barrier 9 lies approximately midway between the ends of the slab.

The slab 10 may be cut from the ingot 5 by any suitable process, but preferably by a process which conserves as much useful material as possible. The uppermost and lowermost portions of the ingot may be used for other purposes, such as contact rectifiers. The intermediate portion, including the barrier 9, may be used for photo-E. M. F. cells. A metal wheel charged with diamond particles is suitable for cutting the ingot 5, a stream of distilled water being used to clear the cut particles from the kerf and to cool the surfaces.

The surfaces of the slab 10 wherein the outcropping of the barrier 9 occurs, may be used in the condition in which they are cut from the ingot 5. There is an advantage, however, in polishing these surfaces in order to facilitate transmission of the exciting light into the interior of the slab 10. These surfaces may advantageously be polished in many ways. One method which has been used is as follows. The surface was first roughed flat with 600 mesh Aloxite, or M-302 optical powder, using an iron lap followed by 1000 mesh Aloxite, and a lead lap in the subsequent polishing with an optical powder such as for instance No. 95 optical powder. Suitable polishing abrasives are obtainable from the Norton Company, the American Optical Company or the Carborundum Company.

In order to facilitate the use of the slab 10 as a photo-E. M. F. cell, contact terminals 12 and 13 are provided on the ends of the slab by a process of rhodium plating. In a rhodium plating process which has been found to be very satisfactory, the end surfaces of the slab are ground flat using a 600 mesh diamond wheel and water

lubrication. Thereafter the end surfaces, including small adjoining portions of the side and edge surfaces, are etched in hot sodium hydroxide solution and washed in distilled water. These etched surfaces are thereupon electroplated with rhodium from a hot solution of rhodium triphosphate slightly acidified with phosphoric acid or sulphuric acid. After washing and drying, the rhodium plating makes excellent contact terminals because it does not loosen from the silicon and is highly resistant to corrosion. Such contacts are remarkably free from noise when used in communication circuits, such as are used to convey sound currents.

The size of the photo-E. M. F. cell or unit 10 of Fig. 2 is not critical, but it has been found that advantageous dimensions are 11 millimeters for length, 5 millimeters for width, and 0.6 millimeter for thickness. The barrier 9 lies advantageously about midway between the terminals 12 and 13.

One arrangement for mounting the photo-E. M. F. cell of Fig. 2 is illustrated in Figs. 3 and 4. Two pairs of spring clips 14 and 15 are secured to a block of insulation 16 by machine screws 17. The photo-E. M. F. cell 10 is slipped between the springs of the pairs of spring clips 14 and 15 with the contact terminals 12 and 13 in contact with the springs. Punched lips 18 prevent the photo-E. M. F. cell 10 from sliding down too far. Conductors 19 and 20 are connected to clips 14 and 15, respectively. When the barrier 9 of the photo-E. M. F. cell 10 is irradiated, a positive potential is developed in conductor 19 with respect to conductor 20 providing that the columnar end of the unit is in contact with clip 14, as shown.

Another arrangement for mounting the unit 10 such as illustrated in Fig. 2, is shown in Fig. 5. The unit 10 is provided with terminal conductors 21 and 22 by soldering. In soldering, the rhodium end surfaces 12 and 13 are 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. The ends of the conductors 21 and 22 are freely tinned, then placed in contact with the respective tinned rhodium surfaces and the joint heated until the solder flows, the excess solder being squeezed from between the conductor and the rhodium plating. A strong bond results. The unit 10 with the conductors 21 and 22 is then insulatingly mounted on a copper block 23. "Victron" or other suitable lacquer is used to secure the unit 10 to the block 23 with a sheet of insulation 24, such as a sheet of cigarette paper, between the unit 10 and the block 23. The conductors 21 and 22 are advantageously held out of contact with the copper block 23 by wrappings 25 and 26, respectively, of friction or rubber tape.

Still another arrangement for mounting the unit 10 of Fig. 2 is illustrated in Figs. 6 and 7 which is adapted to make use of reflected light. The unit 10 is provided with conductors 31 and 32 in the manner described in connection with Fig. 5. The polished faces of the unit 10 are treated to reduce the surface reflection losses by the application of approximately a quarter wavelength thickness of "Victron" lacquer. Two dipings of the polished silicon surfaces in "Victron" lacquer is highly beneficial in improving the response of these photo-E. M. F. cells to light. The coated unit 10 is insulatingly mounted on a copper block 30, the surface of the block adjacent to the unit having been highly polished and advantageously

treated to render it highly reflective of the radiation used for energizing the photo-E. M. F. cell. The unit 10 is supported at its edges by a hollow rectangle 33, cut from an insulating sheet, such as a sheet of cigarette paper. The slab 10, rectangle 33 and block 30 are cemented together by "Victron" lacquer or other suitable cement, and the conductors 31 and 32 are held out of contact with the copper block 30 by wrappings 34 and 35, similar to those described in connection with Fig. 5.

An operational diagram for producing a photo-E. M. F. unit is shown in Fig. 8, some steps of which are used for producing the photo-E. M. F. unit according to this invention. 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 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, the melt may be brought to a temperature of the order of 200° C. above melting point. In an example of practice of this process "high form" crucibles of 50 cubic centimeter capacity obtainable from Thermal Syndicate Ltd., 12 East 46th Street, New York, New York, were employed. A furnace 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 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 centigrade degrees per minute, this being effected by decreasing the power input at the rate of about one-half 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 centigrade degrees per minute.

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 examination of the cooled ingot it is found that a portion of the grain structure is columnar, as heretofore explained. This is, in general, the upper portion of the ingot or the first material to solidify. In the area last to solidify and beyond the columnar grains a non-columnar 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 occurs in a plane normal to the columns and this barrier has extremely important light sensitive electric properties. The barrier ordinarily occurs a short distance above where the columnar and non-columnar zones merge so that it extends across

the columns near their lower ends. The region above the barrier develops a positive thermoelectric potential with respect to an attached copper electrode and may, therefore, be designated as the "P" zone. The region below the barrier develops a negative thermoelectric potential with respect to an attached copper electrode. It will be designated as the "N" zone.

To prepare a photo-E. M. F. cell like that of Fig. 5 for example, a slab of material is cut from the ingot in such a manner as to be bisected approximately by the barrier. The surfaces of the slab parallel to the barrier may be ground flat and electric terminal elements attached thereto in the manner diagrammed in Fig. 8 and described hereinbefore.

Granulated silicon of high purity now available on the market is produced by crushing material found in a large commercial melt. That supplied by Electrometallurgical Company, 30 East 42nd Street, New York, New York, is of a size to pass a 30 mesh screen and to be retained by an 80 mesh screen. The crushed material is purified by treatment with acids until it has attained a purity considerably in excess of 99 per cent. The chemical composition of a typical sample of this material is approximately:

Si	99.85	O	.061
C	.019	H	.001
Fe	.031	Mg	.007
Al	.020	P	.011
Ca	.003	Mn	.002
N	.008		

In some samples amounts up to .03 Ti and .004 Cr have been found.

The results of measurements made in circuits comprising photo-E. M. F. cells made of the same material of which photo-E. M. F. cells of this invention are made, will now be given to assist in the understanding of this invention. It is to be understood that these results are actual results obtained with certain specified photo-E. M. F. units.

Fig. 9 illustrates a test arrangement for determining the location and size of the photo-E. M. F. region in a rectangular slab of silicon cut from an ingot in such a manner that the barrier approximately bisects the slab intermediate the ends thereof. It was a simple matter to determine that the sensitive region was a strip across the face of the slab, probably only a few millimeters wide. This was done by moving a light spot over the face of the slab while the terminals were connected to a milliammeter and noting the positions of the spot for maximum current at a plurality of transverse positions. In order to determine the actual dimensions of the sensitive region pieces of opaque black paper were slotted with variable width slots and slid over the surface of the slab until a maximum response was obtained for a given intensity of illumination of the area exposed by the slot. One such piece of paper is illustrated in Fig. 9. The slab 100 provided with rhodium-plated soldered wire terminals 101 and 102 is connected to a microammeter 103. A sheet of black paper 104 covers the slab except for the surface exposed by slot 105 which lies transversely across the slab 100. In order to find the position of maximum current response with a given width of slot 105 and given intensity of illumination of the surface of the slab exposed by the slot, the surface of the slab is explored by moving the paper 104 with the slot 105 lengthwise across

the slab. For each width of slot the response would vary as typified by the graph of Fig. 14, but would differ from the specific shape there shown dependent upon the location of the barrier and the width of the slot. With a certain slab-type of photo-E. M. F. cell, mounted as shown in Fig. 5, which is 11.4 millimeters long, 5.5 millimeters wide and 0.6 millimeter thick, the data of Fig. 10 was obtained. The slot width is plotted as ordinates and the current at the position of maximum response as abscissae. The curve 106 shows that the response is linear for small slot widths up to about 1.5 millimeters but that beyond this width there is a relatively small increase of response current from 14 microamperes to 18 microamperes for the whole length of the slab which, as mentioned above, was 11.4 millimeters. Therefore, it can be said that for this particular slab a strip of illumination about 1.5 millimeters wide across the slab yields very nearly the total response for a given light flux intensity.

Fig. 11 shows a test arrangement much like that of Fig. 9 but adapted to determine any variation of the photo-E. M. F. region transversely of the slab. The black paper 104 with the slot 105 is rotated 90 degrees with respect to its position in Fig. 9. The data of Fig. 12 was obtained with various slot widths oriented as in Fig. 11 and with the same photo-E. M. F. cell as described above which cell is 11.4 millimeters long, 5.5 millimeters wide and 0.6 millimeter thick. At the position of maximum response for each slot width the response is proportional to the width of the light band as shown by curve 107 of Fig. 12. This shows that there is negligible variation in the photo-E. M. F. region transversely of this slab.

It has happened that an ingot was formed with a double barrier one of which was near the top of the ingot and the other near the bottom. A photo-E. M. F. cell cut from such an ingot and including both barriers exhibits a double peaked response when explored with a narrow light spot. A test arrangement for determining such response is shown in Fig. 13. Such a photo-E. M. F. cell 110, provided with metal terminals 111 and 112, is connected to an ammeter 113. A small transverse strip of the cell is illuminated by light from a source 114 directed by lens 115 through an aperture 116 in a sheet of black paper 117. The cell 110 is moved lengthwise in front of the aperture 116 and the current deflection in the meter 113 is observed. With a certain rod-type of photo-E. M. F. cell, designated rod No. 2, which is 3.15 millimeters in diameter, 30 millimeters long and 24 millimeters between the plated terminals, the data of Fig. 14 was obtained. The width of the light beam was approximately one-half millimeter and its wave-length was 1.1 microns. The current deflection is plotted as ordinates and the distance from one selected end in centimeters is plotted as abscissae. As shown by curves 118 and 119, this photo-E. M. F. cell exhibits two maxima of current response which are of opposite polarity. If both barriers are illuminated simultaneously the effects are opposing in the series circuit including the meter 113. In this particular rod, one barrier is more responsive than the other, as indicated by the height of the peaks of curves 118 and 119. The width of the areas under response curves 118 and 119 is probably due to the fact that the pure silicon of these units is appreciably light transmissive.

The illumination-response characteristics of

the photo-E. M. F. cell which is hereinbefore described in connection with Figs. 9 to 12 as being 11.4 millimeters long, 5.5 millimeters wide and 0.6 millimeter thick are shown by the curves of Fig. 15. The light source used to obtain this data was a 21-candlepower 6- to 8-volt automobile lamp No. 1130 operated at 7.40 volts and a color temperature of 2930° K. The filament was focused in a spot at the barrier at a magnification of about unity. The flux in this beam was varied by inserting Levy line screens whose transmission was determined in the position used. Curve 120 shows the open-circuit voltage and curve 121 shows the short-circuit current dependence on incident light flux in lumens. The voltage is expressed in volts and the current in milliamperes. Curve 122 shows the value of resistance at which the short-circuit current was reduced to one-half.

The spectral sensitivity of a cylindrical type of single-barrier photo-E. M. F. cell is shown in Fig. 16. This cell is 3.15 millimeters in diameter, 26 millimeters long and 21 millimeters between the terminal platings. Curve 125 shows the spectral sensitivity. The ordinates are energy values, the maximum being unity. The abscissae are wave-lengths of the light in microns. The measurements were made using a small spot of light from the spectrometer focused on the barrier. It will be noted that, while the cell has some sensitivity in the visible region, the maximum is out in the infra-red. Since the light penetrates an appreciable thickness of silicon to reach portions of the barrier, the optical transmission of the silicon has an effect on the shape of curve 125. Because of this large response in the deep infra-red, the silicon photo-E. M. F. cells of this invention provide a tool not available heretofore in the optical art.

During the production of silicon ingots according to the method hereinbefore described it was discovered that in a small proportion of the melts, say 3 to 5 per cent, the top of the melt was covered with material which was extruded from the interior during the cooling process. The top surfaces of some such ingots had a pale yellowish and greenish fluorescent appearance. It was discovered by applicant that, if a contact were made to the top surface of such an ingot and some other point of the ingot, an electric current would flow if the top of the ingot were irradiated with infra-red or visible light. The electrons are apparently very efficiently released by the light and driven into the main conducting body of purified silicon. Substantially the full sensitivity is developed whatever may be the size of the surface contact area. This type of photo-E. M. F. cell shows some response for ultra-violet radiation.

An ingot which shows extruded material and the above-mentioned surface layer is shown in vertical section in Fig. 17. The ingot 130 is formed by the solidification of fused silicon powder of high purity in a silica crucible 131. The extruded material forms a hump 132 in the upper surface of the ingot, while the whole surface is covered by the active layer 133. The thickness of this layer 133 is necessarily greatly exaggerated in Fig. 17. It is in fact of microscopic thickness.

A photo-E. M. F. cell according to this invention comprising this sensitive layer 133 may be fabricated by slicing off the top of ingot 130 at the position shown by dot and dash line 134 (Fig. 17), and adding contact terminals as shown in Figs. 18 and 19. An advantageous form of

contact for the sensitive surface layer comprises a ring of sputtered platinum 135. Another way to form a contact ring is to use platinum paint and heat or "fire" the unit at a temperature of 500° to 550° C. The sensitive surface layer is not injured by such firing operation. The other contact 136 attached to the body of silicon 137 may be formed as hereinbefore described by electroplating with rhodium to which a copper wire 138 may be soldered. Similarly, another copper wire 139 may be soldered to the platinum ring 135. This photo-E. M. F. cell may be connected to a load circuit 140 in series with ammeter 141 by means of conductors 138 and 139. The illumination of the light sensitive layer is indicated by the arrows 142. The whole unit may be dipped in "Victron" or other suitable lacquer. The thickness of the lacquer on the sensitive layer may advantageously be made one-fourth the wave-length of the energizing radiation. Such a thickness reduces reflection as hereinbefore described in connection with Figs. 6 and 7.

Another form of photo-E. M. F. cell according to this invention in which the surface of the barrier is illuminated, is illustrated in Figs. 20, 21 and 22. Fig. 22 is a cross section through the cell of Fig. 21 at the plane indicated by the arrows 28. In fabricating one form of such a cell, the columnar zone of a body of fused silicon is cut away down to the barrier, terminal contacts being made to the resulting exposed surface of the barrier zone and the opposite surface of the noncolumnar zone. As shown in Fig. 20, a block of silicon 150 in the form of a parallelepiped is cut from a silicon ingot such as that shown in Fig. 1, having a barrier zone 9 substantially parallel to the top and bottom faces of the block. The columnar zone 7 is at the top and the non-columnar zone 8 at the bottom. The lower surface of the non-columnar zone 8 is provided with an electrical contact 151 by plating with rhodium in the manner hereinbefore described. The upper portion of the columnar zone 7 is then cut away down to the plane represented by the line X-X. This plane extends through the upper layer of the barrier zone, the location of which zone is determined by exploring the vertical surfaces of the block 150 with a small spot of light and noting the current response in a test circuit connected to the upper and lower surfaces of the block 150. The resulting barrier surface 152 is then highly polished and a narrow strip around the periphery of the polished surface is roughened with M-302 emery. Both the polished and roughened portions of surface 152 are then plated with rhodium in the manner hereinbefore described. The rhodium plating is then rubbed off from the polished portion of the surface 152 leaving a strip of plating 153 around the periphery. This strip 153 serves as an electrical contact for the barrier region of the resulting photo-E. M. F. cell. Conductors 154 and 155 may be soldered to the rhodium contacts in the manner hereinbefore described. The illumination of the light sensitive surface is indicated by the arrows 156. When illuminated, conductor 155 assumes a positive potential with respect to conductor 154.

Another photo-E. M. F. cell, similar to that just described but in which the non-columnar material 8 is cut away down to the barrier 9, is illustrated in Figs. 23, 24 and 25. Fig. 25 shows a cross section of the cell of Fig. 24 at the plane indicated by arrows 31. In fabricating this form

of cell, a block of silicon 160 similar to that of Fig. 20, having a columnar zone 7, a non-columnar zone 8 and a barrier region 9 is cut from an ingot of fused silicon. The bottom surface of the columnar zone 7, the columnar zone being at the bottom in Fig. 23, is provided with an electrical contact 161 by plating with rhodium in the manner hereinbefore described. The non-columnar zone 8 is cut away down to the upper portion of the barrier region represented by the plane indicated by the line Y—Y. The resulting barrier surface 162 is polished, roughened around the periphery and plated with rhodium which is partly removed to form contact 163 as explained in connection with the cell of Figs. 21 and 22. Conductors 164 and 165 are soldered to the rhodium plating 161 and 163, respectively. The polished surface 162 is shown illuminated by light rays 166 passing through 30-degree lenses 167. When illuminated, conductor 164 assumes a positive potential with respect to conductor 165.

The edges of the cells of Figs. 22 and 25 may be provided with an opaque insulating coating, such as black pitch, to exclude extraneous light. The 30-degree lenses of Fig. 25 may also be used with the cell of Fig. 22. The use of such lenses is advantageous when these cells are used as exposure meters.

It has been found that individual photo-E. M. F. cells of the kind illustrated in Figs. 22 and 25 are about equally sensitive over the whole exposed barrier surface as determined by exploring the surfaces of several cells with a small spot of light. It is advantageous to cut close to or even into the barrier region. Measurements made on several cells indicate that there is some advantage in cutting away the columnar region of the silicon block as illustrated in Figs. 20, 21 and 22 instead of the non-columnar region as illustrated in Figs. 23, 24 and 25. The columnar material is more transparent than the non-columnar material and accordingly a somewhat larger proportion of the light can reach the light sensitive region. However, both types of cells are useful. The amount of silicon adjacent to the barrier region on the side opposite to that which is illuminated, in these types of cells appears not to be critical.

An ammeter 157 is shown connected to the conductors 154 and 155 of the photo-E. M. F. cell of Fig. 22 and an ammeter 168 is shown connected to conductors 164 and 165 of the photo-E. M. F. cell of Fig. 25.

A coating of "Victron" or other suitable lacquer may be used on the polished surfaces of the cells of Fig. 22 and 25 to reduce reflection losses.

The nature of the boundary or barrier zone 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 0.1 per cent to 0.5 per cent and this should be done if a preliminary sample of a particular lot of material does not form the distinctive barrier structure.

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 zone 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 the ingot into discrete "P" and "N" zones. Where, however, the cooling is precipitate 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 fashion as to render the resulting ingot quite unsatisfactory for photo-E. M. F. cells. The slow cooling rate is important in developing an orderly striation or barrier. Features of the method of preparing effective silicon materials are described and claimed in the application of J. H. Scaff, Serial No. 386,835, filed April 4, 1941, issued as U. S. Patent 2,402,582, June 25, 1946, for Improvements in the preparation of silicon materials. For further information regarding material from which light sensitive electric devices according to this invention may be fabricated, reference is made to the disclosure of this Scaff patent.

"Victron" lacquer, which has been referred to hereinbefore, is a solution of the polystyrene with the addition of a small amount of resin to produce a good lacquering result. It is a commercial product.

Patent No. 2,402,662, of which this application is a division, is itself a continuation in part of application Serial No. 385,425, filed March 27, 1941, issued as U. S. Patent 2,402,839, June 25, 1946, for Electrical translating devices utilizing silicon.

What is claimed is:

1. A photo-E. M. F. cell comprising the upper portion of an ingot of fused silicon the top surface layer of which portion comprises material formed from material from the melt having a yellowish and greenish fluorescent appearance overlying metallic silicon, a conductive terminal adapted to permit illumination of an appreciable portion of said top surface in contact with said top surface, and another terminal in contact with the metallic silicon.

2. A photo-E. M. F. cell comprising a body of silicon of high purity produced by cooling fused silicon powder of a purity in excess of 99 per cent, a surface layer of material extruded from the fused silicon after the surface has solidified, and electrical terminals connected to said body of silicon and said layer, respectively, the terminal connected to said layer being adapted to permit illumination of an appreciable portion of said layer.

3. A photo-E. M. F. cell comprising the upper portion of an ingot of fused silicon the top surface layer of which portion comprises material formed from material from the melt having a yellowish and greenish fluorescent appearance overlying metallic silicon, terminal metal sputtered on said top surface and adapted to permit illumination of an appreciable portion of said top surface, and an electrical contact connected to said metallic silicon.

4. A photo-E. M. F. cell which comprises a body of solidified fused silicon of high purity including a striated zone, said body being cut from an ingot having a striated zone between a columnar zone

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and a non-columnar zone, the striated zone being adapted to be exposed to radiation at right angles thereto, an electrical contact connected to the surface of said striated zone remote from said other zone and adapted to permit radiations to reach an appreciable portion of the surface of said striated zone, and an electrical contact connected to a surface of said other zone remote from said striated zone.

5. The method of fabricating a photo-E. M. F. cell which comprises forming an ingot of fused silicon of high purity having a "P" zone, an "N" zone and a light sensitive barrier zone in the vicinity between the "P" and "N" zones, removing a body of material from said ingot including integrally connected "P" zone, barrier zone and "N" zone material, determining the location of the outcropping of said barrier zone on the exposed surfaces of said body by exploring said surfaces with a small spot of light and noting the current response in a test circuit connected to the "P" zone and the "N" zone material, respectively, removing the material of said body of material on one side of said barrier zone subsequently to the determination of the location of the barrier zone as indicated by said outcropping of said barrier zone to expose a surface which was adjacent to and covered by the removed material before its removal, and connecting electrical contacts to the surface of said barrier zone which was exposed by the removal of said material and to the surface of the remaining material remote from said barrier zone, respectively, the contact connected to the barrier zone being adapted to permit illumination of an appreciable portion of the exposed surface of said barrier zone.

6. A photo-E. M. F. cell comprising the upper portion of an ingot of fused silicon the top surface of which ingot comprises material having a yellowish and greenish fluorescent appearance overlying metallic silicon, said material having been extruded from the fused silicon after the surface had solidified, a conductive terminal adapted to permit illumination of an appreciable portion of said top surface in contact with said top surface, and another terminal in contact with the metallic silicon.

7. A photo-E. M. F. cell comprising the upper portion of an ingot of fused silicon having a purity in excess of 99 per cent, the top surface of which ingot comprises material having a yellowish and greenish fluorescent appearance overlying

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metallic silicon, said material having been extruded from the fused silicon after the surface had solidified, a conductive terminal adapted to permit illumination of an appreciable portion of said top surface in contact with said top surface, and another terminal in contact with the metallic silicon.

8. A photo-E. M. F. cell comprising a body of solidified fused silicon of a purity in excess of 99 per cent including a striated zone, said body being cut from an ingot having a striated zone between a columnar zone and a non-columnar zone and the striated zone being adapted to be exposed to radiation at right angles thereto, an electrical contact connected to the surface of said striated zone remote from said other zone and adapted to permit radiations to reach an appreciable portion of the surface of said striated zone, and an electrical contact connected to a surface of said other zone remote from said striated zone.

9. A photo-E. M. F. cell comprising an integral mass of high purity solidified fused silicon formed by cooling a melt of high purity silicon, said mass having a body portion and a layer-like portion in part adjoining each other, an electric contact connected to a part of said body portion which is remote from said light sensitive portion, and an electric contact connected to the surface of said light sensitive portion remote from said body portion and adapted to permit illumination of an appreciable portion of the surface of said layer-like portion, said layer-like portion being formed of material extruded from the melt during cooling, which material is more light sensitive than the material of said body portion.

RUSSELL S. OHL.

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