May 15, 1951 J. R. FISHER ET AL 2,552,626

SILICON-GERMANIUM RESISTOR AND METHOD OF MAKING IT

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FIG. 1.

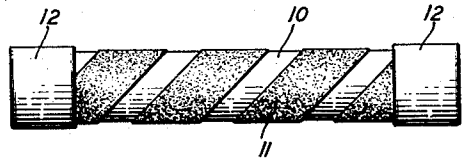

FIG. 2.

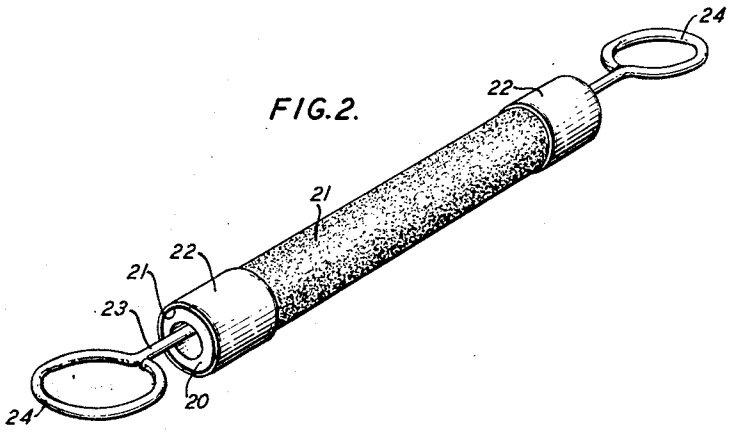

FIG. 3.

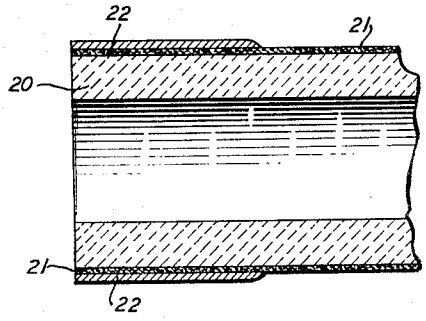

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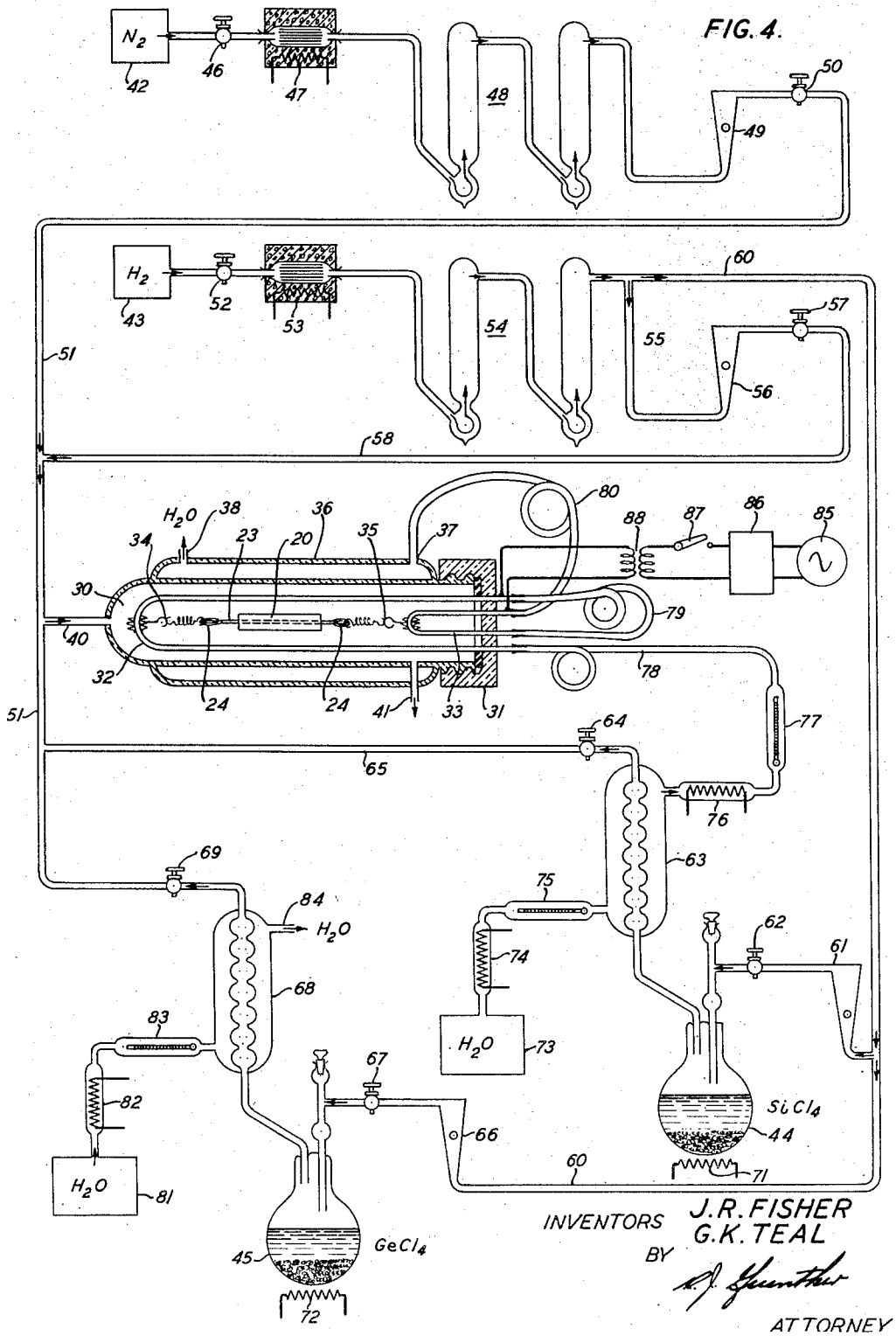
FIG. 4.



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SILICON-GERMANIUM RESISTOR AND METHOD OF MAKING IT

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4 Claims. (Cl. 201—64)

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This invention relates to resistors and more particularly to resistors comprising a film of mixed silicon and germanium and to methods of making such resistors.

Resistors having a relatively high resistance may be made by depositing a thin film of conductive material on an insulating backing. If an extremely high resistance is required, a film material of high resistivity may be used. The making of such resistors often involves obtaining a suitable temperature coefficient of resistance along with a desired resistance value. In general, film materials of relatively high conductivity have low resistance-temperature coefficients and those of relatively high resistivity have high resistance-temperature coefficients. For some applications it is necessary to use film materials of high resistivity in order to obtain a suitable resistance value, but the requirements are such that a low resistance-temperature coefficient is desired.

One object of this invention is to produce a film type resistor having relatively high resistance and a relatively low temperature coefficient of resistance.

A feature of this invention resides in employing a film of mixed silicon and germanium on an insulating backing to produce a resistor of the type desired.

Another feature of this invention lies in codepositing the two materials so that a homogeneous film of a desired characteristic results.

In one embodiment of this invention, a relatively small ceramic tube, such as a porcelain tube is provided with a film of mixed silicon and germanium of very high purity, preferably by the pyrolytic deposition of the materials from a gaseous mixture of their tetrachlorides in hydrogen. The deposition occurs when the hydrogen-chloride mixture is passed over the surface of the heated ceramic tube in a reaction chamber. A good deposit may be obtained with a ceramic tube temperature between 950 and 1150° C. The ceramic tube may be heated by a tantalum wire passing through the bore of the tube.

Other and further objects and features of this invention will appear more fully and clearly from the following description of exemplary embodiments thereof taken in connection with the appended drawings in which:

Fig. 1 is a view in elevation of a resistor made in accordance with this invention;

Fig. 2 is a perspective view of another resistor made in accordance with this invention and includes a supporting element used in the manufacture of the resistor;

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Fig. 3 is a sectional view of a portion of a resistor such as those of Figs. 1 and 2, enlarged to show details of the construction; and

Fig. 4 is a diagram of apparatus which may be used in producing resistance films in accordance with this invention.

The resistor shown in Fig. 1 comprises a tube 10 of insulating material such as a suitable ceramic, having a film 11 of resistance material applied thereto. Contact is made to the resistance film 11 by terminals 12. The film 11 as shown is in spiral form to provide a long path between the terminals 12.

The resistor shown in Fig. 2 is similar to that shown in Fig. 1 except that the film covers all of the surface from terminal to terminal. The insulating tube 20 is completely covered with a film 21 of resistance material and provided with terminals 22. The element 23 forms no part of the finished resistor, but merely provides support for the resistor during processing. The loops 24 are for connecting the support 23 to other parts of the processing apparatus later to be described.

Fig. 3 shows more specifically the construction of one end of these resistors. The tube 20 is coated on its outer surface with the film 21 by a process to be described and a terminal 22 is applied to each end portion of the film 21. The terminals 22 may comprise a film of heat cured metallic paste such as a paste of finely divided silver and a fluxing material such as a glass with sufficient temporary binder and solvent to make the paste workable.

Films of mixed silicon and germanium may be deposited on the surfaces of ceramic tubes by means of the apparatus illustrated in Fig. 4. The ceramic tube 20 mounted on the wire 23, which may be of tantalum, is suspended by the loops 24 in a reaction chamber 30. The chamber 30 is provided with a suitable cover 31 which may be attached by a screw thread. Mounted on the cover and secured in sealing relation therethrough are support and terminal elements or tubes 32 and 33. The support elements 32 and 33 are made of copper tubing or other similar material so that they may also serve as electrical conductors and may be cooled by suitable fluid passing through them. The support wire 23, which also serves as a heater, may be secured to the elements 32 and 33 by suitable resilient supports such as the hook and spring assemblies 34 and 35.

The reaction chamber 30 is provided with a cooling jacket 36 having entrance and exit ports 37 and 38 respectively. Inlet pipe 40 connected

to one end of chamber 30 provides for the entrance of the various gaseous materials used in the deposition process. The waste materials from the chamber are exhausted through the outlet pipe 41.

The gaseous materials used in this process are supplied from a nitrogen tank or reservoir 42, a hydrogen tank or reservoir 43, a silicon tetrachloride boiler 44 and a germanium tetrachloride boiler 45. The nitrogen is used to flush out the chamber initially and the other materials are mixed in the proper proportion to obtain the film or coating desired.

The nitrogen from tank 42 is admitted through valve 46 to a deoxidizing furnace 47 to remove any traces of free oxygen in the gas. The deoxidized gas is then passed through drying towers 48 to remove any traces of water vapor. From the drying towers the gas passes through a flow meter 49 and a valve 50 by way of pipe 51 and inlet 40 to the chamber 30.

Hydrogen from tank 43 passes through similar apparatus including the valve 52, the deoxidizing furnace 53, the drying towers 54, pipe 55, flow meter 56, valve 57, pipe 58 to pipe 51 and then through inlet pipe 40 to the chamber 30. The oxygen and moisture-free hydrogen also may be conducted by pipe 59 to the silicon tetrachloride and germanium tetrachloride boilers 44 and 45 respectively. Hydrogen passing to the silicon tetrachloride boiler goes through flow meter 61, valve 62, boiler 44, reflux condenser 63, valve 64, pipe 65 to the pipe 51 and thence through the inlet pipe 40 to the chamber 30. The hydrogen for the germanium tetrachloride boiler goes from pipe 60 through the flow meter 66, valve 67, boiler 45, reflux condenser 68, valve 69, pipe 51, and inlet pipe 40 to the chamber 30.

The silicon tetrachloride and germanium tetrachloride boilers 44 and 45 are provided respectively with heaters 71 and 72 for boiling off their respective vapors.

The condenser 63 receives cooling water from a supply 73, through a heater 74, and a temperature indicator 75. Cooling water upon leaving condenser 63 passes through another heater 76, a temperature indicator 77, a tube 78, through the support tube 32 in the chamber 30 and thence through the support tube 33 by way of the tube 79. Cooling water leaving tube 33 passes through tube 80, inlet 37 to cooling chamber 36 and thence out through the exit port 38. The tubes 78, 79 and 80 are of an insulating material such as rubber or the like for reasons which will appear upon further description. The condenser 68 may be provided with a separate source of cooling water from the reservoir 81 through the heater 82 and temperature indicator 83. This water is exhausted through the outlet or exhaust pipe 84.

The support and heating wire 23 in the chamber 30 is heated by electric current from the source 85. The circuit is through a suitable regulator 86 by way of closed switch 87, transformer 88, to the support and cooling tubes 32 and 33 and by way of the resilient support means 34 and 35 respectively to wire 23. As previously noted the tubes 78, 79 and 80 are of insulating material. This is to confine the electrical current to the metallic tubing within the chamber 30.

A typical deposition of mixed silicon and germanium on the ceramic tube 20 may be as follows: The valve 50 is opened and the reaction chamber 30 is flushed with nitrogen. After sufficient flushing, the valve 50 is closed and the valve 57 is opened allowing dry, oxygen-free hydrogen to flow through the reaction chamber. While the hydrogen is flowing through the reaction chamber, the switch 87 is closed and the wire 23 is raised to a temperature sufficient to heat the ceramic tube 20 to 1200° C. at which temperature it is maintained for about 30 seconds. The temperature of the tube 20 may be determined by any well-known means such as an optical pyrometer. The tube 20 is now ready to be covered with the silicon-germanium mixture, the thickness and character of the film being determined by the hydrogen flow, the flow of silicon tetrachloride and of germanium tetrachloride, the time of deposition, the temperature of the ceramic tube and the type of ceramic tube used. By suitably controlling these variables, a coherent, smooth film may be obtained on a ceramic base. Successful depositions have been made with germanium tetrachloride concentrations between 0.87 and 8.0 mol per cent relative to silicon tetrachloride.

Preparatory to effecting the deposition, the valves 64 and 69 are opened and the openings of valves 57, 62 and 67 are adjusted to give the desired ratio between the amounts of hydrogen flowing through the tube 58 and the amounts flowing through the boilers 44 and 45. The heaters 74 and 82 are adjusted to give a water temperature of about 3° C. and may be thermostatically controlled. The heater 76 is adjusted to maintain the water entering the cooling system of the reaction chamber 30 at approximately room temperature say 25° C.

After several minutes of flow to establish the equilibrium of the gaseous mixture of hydrogen, silicon tetrachloride and germanium tetrachloride, the temperature of the ceramic tube 20 is rapidly raised to any desired temperature between about 950° C. and 1150° C. and maintained for the period of the deposition which may be 2 minutes at a temperature of 1100° C. During this period the gaseous tetrachlorides are decomposed thermally, the pure liberated silicon and germanium are deposited on the surface of the ceramic tube 20 and the unwanted products of the reaction are discharged through the outlet 41.

If it is assumed that the hydrogen gas emerging from the boilers 44 and 45 is highly saturated, possibly supersaturated, with silicon tetrachloride and germanium tetrachloride respectively, the condensation occurring within the condensers 63 and 68 will reduce the concentration of the chlorides to the saturation values corresponding to the temperatures within the condensers. Therefore, when the mixture enters the reaction chamber 30, it encounters a chamber wall temperature which is somewhat higher than that of the condensers. This differential increases the saturation pressure of the gaseous mixture to a point which is safely above the partial pressure of the chlorides and thereby prevents condensation of the chlorides on the walls of the reaction chamber. The same differential temperature relation is maintained between the condenser and the terminal fixtures 32 and 33 by the cooling water flowing therethrough from the heater 76.

After a suitable deposition time has elapsed, the apparatus is shut down and the ceramic tube is removed. The germanium-silicon film may be provided with contacts as previously set forth with respect to Figs. 2 and 3. If a longer film such as illustrated in Fig. 1 is desired, the unwanted material may be ground off or otherwise removed with suitable apparatus.

Although the invention has been disclosed by exemplary embodiments thereof, it is not intended that it be limited thereby but by the scope of the appended claims only.

What is claimed is:

1. A resistor comprising a ceramic support, a thin film on said support of a material consisting of a mixture of silicon and germanium, and spaced electrical connecting means secured to said film, the germanium constituting from of the order of 2 to the order of 18 per cent by weight of the film.

2. A resistor comprising a ceramic support, a thin film of mixed silicon and germanium on said support, and spaced electrical connecting means in contact with said film, the atomic ratio of silicon to germanium in said film being about 11 to 1.

3. An electrical film resistor comprising an alloy of silicon and germanium, the germanium constituting of the order of 18 per cent by weight of the film and means for supporting said film.

4. The method of making an electrical resistor, which comprises simultaneously introducing silicon tetrachloride and germanium tetrachloride into a chamber having a body therein, the germanium tetrachloride concentration relative to silicon tetrachloride being between substantially 0.87 and 8.0 mol per cent,

and maintaining an atmosphere of hydrogen and a temperature of the order of 1100° C. in the chamber, whereby silicon and germanium are deposited simultaneously upon said body in a film having a high resistivity and a low temperature coefficient of resistance.

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