

May 18, 1948.

K. H. STORKS ET AL

2,441,603

ELECTRICAL TRANSLATING MATERIALS AND METHOD OF MAKING THEM

Filed July 28, 1943

2 Sheets-Sheet 1

FIG. 1

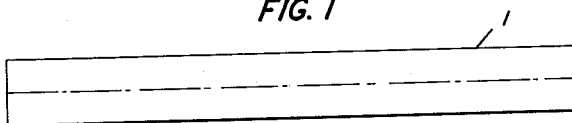


FIG. 2



FIG. 3

FIG. 4

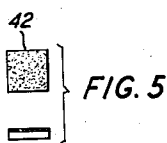
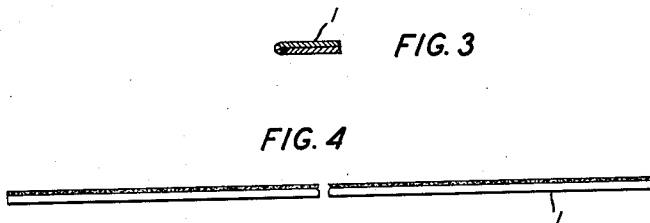
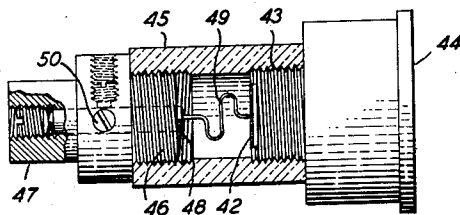


FIG. 7



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2 Sheets-Sheet 2

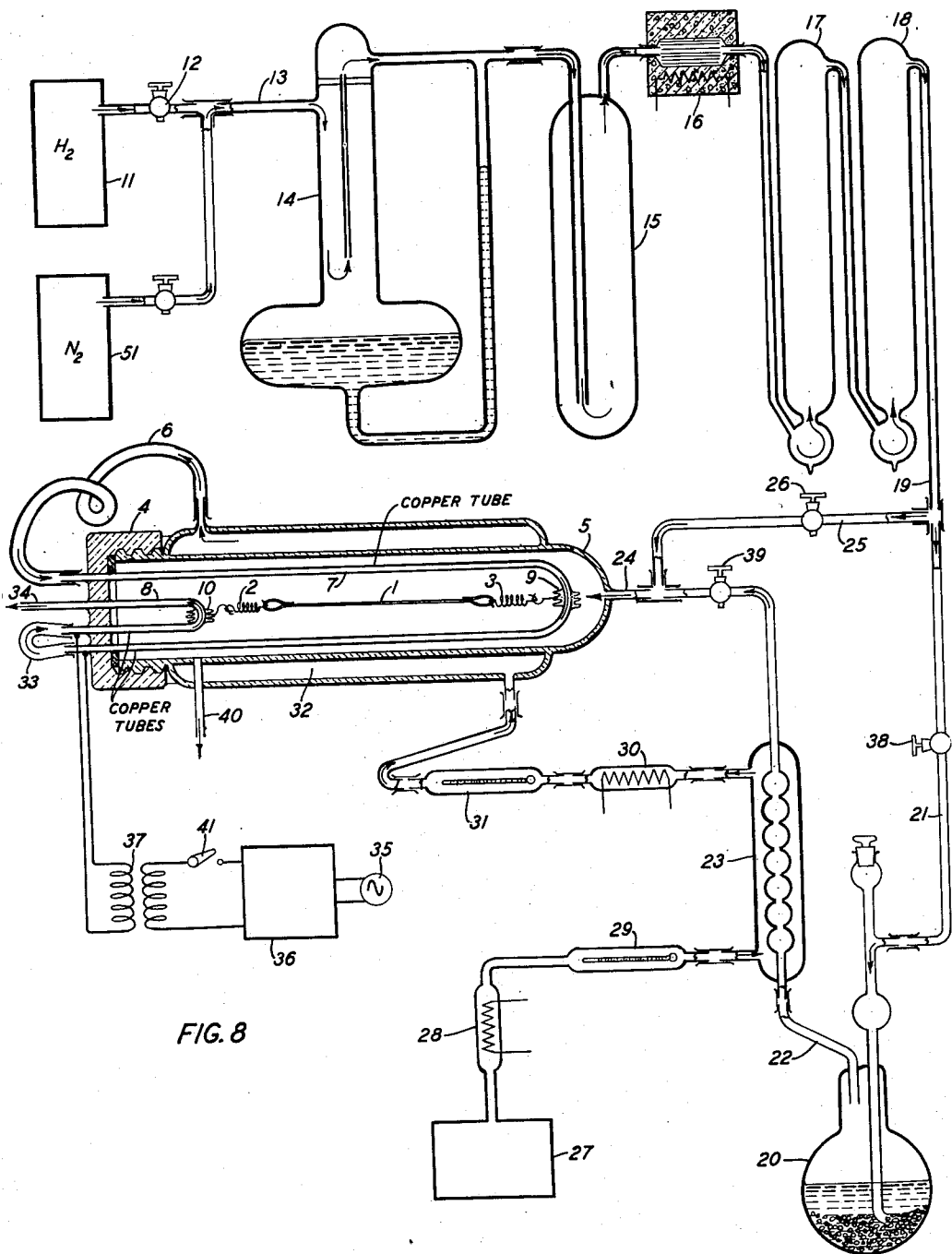


FIG. 8

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2,441,603

ELECTRICAL TRANSLATING MATERIALS
AND METHOD OF MAKING THEM

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Application July 28, 1943, Serial No. 496,414

10 Claims. (Cl. 175-366)

1

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

The objects of the invention are to realize the optimum electrical characteristics for rectifying and other translating devices, including an increased electrical efficiency; to obtain an improved and a more uniform rectification material for use in these devices; to improve the process by which this material is produced; and to effect other improvements in materials and devices of this character and in the methods by which they are manufactured.

With the extension of signaling frequencies in the radio and allied arts into the ultra-high frequency range where waves of a few centimeters in length are employed for signaling purposes it has become necessary to develop new types of apparatus for receiving, translating and utilizing the signal energy at these extreme frequencies. One of the problems has been to devise a satisfactory translating device which is capable of detecting, converting or otherwise translating signal waves having frequencies of the order mentioned. Up to the present time the most promising solution of this problem has been a translating or rectifying device of the point-contact type. In one form a fine tungsten wire is mounted so that its free end engages the surface of an element having suitable rectifying properties, such as a crystal of elemental silicon. More specifically the silicon crystal elements of these prior rectifiers have been prepared by melting powdered silicon of relatively high purity in a furnace and cutting the resulting ingot into small wafers of suitable diameter and thickness. The crystal wafer is then mounted on a terminal block, and the fine tungsten wire is adjusted so that its end makes a point contact with the surface of the crystal.

In accordance with the present invention it is possible to increase the efficiency and usefulness of these translating devices by means of a translating element made by an improved process of depositing elemental silicon on metallic filaments and of causing the filament material to alloy with the silicon in a prescribed way. The translating element made by this improved process consists of crystallized layers of a multi-phase system of thermally deposited silicon and a suitable metal such as tantalum, which may be supported on a backing strip of some suitable metal, which may also be tantalum. In the process by which these rectifying elements are prepared a strip or filament of tantalum is

2

heated to a predetermined temperature in a reaction chamber, and a vaporous mixture of silicon tetrachloride and hydrogen is introduced into the chamber under closely regulated conditions. By carefully controlling the manufacturing parameters, that is, the concentration of the vapor mixture admitted to the chamber, the temperature of the filament, the temperature of the chamber walls and filament terminals during the deposition process and the duration and sequence of the deposition processes and heat treatments applicants have found that marked improvements may be realized in the electrical performance of the transmitting devices made from the material thus produced.

Accordingly, a feature of the invention is a method of depositing silicon on metal strips for use as translators in which a vapor mixture including silicon tetrachloride of predetermined concentration is administered to a reaction chamber containing a suspended metallic filament, in which the filament is heated to a predetermined temperature and maintained uniformly at this temperature during the decomposition of the silicon tetrachloride, and in which the walls of the reaction chamber and the terminals on which the filaments are suspended are maintained at a relatively low temperature by a cooling system to prevent the formation of reaction products which otherwise tend to contaminate the deposited silicon and to impair its usefulness. More specifically, the vapor administered to the reaction chamber is a mixture of silicon tetrachloride and hydrogen, and the concentration of this mixture is controlled by a condenser associated with the cooling system of the reaction chamber in such a way that the partial pressure of the silicon tetrachloride in the reaction chamber is always below the pressure of saturation. In this manner the silicon tetrachloride is prevented from condensing on the cool walls of the reaction chamber during the deposition process.

Another feature of the deposition process is the method of cooling the reaction chamber in which the cooling liquid, after being raised to a temperature above that required for the condenser, is passed in succession through a jacket surrounding the reaction chamber and through conduits forming the suspension terminals of the metallic filament on which the deposition is taking place.

Another feature of the invention is the method of preparing the rectifier material in which successive layers of silicon are deposited on a metal-

3

lic filament and in which each layer thus deposited is fused and crystallized before the succeeding layer is deposited.

Another feature of the invention is the method of preparing rectifier material in which the silicon is alloyed with the filament material in a controlled manner to give a chemical system of a preferred composition, a preferred phase structure and a smooth surface contributing to low noise output. This end is greatly aided by the controlled quenching of the alloy in flowing hydrogen gas.

Another feature of the invention is a method whereby the thermal deposit of the silicon is confined to one side of the metal filament or strip. This end is achieved by folding the strip so that only one side thereof is exposed within the reaction chamber.

Other features and advantages of the invention will be discussed more fully in the following detailed specification.

In the drawings accompanying the specification:

Fig. 1 illustrates a filament or strip (greatly enlarged) of backing metal for the rectifying elements;

Fig. 2 shows the folded metal strip with supporting terminal springs secured thereto;

Fig. 3 is a cross-section of a folded strip;

Fig. 4 is a side view of the metal strip illustrating a deposited layer of silicon;

Figs. 5 and 6 illustrate units cut from the prepared strip and ready for assembly;

Fig. 7 is a view partly in cross-section of a translating device including one of the rectifier elements; and

Fig. 8 illustrates the apparatus used for depositing the silicon on the metal backing strips.

Different methods have been employed heretofore for obtaining silicon in suitable form for rectification elements having the physical and electrical characteristics essential to good performance in the ultra-high frequency range. One of the obstacles commonly encountered in these prior methods has been the difficulty of attaining the high degree of silicon purity necessary for best results. Experience shows that where metallurgical methods are used to derive the silicon material it should have a purity close to 100 percent. But the character and amounts of the small percentage of impurities are important and very difficult to control. The strong affinity which silicon in its elemental state has for other elements makes it extremely difficult to obtain it in crystalline form in bodies of substantial size and to exclude the presence of impurities in varying and uncontrolled amounts.

Applicants' method overcomes the difficulties above outlined by deriving the elemental silicon from one of its compounds which can be readily purified, depositing it in the form required and fusing the deposit to crystallization under conditions which insure the desired degrees of purity and of alloying with a metal to give suitable electrical impedance and rectification characteristics. More particularly, silicon tetrachloride vapor mixed with hydrogen is administered to a reaction chamber where it is decomposed thermally to liberate the elemental silicon which then deposits on a filament of metal, such as tantalum. However, experience shows that other reactions are likely to take place within the chamber when the temperature is raised to a value sufficient to cause decomposition of the silicon tetrachloride vapor. For example, reactions may occur between

4

the vapors within the chamber and the materials of which the chamber walls and fixtures are composed, resulting in products which deposit as impurities on the filament along with the liberated silicon. In applicants' process these objectionable reactions are prevented by a novel method of controlling the temperature of the reaction chamber walls and fixtures in conjunction with the pressure of the vapor mixture administered to the chamber. To this end a vapor mixture of hydrogen and silicon tetrachloride having a high saturation of the tetrachloride is prepared in apparatus external to the reaction chamber, and this mixture is passed through a reflux condenser on its way to the reaction chamber. A cooling liquid at a predetermined temperature passes through the condenser to reduce the saturation of the vapor mixture to a definite value before the mixture is permitted to enter the chamber. The cooling liquid after leaving the reflux condenser is raised to a higher temperature and is then circulated through the walls and terminal fixtures of the reaction chamber to maintain them at the corresponding temperature during the decomposition of the tetrachloride vapor. This increment between the temperature at which the saturation of the vapor mixture is fixed before its introduction into the chamber and the temperature of the chamber walls insures that the partial pressure of the tetrachloride vapor within the chamber is always less than the pressure of saturation. By this arrangement, therefore, it is possible to maintain the temperature of the chamber walls and terminal fixtures sufficiently low to prevent reactions taking place which would contaminate the silicon deposition and yet sufficiently high to prevent condensation of the tetrachloride vapor within the chamber.

In the drawings Figs. 1 to 3 illustrate the metallic filament or ribbon which is used as the base for the thermal deposit of silicon. It will be understood, of course, that the invention is not limited to a particular metal for the filament; the particular metal or combination of metals found to give the results desired may be chosen. Experiments have been made with such metals such as tantalum, platinum, tungsten and molybdenum, and of these it is found that tantalum has the least tendency to enter into solution with the silicon layer. This metal, therefore, gives excellent results where a high degree of silicon purity is desired and where the alloying is subjected to control.

The filament 1 of the desired metal, such as tantalum, is formed with the requisite dimensions and is then prepared for the reaction chamber shown in Fig. 8. This preparation consists in folding the ribbon along the middle, as indicated by the dotted line in Fig. 1, turning over and spot-welding the ends to form loops, and attaching thereto a pair of retractile springs 2 and 3 as illustrated in Fig. 2. The purpose of folding the ribbon upon itself is to restrict the deposit of the silicon to only one of the ribbon surfaces. After the ribbon is thus prepared the head 4 of the reaction chamber 5 is unscrewed and removed, the circulating hose 6 being first detached, molded or otherwise fixed in the head 4 are the terminal and cooling fixtures for suspending the filament 1. These fixtures comprise a large U-shaped tube 7 and a smaller U-shaped tube 8. These tubes are preferably of copper, and they serve to conduct the cooling liquid through the heat distributing terminals 9 and 10, between which the filament 1 is suspended by the retractile

5

springs 2 and 3. Following the suspension of the filament between the terminals 9 and 10 the head 4 is screwed back in place, closing the open end of the chamber 5. The cooling pipe 6, the purpose of which will be explained hereinafter, is also attached as shown in the drawing.

The remaining apparatus shown in Fig. 8 is for the purpose of administering the vapor mixture to the reaction chamber and for heating the chamber to bring about the vapor decomposition. The hydrogen is derived from a supply tank 11 which is connected by way of valve 12 and feed pipe 13 to a flow meter 14. The purpose of the meter 14 is to maintain a uniform flow of gas under varying external conditions. The hydrogen gas after passing through the regulating flow meter 14 enters a trap 15 having liquid nitrogen therein for the purpose of trapping any mercury vapor that may escape from the meter 14. Following the trap 15, the gas enters a deoxidizing furnace 16 for the purpose of removing any traces of free oxygen that may be mixed with the hydrogen gas. On leaving the furnace 16 the hydrogen and any water vapor that may be formed in the furnace enter the drying towers 17 and 18. These towers may be provided with phosphorous pentoxide for removing all traces of water vapor, thus permitting only pure hydrogen to flow into the outlet pipe 19.

The silicon tetrachloride vapor is derived from the vessel 20 where it is first mixed with the hydrogen gas under conditions that give the mixture a high degree of saturation. The mixture is effected by leading the pure hydrogen gas through the inlet pipe 21 into the liquid tetrachloride. The hydrogen gas, after bubbling through the liquid tetrachloride, escapes through the outlet pipe 22 into the reflux condenser 23. After leaving the condenser the vapor mixture passes through the intake pipe 24 and thence into the reaction chamber 5. A by-pass pipe 25 is also provided with a valve 26 for diluting the vapor mixture, if desired, by passing some of the hydrogen directly into the reaction chamber.

The water for the cooling system is taken from a source 27 and raised to a predetermined temperature, preferably a few degrees below room temperature, by means of a heater 28. After passing through the thermometer chamber 29, which gives a continuous indication of the temperature, the liquid enters the reflux condenser 23 to fix the concentration of the vapor emerging from the vessel 20. After leaving the condenser 23 the liquid passes through a second heater 30 which raises its temperature to a predetermined value, preferably about room temperature. From the heater 30 the liquid passes through thermometer chamber 31 and thence into the cooling jacket 32 surrounding the walls of the reaction chamber 5. After passing through the cooling jacket 32 the liquid emerges into the pipe or hose 6. The purpose of the pipe 6 is to reduce the temperature of the liquid which has been heated in the jacket 32 by radiating or otherwise extracting some of the heat therefrom. After passing through the pipe 6 the liquid reenters the reaction chamber flows through the copper tube 7, through the terminal 9 and thence out of the chamber into a second cooling tube 33. From the tube 33 the liquid reenters the chamber a second time and flows in the copper tube 8 through the terminal 10 and finally out by way of the waste pipe 34.

The necessary heat for producing the vapor decomposition within the chamber is derived from a source of current 35, and a suitable regulator

6

36 serves to maintain the voltage necessary to produce the required temperature within the chamber. The energy from the source 35 is supplied to the suspended filament 1 within the chamber by connecting the secondary winding of the transformer 37 to the circulating pipes 7 and 8, thus causing current to flow through the filament by way of terminals 9 and 10 and suspension springs 2 and 3.

The sequential steps of the process will now be described in detail, assuming specific temperatures values and other factors which have been found to give good results. A strip 1 of annealed tantalum is cut to suitable length and folded as seen in Figs. 2 and 3. Before folding, the strip may be washed if necessary in acetone to remove any grease that may be present. Also a matte finish may be given the surface of the strip by blasting it with fine mesh silicon carbide. After thorough cleaning, the strip is folded as above explained, and springs 2 and 3 are attached either by welding or as indicated in the drawing. The prepared filament 1 is then mounted within the reaction chamber as shown in Fig. 8.

Dry tank hydrogen is now passed over the filament for several minutes. To this end the valves 12 and 26 are opened and valves 38 and 39 are closed. Hydrogen from the tank 11 passes through the flow meter 14, through the liquid trap 15, furnace 16 and thence through the drying towers 17 and 18 into the supply pipe 19. From thence it flows through the by-pass pipe 25 into the reaction chamber and out through the waste pipe 40. While hydrogen is flowing through the chamber, the switch 41 is closed and the filament 1 is raised to a temperature of 1200° C., where it is maintained for a period of about thirty seconds. Thereupon the filament is given a flash to the melting point of silicon, following which it is permitted to cool rapidly to room temperature. The temperature of the filament within the chamber is determined by any well-known means, such as an optical pyrometer.

The filament is now ready for the deposition process which consists in depositing a plurality, preferably three, separate layers of silicon, each layer being fused before the succeeding layer is deposited. Preparatory to the first step in the deposition process the valve 39 is opened and the openings of valves 26 and 38 are adjusted to give the desired ratio between the amount of hydrogen flowing through the by-pass pipe 25 and the amount flowing through the pipe 21 into the tetrachloride vessel 20. This ratio, which may be of the order of 1:1, may be determined by any suitable method, one of which is to observe the rate at which bubbles emerge from the liquid tetrachloride in the vessel 20. The flow of hydrogen in the meter 14 is fixed at 35 millimeters pressure of mercury across the capillary. The heater 28 is adjusted to maintain the water entering the condenser 23 at a temperature about 3 or 4 degrees below room temperature, which may be assumed to be 67° F., and the heater 30 is adjusted to maintain the liquid emerging from the condenser at 67° F.

After several minutes of flow to establish the equilibrium of the vapor mixture of hydrogen and silicon tetrachloride the temperature of the filament is raised to 935° C., and is maintained at that value for about ten minutes. During this period the silicon tetrachloride vapor is decomposed thermally, the liberated silicon is deposited on the surface of the filament 1, and the un-

wanted products of the reaction are discharged through the waste pipe 40.

If it is assumed that the hydrogen gas emerging from the vessel 20 is highly saturated, possibly super-saturated, with silicon tetrachloride, the condensation occurring within the condenser 23 will reduce the concentration of tetrachloride to the saturation value corresponding to the temperature within the condenser. When, therefore, the mixture enters the reaction chamber, it encounters a chamber wall temperature which is somewhat higher than that of the condenser. This differential increases the saturation pressure of the vapor to a point which is safely above the partial pressure of the tetrachloride and thereby prevents condensation of the tetrachloride on the walls of the chamber. The same differential temperature relation is maintained between the condenser and the terminal fixtures within the chamber 5 by means of the cooling pipes 7 and 8 and the external cooling tubes 6 and 33 through which the liquid is circulated before it finally emerges from the waste pipe 34.

After deposition has proceeded for a period of about ten minutes as described, the flow of tetrachloride vapor is stopped by closing the valves 38 and 39, permitting the continued flow of hydrogen into the deposition chamber. After about three minutes the filament temperature is raised to 1200° C., and maintained there for two minutes. Thereupon the temperature is quickly raised to the melting point of silicon, following which it is quenched in the hydrogen, which is a good heat conductor, to about 895° C., forcing the fused silicon to rapidly crystallize.

The second and third layers of silicon are deposited, fused and quenched under conditions the same as those above described for the deposition of the first layer.

By this method pure silicon is deposited on the tantalum, a diffusion of the tantalum into the silicon takes place to form a polyphase structure, and the degree of the alloying action is closely controlled by quenching the fused structure in hydrogen gas. In this way a superior rectifying material is obtained.

The filament is now removed from the chamber and is cut into rectangles or discs as illustrated in Figs. 5 and 6 for use in the rectifier assemblies. The assembled rectifier, greatly enlarged, is illustrated in Fig. 7. One of the silicon units 42 is included in the assembled device and is mounted on the threaded metallic stud 43. The mounting of the silicon unit on the stud 43 may be accomplished by any suitable method. For example, the tantalum side of the unit 42 may be welded to the surface of the stud 43. Following the attachment of the silicon unit 42 to the stud 43, which is integral with the metallic base member 44, the stud is screwed into one end of the ceramic insulating cylinder 45. In like manner the threaded stud 46, which is integral with the metallic cap 47, screws into the opposite end of the cylinder 45. The cap member 47 contains a central bore for receiving the cylindrical metallic contact holder 48; and this holder is adjusted within the bore until the tip end of the tungsten contact wire 49, the opposite end of which is soldered in the holder 48, makes contact with the silicon surface of the element 43. When the desired degree of force is applied to the contact engagement of the wire 49 with the silicon element 43, the set screws 50 are tightened to seize the holder 48.

The vessels and interconnecting pipes forming

the system shown in Fig. 8 are of glass. The unions between sections of pipe are preferably of copper, the valves are of bronze, and the valve packing is protected from the vapors in the system by lead washers on the valve stem. These precautions are taken to eliminate any source of contamination and to prevent any unwanted substance from finding its way into the reaction chamber.

The tank 51 contains nitrogen which may be used for flushing the system to clean out impurities and to prevent the entry of oxygen, water vapor, or other substances.

What is claimed is:

1. The method of making an electrical translating element which comprises suspending a metallic filament in a reaction chamber, administering a vapor mixture including silicon tetrachloride to said chamber, heating said filament to a predetermined temperature for effecting the decomposition of the silicon tetrachloride and the deposition of a layer of silicon on said filament, cooling said reaction chamber to a predetermined temperature to prevent the contamination of said silicon layer by the formation of undesired reaction products, and controlling the pressure of the vapor mixture before it enters the reaction chamber to prevent the condensation of the silicon tetrachloride within said chamber.
2. The method of making an electrical translating element which comprises suspending a metallic filament in a reaction chamber, administering a vapor mixture including silicon tetrachloride to said chamber, heating said filament to a predetermined temperature for effecting the decomposition of the silicon tetrachloride and the deposition of a layer of silicon on said filament, cooling said reaction chamber to a predetermined temperature to prevent the contamination of said silicon layer by the formation of undesired reaction products, and establishing a differential between the saturation pressure of the vapor mixture before and after it enters the reaction chamber to prevent the condensation of the silicon tetrachloride within said chamber.
3. The method of making an electrical translating element which comprises suspending a metallic filament in a reaction chamber, passing a vapor mixture including silicon tetrachloride through a condenser and thence into said chamber, heating said filament to effect the decomposition of the silicon tetrachloride and the deposition of a layer of silicon on said filament, passing a stream of liquid first to said condenser and then to the walls of said reaction chamber, controlling the temperature of said liquid at a given value as it passes to said condenser for fixing the concentration of said vapor mixture, and controlling the temperature of said liquid at a higher value as it passes to the walls of said reaction chamber in order to increase the saturation pressure of said vapor mixture above the partial pressure of the silicon tetrachloride.
4. The method of making an electrical translating element which comprises fixing a metallic filament in a reaction chamber, administering a vapor mixture of silicon tetrachloride and hydrogen to said reaction chamber, electrically heating said metallic filament for effecting the decomposition of the silicon tetrachloride in said mixture and the deposition of a layer on said filament, cooling said reaction chamber to a predetermined temperature to prevent reaction between the silicon tetrachloride and the walls of said chamber and the consequent formation of contaminating

products, and controlling the concentration of the silicon tetrachloride in said vapor mixture before it enters the reaction chamber to prevent the condensation of the silicon tetrachloride within said chamber.

5. The method of making an electrical translating element which comprises suspending a metallic filament between two terminals in a reaction chamber, passing a vapor mixture including a silicon compound and a gas through a condenser and into said chamber, applying a voltage to said terminals for heating said filament to a predetermined temperature for effecting the decomposition of the silicon compound and the deposition of a layer of silicon on said filament, passing a stream of cooling liquid first to said condenser and thence in series through the cooling jacket of said reaction chamber and through said suspending terminals, controlling the temperature of said liquid at a given value as it passes to said condenser to fix the concentration of said vapor mixture, and controlling the temperature of said liquid at a higher value as it passes to said cooling jacket and terminals for increasing the saturation pressure of said vapor mixture and preventing the condensation of the silicon compound on the walls of said reaction chamber and on said suspending terminals.

6. The method of making an electrical translating element which comprises suspending a metallic filament in a reaction chamber, administering a vapor mixture including a compound of silicon to said reaction chamber, heating said filament to a predetermined temperature a number of times in succession for effecting the decomposition of the silicon compound and the deposition of a corresponding number of separate layers of silicon on said filament, heating said filament to a higher temperature, following the deposition of each layer, to fuse, crystallize, and to quench the deposited layer to give a desired phase structure and smooth surface, and cooling said reaction chamber to a predetermined temperature to prevent the contamination of said silicon layers by the formation of undesired reaction products.

7. The method of making an electrical translating element which comprises folding a metallic

strip at its middle to conceal one of its surfaces and to leave the other surface exposed, suspending said folded strip in a reaction chamber, administering to said reaction chamber a vapor mixture including a compound of silicon, heating said metallic strip to a predetermined temperature to effect the thermal decomposition of said silicon compound and the deposition of a layer of silicon on the exposed surface of said metallic strip, cutting said strip with the deposited silicon thereon into units, and utilizing the metallic surface of said units for mounting them.

8. The method of making rectifier material which comprises fusing silicon in the presence of tantalum to cause a diffusion of the tantalum into the silicon and the formation of a polyphase structure, and quenching said structure to control the degree of diffusion.

9. The method of making rectifier material which comprises fusing silicon in the presence of a body of tantalum to form a polyphase structure of silicon and diffused tantalum on said tantalum body, and quenching the fused structure in hydrogen.

10. The method of making rectifier material which comprises depositing a plurality of successive layers of silicon on a body of tantalum, fusing each successive layer to effect a diffusion of the tantalum into the deposited silicon, and quenching each fused layer in succession to crystallize the silicon and to control the degree of diffusion.

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