

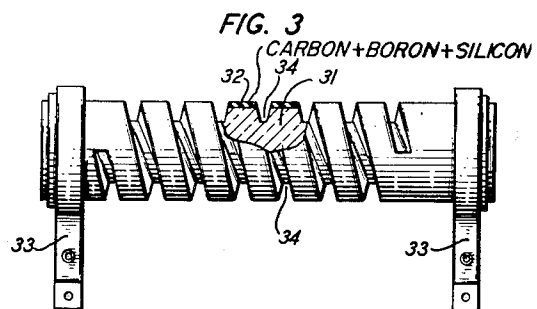
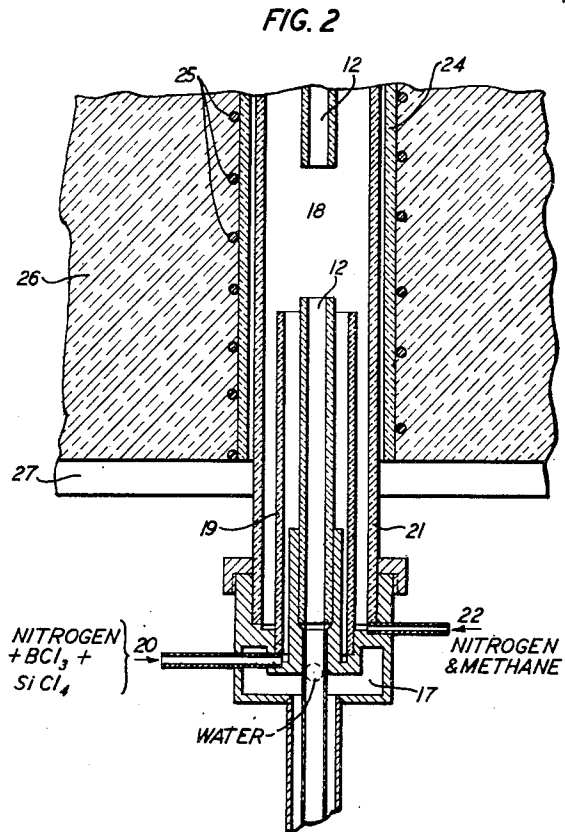
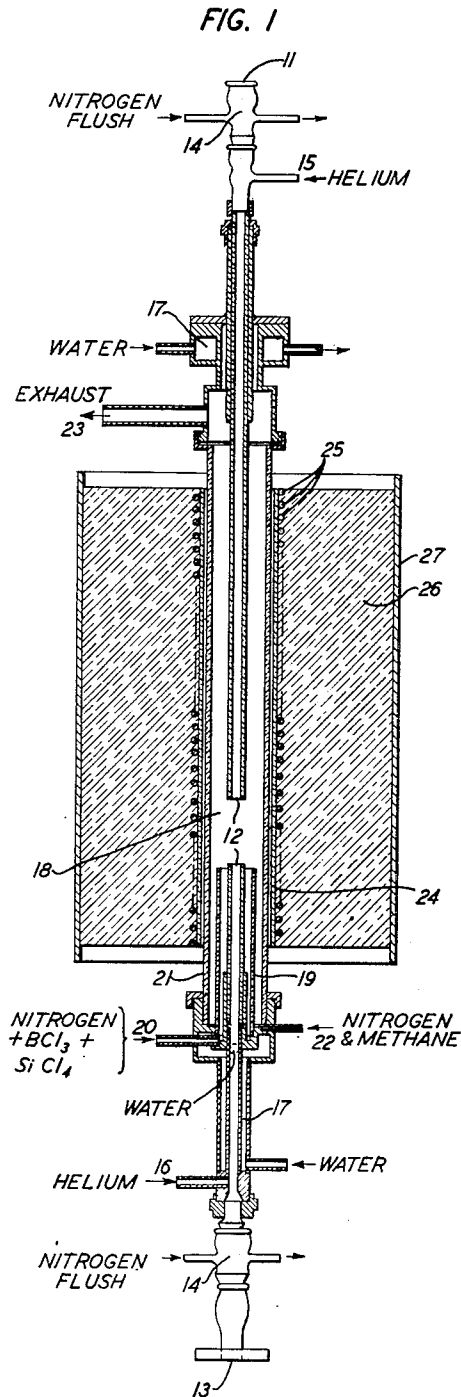
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METHOD OF MAKING ELECTRICAL CARBON-FILM RESISTORS

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METHOD OF MAKING ELECTRICAL CARBON-FILM RESISTORS

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5 Claims. (Cl. 117-46)

This invention relates to methods of depositing carbon films containing materials codeposited with carbon, and particularly to improvements in the method of making carbon-film resistors.

Because the inductive effects and skin effects associated with wire-windings become increasingly troublesome in circuits carrying high-frequency currents, wire-wound resistors are often undesirable for use in such circuits. Although carbon-coated resistors are relatively free of these disadvantages of wire-wound resistors and may thus be preferred for high-frequency currents, they themselves often show larger temperature coefficients of resistance than do metal windings. These thermal variations in resistance value may limit the carbon-film resistor to uses in which resistance fluctuation with temperature can be tolerated.

Resistors having boron codeposited with carbon in the film and the method of making such resistors are taught in United States Patent 2,671,735 issued March 9, 1954 to R. O. Grisdale, A. C. Pfister and G. K. Teal. The inclusion of boron in carbon films, as taught by the patent, greatly improves the temperature coefficient of resistance of such films as compared with unmodified films of carbon alone.

The present invention, relating to the production of films in which silicon is codeposited with boron and carbon, renders carbon-film resistors even more useful and facilitates their production. While retaining or even decreasing the low thermal coefficients of resistance characteristic of the borocarbon films, the new films show increased adherence and coherence of the deposit, making them more stable to the adverse influences of heat, moisture and abrasion.

In the new method, vapors of volatile silicon and boron compounds are admixed with a carbonaceous gas and passed over a non-conducting base heated to a temperature sufficient to decompose the gaseous compounds. Upon decomposition, boron, carbon and silicon are left in a thin film on the non-conducting core, which can then be subsequently fashioned into a resistor.

In the accompanying drawings:

Fig. 1 is a front view, partly in section, of a suitable type of apparatus in which deposition may be accomplished; and

Fig. 2 is a front view, in section, of a portion of Fig. 1 enlarged to show the detailed construction of the apparatus of Fig. 1 in the region of the reaction zone; and

Fig. 3 is a front view, partly in section, of a resistor made according to the present invention.

The apparatus shown in Fig. 1 is of a design which has given especially satisfactory film deposits. Substantially continuous lengths of the non-conducting core on which a film of silicon and borocarbon is to be deposited are fed downward through the upper aperture 11, descend through the apparatus through the guide tubes 12, and emerge covered with a film at the lower aperture 13. Mechanical means (not shown) are provided for moving the continuous core piece through the guide tubes 12 by

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pushing and pulling, with, generally, a rate of travel of the core through the apparatus between 6 inches per minute and 1½ inches per minute being maintained. The guide tubes 12 are mounted such that one end of each tube opposes, on a common vertical axis which is the longitudinal tube axis, an end of the other of the two tubes, a separation 18 of approximately 2 inches, measured along the common axis, being maintained between the open opposing ends of the tubes. Cross streams of an inert gas, conveniently nitrogen, are passed through the seal-fittings 14 at the extreme ends of the guide tubes. The gas flush and flexible rubber diaphragms, seated at the apertures 11 and 13 and punctured to permit the passage of the core piece through the apparatus, act to keep air from entering the guide tubes 12.

Other streams of inert gas, conveniently helium, are fed into the upper and lower guide tubes 12 at the points 15 and 16, respectively, in the diagram. These oppositely directed gas streams keep the coating gases from entering the guide tubes 12, and escape at the break 18 in the guide tubes, merging there with the film-coating gases. It is at this axial break 18 that the core piece is exposed to the coating atmosphere and in this region deposition of the film takes place.

Water is led through cooling chambers 17 in the upper and lower portions of the apparatus. The chambers serve to confine heat to the portion of the apparatus between them; the lower chamber, in addition, functions to cool the inert gas entering the inlet 16, which gas in turn then lowers the temperature of the filmed cores before they emerge at the aperture 13.

Immediately beneath the reaction zone 18, and beginning at the upper end of the lower guide tube 12, a second tube 19 concentrically surrounds the lower of the two guide tubes. This second tube, conveniently 1¼ inches in diameter, is connected to a gas line 20 through which carrier gas, preferably nitrogen, saturated with vapors of a boron compound and a silicon compound, preferably boron trichloride and silicon tetrachloride, is eventually led to the reaction zone 18.

Concentric with both the guide tubes 12 and the second duct 19 for reactants, there is a larger cylindrical jacket 21, conveniently having an outside diameter of 2 inches. The jacket 21 shields the reaction zone 18, and is sealed above and below the reaction zone around the tubes passing through it, but has an inlet 22 for the admission of a carbonaceous gas, preferably methane, and an outlet 23 for removing all excess and unreacted active components, inert carrier, diluent, and the gaseous decomposition products formed in the zone 18.

Immediately surrounding the jacket 21 is a refractory furnace core 24 on which is wound electrical resistance wire 25. The furnace core 24 has, conveniently, an inside diameter of 2 inches, so that it fits snugly over the jacket 21. The surface of the furnace core 24 may be corrugated to hold the wire windings 25 in position. Current passed through the windings 25, which are preferably of a platinum-rhodium alloy, furnishes the heat required to bring the apparatus to a desired temperature.

The entire core 24 and windings 25 are embedded in a thermal insulating material 26, conveniently a granular refractory material, the whole being then protected by a metal casing 27.

In Fig. 2 is given a detailed view of that portion of the apparatus of Fig. 1 surrounding the deposition chamber 18. In Fig. 2 are shown the guide tubes 12, the concentric tube 19 for reactants and the inlet tube 20, the cylindrical jacket 21 and its corresponding inlet 22, the furnace core 24, resistance winding 25, the insulating sheath 26 and metal casing 27, and a portion of the lower cooling chamber 17.

The guide tubes 12, reactant tube 19, and cylindrical

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jacket 21 are preferably made of a heat-resistant ceramic such as McDanel high-temperature combustion-tube porcelain. The furnace core is, similarly, composed of heat resistant ceramic, and an alundum material, such as Norton No. 8707 RA98, has proved convenient.

The resistor of Fig. 3 is made up of a non-conducting base 31, generally a ceramic composition, at the surface of which is deposited a layer 32 of carbon, boron, and silicon, as indicated. Metal terminals 33 are fastened to the end of the resistor to make electrical contact with the carbon layer. A thin metal film covering the portion of the carbon layer at which the metal terminals are applied may facilitate making electrical contact. In the resistor shown a helical groove 34 has been cut through the surface into the ceramic base to increase the length of the current path through the carbon layer.

In a preferred example, nitrogen has been used as a carrier gas, functioning to transport the vapors of volatile boron and silicon compounds to the reaction zone where they are decomposed and deposition occurs. Nitrogen does not interfere chemically in the proper thermal decomposition of the compounds which it carries, and other gases preferably having a similar property, such as argon, helium, carbon monoxide or hydrogen, can be used. If unreactive with the boron and silicon containing materials at ordinary temperatures, the carbonaceous gas needed in the deposition can also be employed as a carrier. As the presence of water vapor and oxidizing impurities such as oxygen may be detrimental to the formation of a suitable deposit, the carrier is preferably dried and oxygen removed. Admixture of small amounts of hydrogen and passage over a palladinized alumina catalyst has, for example, been used to convert oxygen as an impurity to water vapor. Water vapor itself may be removed by contact of the gas with a drying agent, and passage of the gas over calcium hydride, for example, has been successfully used as a drying step. Because nitrogen is readily available dry and with a high degree of purity, it is often used as a gaseous vehicle in the deposition process.

Any of the volatile boron compounds suggested in United States Patent 2,671,735, mentioned previously, may be used as the source of the boron ultimately deposited in the resistor film. Diborane, borane halides, boron trihalides, alkyl, aryl, and mixed alkyl-aryl borines, and borines in which one or more alkyl or aryl groups has been replaced by a halogen are suitable, as there suggested. Any boron compound capable of being introduced into the furnace may be employed, though preferably the boron compound chosen should be volatile at temperatures low enough to render its vaporization a convenient process. Practical considerations dictate the use of a material which is non-corrosive to the apparatus or the base on which the deposit is to be laid.

The carbonaceous gases amenable to use in the deposition are usually gaseous or readily-volatizable paraffinic and aromatic hydrocarbons, such as methane, ethane, propane, butane, benzene, toluene and xylene, or partially halogenated hydrocarbons, as taught in the aforementioned United States Patent 2,671,735 issued to Grisdale, Pfister and Teal.

Those compounds chosen to furnish silicon for deposition are also, generally, those with high vapor pressures at conveniently low temperatures. Silanes, halogen substituted silanes, silicenes and halogenated silicenes are in this category. Thus, silane, and di-, tri-, and tetrasilane, SiH_4 , Si_2H_6 , Si_3H_8 , Si_4H_{10} , all have normal boiling points below 85°C . Halogen substituted silanes, such as SiH_3Br , SiH_3Cl , SiH_2Br_2 , SiH_2Cl_2 , SiHBr_3 , SiHCl_3 , SiHF_3 , SiCl_4 , SiF_4 , Si_2Cl_6 , Si_2F_6 can be employed, as all are relatively volatile. Again, practical consideration favors those compounds most easily handled or those readily available at low cost. If fluorosilanes are used, for example, special materials resistant to fluorine

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liberated upon decomposition are required in the construction of the apparatus.

Compounds which are both carbonaceous and silicon-containing can be employed in the deposition technique. Examples of such compounds are relatively volatile members of the class



where R_1 , R_2 , R_3 , R_4 are hydrogen, aryl or alkyl radicals, or halogens. Typical compounds are methyl silicene, $\text{SiH}_3(\text{CH}_3)$, di- and tetramethyl silicenes, $\text{SiH}_2(\text{CH}_3)_2$ and $\text{Si}(\text{CH}_3)_4$, methyltriphenyl silicene, $\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)_3$, tetraethyl silicene, $\text{Si}(\text{C}_2\text{H}_5)_4$, tetrabenzyl silicene, $\text{Si}(\text{C}_6\text{H}_5\text{CH}_2)_4$, chloromethyl silicene, $\text{SiH}_2\text{ClCH}_3$, and dichlorodimethyl silicene, $\text{SiCl}_2(\text{CH}_3)_2$. Hexamethyl disilicene, $\text{Si}_2(\text{CH}_3)_6$, is an example of volatile higher silicene homologues which are adaptable to the deposition technique.

Although, in a preferred technique which has been particularly successful in forming good siliconborocarbon films, boron trichloride, silicon tetrachloride, and methane are chosen, so that each of the materials in the final deposit originally enters the gas stream as a compound containing only that material and non-deposited constituents, modification of the procedure to use those volatile substances containing both carbon and boron, or carbon and silicon, is possible. Any desired ratio of carbon to silicon and carbon to boron in the final gas mixture is obtainable by proper dilution of the pure compounds containing both carbon and a second depositable constituent, the dilution being made with appropriate carbonaceous gases which are silicon or boron free, or with silicon or boron compounds containing no carbon.

Although it is possible to stream mixtures of some of these pure gases directly to the heated surface at which deposition is to take place, considerations of flow rates and the rate of deposition preferably call for a dilution of the mixture of gaseous pure compounds with an inert gas. As with the carrier gas discussed above, a water-free substance chemically inert or reducing in character best serves the purpose. Again, argon, helium, hydrogen, or nitrogen are examples of satisfactory diluents. Some diluent gas is most easily introduced with the mixed stream of boron and silicon components, the balance of desired diluent being added with the carbonaceous component, but mixture with any or all of the reacting gases suffices, and the dilution may occur at any point in the system including the area immediately surrounding the heated base on which deposition is to occur.

The flow of gases about the heated base should be such that a turbulence sufficient to get a homogeneous, uniform coating of deposit on all portions of the base results. The flow rate is largely determined by the geometry of the deposition apparatus. Once a rate suitable for giving a uniform deposit is reached, it is generally more convenient to vary the composition of the gas mixture or the time for which contact between the heated base and the mixture is maintained as the variables controlling the thickness and chemical make-up of the deposit, rather than altering the rate of flow of the depositing gas mixture.

The temperatures at which the most satisfactory depositions occur lie within the approximate limits 1000°C . to 1400°C . and preferably between 1100°C . and 1300°C . Lower temperatures do not generally give good deposits, and at higher temperatures some materials from which the resistor bases are manufactured may become unstable. Further, the design of apparatus to withstand such higher temperatures becomes difficult. Deposition temperatures of 1125°C . to 1200°C . are found best. An optimum operating temperature is 1150°C .

A temperature sufficiently high to decompose the boron, silicon or carbon-donating gases to form a deposit is required. If suitable substances having low decomposition

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temperatures are chosen, a film can be deposited at temperatures as low as 600° C., though the characteristics of the films which are most sought often diminish in the films at deposition temperatures of 900° C. to 950° C. and lower.

The resistor bases on which the deposit is laid are generally of a ceramic composition, though any non-conducting material stable at an elevated deposition temperature would suffice. A number of suitable ceramic materials is suggested in the previously-mentioned patent of Gris-
dale, Pfister and Teal, United States 2,671,735. The cer-
amics may be either vitreous or porcelain-like in nature
and a particularly suitable ceramic composition is de-
scribed in United States Patent 2,386,633, issued October
9, 1945 to M. D. Rigterink. Bodies shaped of this materi-
al are fired at approximately 1250° C. after being shaped
from a paste of 15 parts flint ground to 325 mesh, 50 parts
of kaolin, sufficient water to give a proper consistency,
and 35 parts of a fired mixture of 60 parts kaolin, 10 parts
magnesium carbonate, 10 parts calcium carbonate, 10
parts strontium carbonate and 10 parts barium carbonate,
said mixture being previously calcined at 1200° C. and
ground thereafter to 325 mesh.

In a deposition technique employing the apparatus sche-
matized in Fig. 2, boron trichloride, silicon tetrachloride
and methane, as mentioned previously, were the com-
pounds chosen to furnish the film constituents upon de-
composition. Nitrogen was used as a carrier and diluent,
and helium was the gas employed as a flush. All methane,
helium and nitrogen used in this specific deposition tech-
nique were dried by passage over calcium hydride before
introduction into the system. Since oxygen-free methane,
and nitrogen and helium both having low oxygen analyses
were used directly, no further purification to remove
oxygen was found to be necessary.

In the preferred example, liquid boron trichloride, used
as the boron-contributor, was kept in a glass bubbler ap-
paratus through which nitrogen could be passed. The
bubbler was surrounded by a mechanically agitated bath
of trichloro ethylene at the normal freezing point of tri-
chloroethylene, -36° C. A cooling medium of Dry Ice
and acetone in a suitable flask was immersed in the vessel
containing trichloroethylene.

The silicon containing compound chosen in the pre-
ferred example was liquid silicon tetrachloride, kept in
a second bubbler similar to that used for boron trichloride.
A temperature of 0° C. was maintained by immersion of
the bubbler in a water-ice bath.

For both substances, dried nitrogen was passed through
the liquid using a tube having an outlet beneath the liquid
level, the outlet being fitted with a fritted glass disk to
cause the release of small gas bubbles into the liquid. A
given volume of carrier gas, essentially saturated with
either boron trichloride or silicon tetrachloride at a fixed
temperature, had, then, a content of either of the two non-
inert vapors which could be calculated from knowledge of
the vapor pressure of boron trichloride or silicon tetrachlo-
ride in the carrier nitrogen at that temperature. Sub-
sequent dilution with nitrogen to give a desired composi-
tion of the final gas mixture could then be accomplished.

In an apparatus of the construction shown, a total rate
of flow of gases between 600 cubic centimeters per minute
and 1200 cubic centimeters per minute has proved effica-
cious for the particular existing geometry. A total rate
of flow of 800 cubic centimeters per minute has been
found as most desirable, and the depositions are generally
done with this amount of gas passing. Any deposition ap-
paratus, of which the one described is an example, may
have an almost unique geometry which may affect the
optimum flow-rate value in that apparatus.

Suitable borocarbon films containing codeposited silicon
can be conveniently produced from gas mixtures in which
the ratio of the number of boron atoms to the number of
carbon atoms in the mixture lies between the limits 1.00
and 0.01. For the preferred example in which methane,

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boron trichloride and silicon tetrachloride compose the
active ingredients in the gaseous deposition mixture, the
composition range set forth above corresponds to mix-
tures in which the percent by volume of boron trichloride
in the combined boron trichloride and methane lies be-
tween 50 percent and one percent. Though increased
amounts of boron may be used in the depositing gas, the
resultant films may have higher surface resistances in ohms
per square, than are of interest at present. More com-
monly used resistance values are obtained when the boron
content of the depositing gas is reduced so that the afore-
mentioned atomic ratio lies between the values 0.33 and
0.01 corresponding to a value of the ratio

$$\frac{\text{BCl}_3}{\text{BCl}_3 + \text{CH}_4}$$

lying between 25 volume percent and one volume percent.
Deposits having specially favorable thermal coefficients
of resistance are obtained when the boron-carbon atomic
ratio lies between the values 0.25 and 0.026 with an
optimum value for the ratio, giving the films with least
resistance change with temperature, appearing at 0.18.
In volume percent, these figures correspond to 20 volume
percent, two and one-half percent and an optimum of 15
percent boron trichloride by volume, respectively, in the
quantity

$$\frac{\text{BCl}_3}{\text{BCl}_3 + \text{CH}_4}$$

Similarly, the ratio of the number of silicon atoms to
the number of carbon atoms in the depositing gas mix-
ture is best kept between the limiting values 3.00 and
0.01. When silicon tetrachloride and methane are used
in the deposition, as in the preferred example, this range
of the silicon to carbon ratio corresponds to a percent
by volume of silicon tetrachloride in the gaseous mixture
of silicon tetrachloride and methane lying between 75
volume percent and one volume percent.

The lower limit on the silicon-carbon ratio may be con-
veniently raised to 0.053 or five volume percent of silicon
tetrachloride in the silicon tetrachloride-methane mixture.

Better films are deposited with the ratio of the number
of silicon atoms to the number of carbon atoms in the
mixture having values between 0.67 and 0.11 and particu-
larly good films are obtained with an optimum ratio of
0.43. Measured by the quantity

$$\frac{\text{SiCl}_4}{\text{SiCl}_4 + \text{CH}_4}$$

these ratios take the values 40 volume percent, ten volume
percent and an optimum of 30 volume percent,
respectively.

The geometry of the furnace may be influential in
determining which gas compositions are most effective
in producing good deposits. The limits on composition
ratios and the optimum values of those ratios recited
above have been determined using a furnace of the type
shown in Fig. 1. Variations in furnace geometry may
also affect the optimum gas composition values listed,
but suitable resistance films are produced by keeping
within the limits set on the boron-to-carbon and silicon-
to-carbon ratios mentioned earlier.

The final film thickness is usually kept at the same
order of magnitude as for boron-carbon films, between
10⁻⁶ and 10⁻⁴ centimeters. By increasing or decreasing
the time in which a portion of the ceramic base remains
in the reaction zone, the film thickness can be increased
or decreased. Thicker films with resistance values of 100
ohms per square, and films thin enough to give a re-
sistance of 2500 ohms per square have been produced,
as well as those with intermediary resistance values. A
film with resistance as high as 10⁵ ohms per square can
be obtained.

It is not known how the silicon borocarbon film differs
structurally from the borocarbon film, or whether silicon

is present as silicon carbide or in elemental form in solid solution with carbon. The silicon borocarbon films show striking improvement, however, in some characteristics considered particularly desirable in a resistor film.

The silicon borocarbon films show a decreased susceptibility to oxidative changes in the film upon exposure to high temperatures. Where resistors may overheat, such an increased chemical stability and resistance to oxidation is of particular importance.

Increased adherence of the silicon borocarbon films is shown by "rub-up" tests in which the change in film resistance caused by abrasion under controlled conditions is measured. Whereas borocarbon films usually show a 10 to 15 percent increase in resistance from mechanical loss of film material, the more adherent films containing silicon showed resistance changes less than five percent.

In a check of resistance stability, test resistors were separately encased in glass and heated to 400° C. for one hour while the containers enclosing them were evacuated. During the sealing, pumping, and baking operations, borocarbon films generally showed six to eight percent changes in resistance values. The more stable and more densely compacted silicon-borocarbon films showed an average change of as little as 1.5 percent in resistance value, as measured on films for which the boron-carbon atom ratio was 0.33 and the silicon-carbon atom ratio was 3.00 in the depositing gas. Increased coherence and adherence of the films can also be correlated with a greater tendency of the films to retain their fixed resistance values in humid atmospheres. Penetration of less coherent films by moisture appears to be the cause of resistance value fluctuations in plain borocarbon films.

In addition to increased adherence and better behavior of the films in heat and moisture, the thermal coefficients of resistance of the silicon borocarbon films retain the small negative values which originally made plain borocarbon films desirable. The films with silicon can be made such that their thermal resistance coefficients fall within the envelope surrounding the curves representing the best behavior of the thermal coefficients of borocarbon films. The silicon borocarbon films can thus be made at least as good as borocarbon films, with respect to their thermal resistance variation, and in many cases the silicon films may better the borocarbon films by a factor of 50 percent in their reduced thermal resistance coefficients.

Although specific embodiments of this invention have been shown and described, it will be understood that they are but illustrative and that various modifications may be made therein without departing from the scope and spirit of the invention.

What is claimed is:

1. The method of making borocarbon-film electrical resistors with increased stability against heat, moisture, and abrasion due to increased adherence and coherence of the film, which method comprises contacting at an elevated temperature a non-conducting core with a gaseous mixture comprising chemically-bound carbon, chemically-bound boron, and chemically-bound silicon, in which mixture the ratio of the number of bound boron atoms to the number of bound carbon atoms lies between 1.00 and 0.01 and the ratio of the number of bound silicon atoms to the number of bound carbon atoms lies between 3.00 and 0.01.

2. The method of making borocarbon-film electrical resistors as described in claim 1 wherein the chemically-bound carbon is present as a compound selected from the group consisting of hydrocarbons and halogenated hydrocarbons, the chemically-bound boron is present as a compound selected from the group consisting of borane halides and boron trihalides, and the chemically-bound silicon is present as a halogen substituted silane.

3. The method of making borocarbon-film electrical resistors as described in claim 1 wherein the chemically-bound carbon is present as methane, the chemically-bound boron is present as boron trichloride, and the chemically-bound silicon is present as silicon tetrachloride.

4. The method of making borocarbon-film electrical resistors with increased stability against heat, moisture, and abrasion due to increased adherence and coherence of the film, which method comprises contacting at an elevated temperature a non-conducting core with a gaseous mixture comprising chemically-bound carbon, chemically-bound boron, and chemically-bound silicon, in which mixture the ratio of the number of bound boron atoms to the number of bound carbon atoms lies between 0.33 and 0.01 and the ratio of the number of bound silicon atoms to the number of bound carbon atoms lies between 0.67 and 0.11.

5. The method of making borocarbon-film electrical resistors as described in claim 4 for which the chemically-bound carbon is present as methane, the chemically-bound boron is present as boron trichloride, and the chemically-bound silicon is present as silicon tetrachloride.

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