Dec. 17, 1968 R. L. CORMIA 3,416,959

METHOD OF FORMING CARBON RESISTOR FILMS

Filed Feb. 26, 1965

Fig. 1.

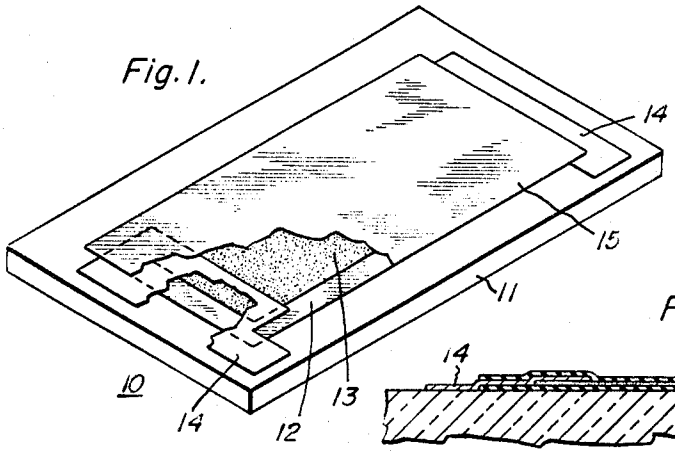


Fig. 2.

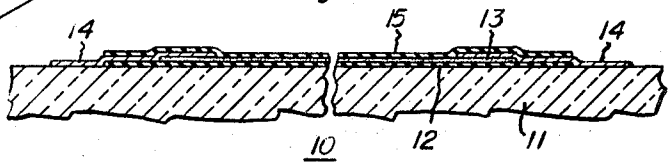
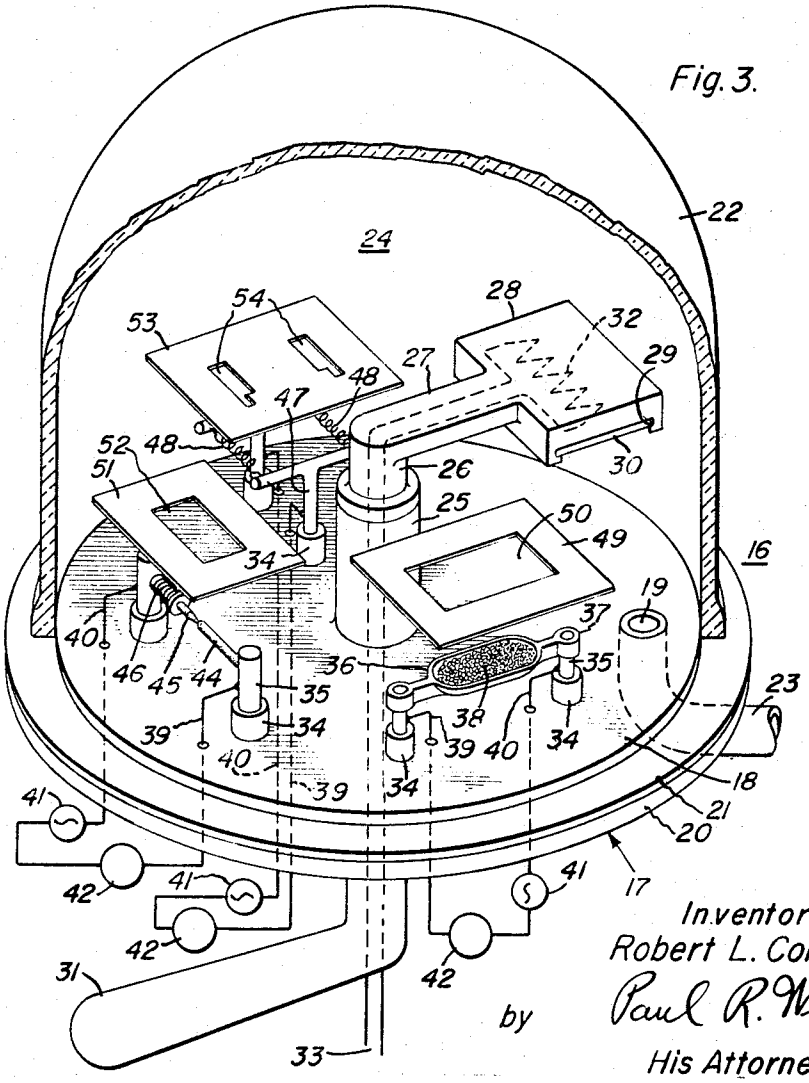


Fig. 3.



Inventor:
Robert L. Cormia,
by Paul R. Webb II
His Attorney.

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METHOD OF FORMING CARBON RESISTOR FILMS

Robert L. Cormia, Schenectady, N.Y., assignor to General Electric Company, a corporation of New York

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ABSTRACT OF THE DISCLOSURE

Carbon films having a resistance of 5000 ohms per square with less than .3% change in permanent resistance after a 10 minute heat treatment at 400° C. are formed by successive depositions in a pressure range between 1×10^{-9} to 5×10^{-5} millimeters of mercury of a silicon monoxide layer, a carbon layer, metallic contacts, and a silicon monoxide overcoating atop a non-conductive substrate. The substrate preferably is heated to a temperature between 200° to 600° C. during the depositions and all depositions are effectuated without a breaking of the vacuum of the chamber. Resistors of a desired ohmic value are obtained either by a careful monitoring of the deposition rate or by a selective oxidation of a portion of the carbon film prior to the deposition of the silicon monoxide overlayer.

This invention relates to methods of making electrical resistors, and more particularly to resistors methods of making evaporated carbon resistors.

Carbon resistors which have been prepared by painting a carbon film on a substrate have posed various problems in the employment of these resistors. Such resistors have exhibited a poor adherence of the carbon film to the substrate. A serious problem is also encountered in that the resistance of such a resistor changes substantially upon exposure to an elevated temperature.

Thus, it would be desirable to provide a method of forming a carbon resistor which exhibits good adherence to its substrate, stability during operation, and a minimum amount of change in resistance due to the elevation of the temperature of the resistor. The present invention therefore is directed to methods of making evaporated carbon film resistors wherein the problem of instability, poor adherence and changing resistance due to temperature change are substantially reduced or eliminated.

It is an object of my invention to provide a method of forming a carbon resistor which is operable over a wide temperature range with a minimum change in resistance.

It is another object of my invention to provide a method of forming a resistor wherein the carbon film exhibits good adherence to its substrate.

It is another object of my invention to provide a method of forming a carbon resistor which is stable during operation.

It is a further object of my invention to provide a method of forming a carbon resistor having a predetermined resistance value.

In carrying out my invention in one form, an electrical resistor is formed which comprises an electrically non-conductive substrate, a layer of silicon monoxide adhering firmly to the substrate, a layer of carbon with a predetermined resistance value adhering to the silicon monoxide layer, a pair of spaced apart electrically conductive electrodes adhering to the carbon layer, and a second layer of silicon monoxide adhering to the carbon layer.

These and various other objects, features and advantages of the invention will be better understood from the following description taken in connection with the accompanying drawing in which:

FIGURE 1 of the drawing is a perspective view of a resistor formed by the method of my invention;

FIGURE 2 is a sectional view of the resistor shown in FIGURE 1 of the drawing; and

FIGURE 3 is a perspective view of apparatus for forming an electrical resistor in accordance with my invention

In FIGURES 1 and 2 of the drawing, there is shown generally at **10** a resistor formed by the method of my invention. This resistor comprises a substrate **11** of an electrically non-conductive material such as slide glass Pyrex glass, or a glazed ceramic, which substrate provides a smooth surface for subsequent condensation of materials thereon. A layer **12** of silicon monoxide is shown adhering firmly to substrate **11**, A layer **13** of evaporated carbon, which has a predetermined resistance value, adheres to silicon monoxide layer **12**. A pair of spaced apart electrically conductive electrodes **14** of aluminum adhere to carbon layer **13**. A second layer **15** of silicon monoxide adheres to carbon layer **13** and is shown covering a portion of electrodes **14**.

While the substrate **11** is described as being composed of slide glass, Pyrex glass or a glazed ceramic, other substrates, which are electrically non-conducting, and stable at temperatures of evaporation and operation are suitable. Carbon layer **14** which is evaporated on the surface of silicon monoxide layer **12** is of various thicknesses depending upon the predetermined resistance value desired. Thus, after a predetermined resistance value is selected for the resistor, the carbon layer is evaporated onto layer **12** in an appropriate thickness to provide this resistance value for the device. Electrodes **13** are shown as being of aluminum. However, any electrically conductive material which is stable at the evaporation temperature and the operating temperature is employable. Thus other materials such as niobium, tantalum, gold, chromium and copper are useable as electrode materials Other electrode configurations are also suitable.

Layers **12** and **15** of silicon monoxide are shown as of identical dimensions which do not cover the entire surface of substrate **11**. However, these layers may be made of varying dimensions and are not limited to the dimensions shown with relationship to the substrate.

In FIGURE 3 of the drawing, apparatus is shown generally at **16** for forming electrical resistors in accordance with my invention. A metal base **17** has a raised center portion **18** with an aperture **19** therein and an outer rim **20** on which is positioned a rubber gasket **21**. A glass bell jar **22** is positioned on gasket **21** adjacent the edge of center portion **18** of base **17**. An evacuation line **23** is connected to aperture **19** and to a pump (not shown) to evacuate a chamber **24** defined by bell jar **22** and center portion **18** of base **17**.

A centrally located insulating sleeve **25** is shown extending through center portion **18** of base member **17**. Sleeve **25** positions therein a pivotal rod **26** with an arm **27** extending therefrom. Arm **27** supports a member **28** on the underside of which is provided a recess **29** to support an electrically non-conductive substrate **30** therein. Rod **26** is moved from outside chamber **24** by any suitable means, such as, an arm **31**. Heating means **32** in the form of an electrically insulated coil imbedded in member **28** or affixed to the lower surface of this member provides heating for substrate **30**. Leads **33** from coil **32** extend through arm portion **27**, and rod **26** to an appropriate power source (not shown) which has an adjustable power control (not shown). In addition to the pivotal action of member **28** by corresponding movement of handle **31** outside chamber **24**, rod **26** may be raised and lowered by pressure exerted on handle **31**.

A first pair of insulating sleeves **34** are positioned on center portion **18** of base member **17** and support therein a pair of electrically conductive rods **35**. An electrically conductive boat **36**, for example, of tantalum is supported at opposite ends of rods **35** by means of a pair of brackets **37**. A quantity of silicon monoxide **38** in particle form is provided in boat **36** for subsequent evaporation. A pair of leads **39** and **40** connect opposite rods **35** to a power source **41** which is regulated by an adjustable power control **42**. A second pair of electrically insulating sleeves **34** are positioned on center portion **18** and support therein a pair of electrically conductive rods **35**. A similar pair of leads **39** and **40** are connected to a power source **41** which is regulated by an adjustable power control **42**. A carbon rod **44** is supported in the side wall of one of rods **35** and extends outwardly therefrom. A pointed carbon rod **45** is mounted on the other electrically conductive rod **35** by means of a conventional spring loaded device **46** whereby the point of rod **35** is in contact with the end of carbon rod **44** thereby providing a carbon source for evaporation. A third pair of electrically insulating sleeves **34** are positioned on center portion **18** and support therein a pair of T-shaped members **47**. A similar circuit comprising a pair of leads **39** and **40** are connected to a power source **41** which is regulated by an adjustable power control **42**. An electrically conductive wire coil **48**, for example of tungsten, is connected between both opposite ends of T-shaped members **47**. An aluminum evaporant in rod or other form is positioned within each coil **48**.

A mask **49** with a rectangular opening **50** is shown positioned above boat **36** and supported in any suitable manner (not shown). A mask **51** with a smaller rectangular opening **52** is shown above carbon rods **44** and **45** and supported in any suitable manner (not shown). A third mask **53** with a pair of openings **54** is shown supported above T-shaped members **47** and wire coil **48** whereby openings **54** are in registry with wire coil **48**. Mask **53** is supported in any suitable manner (not shown).

I discovered that an electrical resistor is formed on a substrate by positioning an electrically non-conductive substrate within a chamber, evacuating the chamber to a pressure range of 1×10^{-9} to 5×10^{-5} millimeters of mercury, heating the substrate to a temperature in a preferred temperature range of 200° C. to 600° C., evaporating carbon within the chamber and condensing a layer of carbon on the substrate, evaporating an electrically conductive metal within the chamber and condensing the metal as a pair of spaced apart electrodes on the carbon layer, and evaporating silicon monoxide within the chamber and condensing a layer of silicon monoxide on the carbon layer.

I discovered further that an electrical resistor could be formed on a substrate by employing the above steps but prior to evaporating carbon, silicon monoxide is evaporated within the chamber and condensed as a layer of silicon monoxide on the substrate whereby the subsequent evaporation of the carbon in the chamber provides condensation of a layer of carbon on the silicon monoxide layer.

An electrical reisstor is also formed on a substrate which includes either of the above series of steps and additionally the steps of providing a boron vapor within the chamber while the carbon is evaporated within the chamber thereby condensing a layer of carbon with two to ten weight percent of boron on the silicon monoxide layer or on the electrically non-conductive substrate.

I found that a suitable substrate, on which my improved electrical resistor is formed, must be of an electrically non-conducting material. For example, slide glass, Pyrex glass, or a glazed ceramic is suitable. Addiitonally, other materials which are characterized by being electrically non-conductive, and stable at temperatures of evaporation and operation are suitable for employment as substrates.

I found that an improved electrical resistor is formed in accordance with my invention by employing a chamber wherein a conventional pressure range of 1×10^{-9} to 5×10^{-5} millimeters of mercury is employed. I found further that it is necessary to heat the substrate during evaporation and condensation of the various layers. While the precise temperature of the substrate heating is not critical, I have found that a preferred temperature range from 200° C. to 600° C. provides a desirable range whereby the layers evaporated and condensed on the substrate adhere firmly to the substrate. I found that silicon monoxide can be evaporated within the chamber and condensed as a layer of silicon monoxide on the substrate by employing various sources of silicon monoxide. For example, I prefer to employ a boat of an electrically conducting material which contains silicon monoxide particles and which boat is connected electrically to a power source to evaporate the silicon monoxide and subsequently condense the silicon monoxide substrate.

I found that the resistance value of the evaporated carbon layer is predetermined by controlling the thickness of the carbon layer deposited on the silicon monoxide layer or on the substrate thereby providing a predetermined resistance value. A pair of carbon rods is shown as the preferred way to provide a carbon source which source is connected electrically to a power source to provide for evaporation of the carbon from the carbon rods onto the layer of silicon monoxide or onto the substrate. Various other suitable means of evaporating carbon for condensation are also employable in this process. Additionally, if it is desired the layer of carbon is deposited on the substrate or on the first layer of silicon monoxide on the substrate and thereafter the thickness of the carbon may be adjusted to provide a predetermined resistance value. For example, this is accomplished by providing a source of oxygen to the bell jar whereby the carbon condensed on the substrate or on the silicon monoxide layer is oxidized to the desired thickness to provide the predetermined resistance value. The carbon may be deposited directly on the substrate or it may be deposited on a first layer of silicon monoxide which has been previously deposited on the substrate.

Additionally, boron is added with the carbon to provide a carbon layer containing 2 to 10 weight percent of boron. This is accomplished in various suitable manners. For example, the carbon is evaporated from a carbon source while a boron vapor is provided within the chamber during the carbon evaporation to condense a layer containing carbon and two to ten weight percent of boron on the substrate or on the silicon monoxide layer. A carbon compound containing a sufficient weight percent of boron to provide two to ten weight percent boron in the condensed layer of carbon on the substrate is also a suitable manner to accomplish the provision of a layer of carbon with the above percentage of boron. Other boron compounds are suitable within the system to provide the desired weight percent of boron within the carbon layer deposited on the substrate or the silicon monoxide layer.

I found that a number of materials are employable as electrode materials. For example, aluminum, niobium, tantalum, gold, chromium and copper are suitable as such electrode materials. While a particular electrode configuration is described above and shown in the drawing, other electrode configurations are sutable.

I found further that the resistor is formed in an operation whereby the vacuum is not broken. This is accomplished by employing masks within the evacuated chamber and moving the substrate from mask to mask to provide the desired layers in the proper sequence. If it is desired, the substrate is made stationary within the chamber and the mask and sources rotated.

In the operation of the apparatus shown in FIGURE 3 of the drawing to provide an improved electrical re-

sistor in accordance with my invention, silicon monoxide particles **38** are provided in boat **36**, carbon rods **44** and **45** are employed, and a pair of wire coils **48** of tungsten with an aluminum evaporant rod positioned in each of the coils are used. A substrate **30**, such as, of Pyrex glass, is inserted in recess **29** of member **28**. Bell jar **22** is positioned on rubber gasket **21** and its inner edge is adjacent to center portion **18** of base member **17**. The pump (not shown) evacuates chamber **24** to a pressure in the pressure range of 1×10^{-9} to 5×10^{-5} millimeters of mercury. Substrate **30** is heated then to a temperature in the preferred temperature range of 200° C. to 600° C. by heating coil **32** contained within member **28**.

Member **28** is pivoted by means of handle **31**, which is located outside of bell jar **22**, to mask **49** and lowered so that substrate **30** is in registry with opening **51** in mask **49**. First control **42** is operated thereby heating gradually silicon monoxide particles **38** in boat **36** to cause these particles to evaporate. The silicon monoxide evaporates from particles **38** and condenses as a layer of silicon monoxide **12** on the surface of substrate **30**. The heating is then discontinued.

Handle **31** is moved to raise member **28** from mask **49** and to pivot member **28** to mask **51**. Handle **31** is then depressed thereby lowering member **28** to mask **51** and providing the center portion of substrate **30** in registry with opening **52** of mask **51**. Second control **42** is then operated thereby heating the carbon source of rods **44** and **45** and causing evaporation of carbon from the point of rod contact. This carbon which is evaporated condenses as a layer of carbon **13** on the silicon monoxide layer. The thickness of this layer is controlled to provide a predetermined resistance value for the resistor. The heating is then discontinued.

Handle **31** is moved upward to raise member **28** and is moved to pivot member **28** to mask **53**. Member **28** is then lowered to be in contact with or in close relationship to mask **53** whereby two spaced apart portions of carbon layer **13** of the coated substrate are in registry with the pair of spaced apart openings **54** in mask **53**. Third control **42** is then operated thereby heating tungsten wire coils **48** and causing an evaporation of the electrically conductive aluminum evaporant positioned therein which aluminum condenses as a pair of spaced apart electrodes **14** on the carbon layer **13**. The heating is then discontinued.

Handle **31** is then employed again to raise member **28** away from mask **53** and move member **28** to the mask **49**. Member **28** is then lowered to contact or be in close relationship to mask **49** whereupon carbon layer **13** and a portion of both electrodes **14** of the coated substrate **30** are in registry with opening **50** in mask **49**. First control **42** is operated again to heat up gradually the silicon monoxide particles **38** in boat **36** to evaporate additional silicon monoxide which condenses as a second layer of silicon monoxide **15** on the carbon layer **13** and a portion of both electrodes **14**. The heating is then discontinued.

Member **28** is then raised from mask **49**. The substrate heating provided by coil **32** is then discontinued. The apparatus is allowed to cool to room temperature within chamber **24**. Chamber **24** is then returned to atmospheric pressure whereupon bell jar **22** is removed. Substrate **30** with the carbon resistor formed thereon is then easily removed by sliding substrate **30** from recess **29** on member **28**.

In the above operation of this device, an electrical resistor is also formed by depositing a first layer of carbon on the substrate. A pair of spaced apart electrodes are then condensed on the carbon layer. A layer of silicon monoxide is then condensed on the carbon layer and covers partially the electrodes. Furthermore, in the operation of this device, a source of boron such as provided in a carbon-boron compound is substituted for the carbon rods **44** and **45**, a separate boron vapor is provided within the chamber, or a separate boron compound is positioned adjacent to and heated separately during the evaporation of the carbon whereby a carbon layer containing two to ten weight percent of boron is deposited either directly on the substrate or on the silicon monoxide layer. While it is not shown in the drawing, a separate source of oxygen can be provided to chamber **24** after the carbon layer is deposited directly on the substrate or on the silicon monoxide layer to etch the carbon layer to the correct thickness for a predetermined resistance value for the carbon resistor.

Several examples of electrical resistors which were made in accordance with the present invention are as follows:

In the first four examples, apparatus was set up in accordance with FIGURE 3 of the drawing to form electrical resistors in accordance with my invention. In each of these examples, silicon monoxide particles were employed in an electrically conductive boat, a pair of carbon rods were employed for the carbon source, and tungsten wire coils with an aluminum evaporant were employed for the source of metal for the electrodes. In each example, a Pyrex glass substrate was positioned within the chamber after which the bell jar was placed on the rubber gasket. The pump (not shown) evacuated the chamber to a pressure of 2×10^{-6} millimeters of mercury. The substrate was heated by the substrate heater to a temperature of 400° C. Silicon monoxide was evaporated from particles through a mask and condensed as a layer of about 2,000 A. thick on the substrate. A layer of carbon was then evaporated from the carbon rods through a mask and deposited as a layer on the silicon monoxide layer. In each of the four examples, the thickness of the carbon varied but the thickness was less than 1000 A. thick for each four layers. During this second evaporation, the temperature of the substrate was raised from 400° C. to 450° C. The substrate temperature was then lowered to 200° C. during the evaporation of the aluminum through a mask and condensation as a pair of spaced apart electrodes on the carbon layer. A second layer of silicon monoxide was then evaporated from particles through a mask and condensed on the carbon layer to provide a layer of about 3000 A. thickness while the substrate temperature was maintained at about 300° C. Subsequently, substrate heating was discontinued and the device allowed to cool to room temperature. The chamber was returned to atmospheric pressure after which the bell jar was removed.

The electrical resistors formed by this method each provided an electrically non-conducting substrate, a layer of silicon monoxide adhering firmly to the substrate, a layer of carbon with a predetermined resistance value adhering to the silicon monoxide layer, a pair of spaced apart electrically conductive electrodes adhering to the carbon layer, and a second layer of silicon monoxide adhering to the carbon layer. These resistors exhibited temperature coefficient of resistivity values from —400 p.p.m./degree C. to —700 p.p.m./degree C. from room temperature to 150° C.

While each of the above resistors had a carbon layer less than 1000 A. thick, this thickness varied from Example 1, which had the thinnest layer, to Example 4, which had the thickest layer. These examples are set forth below in Table I which recites the resistance in ohms per square of each resistor; the percentage of permanent resistance change after a ten minute heat treatment at 400° C., and the percentage of permanent resistance change after a 175 hour heat treatment at 150° C.

TABLE I

Example Number	Resistance, Ohms/□	ΔR, 400° C., percent	ΔR, 150° C., percent
1	5,000	<0.3	<0.3
2	4,000	<0.3	<0.3
3	1,600	<0.3	<0.3
4	1,220	<0.3	

In Examples 5–7, apparatus was set up in accordance with FIGURE 3 of the drawing to form electrical resistors in accordance with my invention. In each of these examples, silicon monoxide particles were employed in an electrically conductive boat, a pair of carbon rods were employed for the carbon source, and tungsten wire coils with an aluminum evaporant were employed for the source of metal for the electrodes. In each example, a glazed ceramic substrate was positioned within the chamber after which the bell jar was placed on the rubber gasket. The pump (not shown) evacuated the chamber to a pressure of 2×10^{-6} millimeters of mercury. The substrate was heated by the substrate heater to a temperature of about 300° C. A layer of carbon was evaporated from the carbon rods through a mask and deposited as a layer less than 1000 A. thick on the substrate. The substrate temperature was then lowered to 200° C. during the evaporation of the aluminum through a mask and condensation as a pair of spaced apart electrodes on the carbon layer. A layer of silicon monoxide was then evaporated from particles and through a mask and condensed onto the carbon layer to provide a layer of about 3000 A. thickness while the substrate temperature was maintained at about 300° C. Subsequently, substrate heating was discontinued and the device allowed to cool to room temperature. The chamber was returned to atmospheric pressure after which the bell jar was removed.

The electrical resistors formed by this method each provided an electrically non-conducting substrate, a layer of carbon with a predetermined resistance value adhering firmly to the substrate, a pair of spaced apart electrically conductive electrodes adhering to the carbon layer, and a layer of silicon monoxide adhering to the carbon layer. These resistors exhibited temperature coefficient of resistivity values from —400 p.p.m./degree C. to —700 p.p.m./degree C. from room temperature to 150° C.

Examples 5–7 are set forth below in Table II which recites the resistance in ohms per square of each resistor; the percentage of permanent resistance change after a ten minute heat treatment at 400° C., and the percentage of permanent resistance change after several hundred hours heat treatment at 150° C.

TABLE II

Example Number	Resistance, Ohms/□	ΔR, 400° C., percent	ΔR, 150° C., percent
5	2,000	<0.5	<0.5
6	2,000	<0.5	<0.5
7	2,000	<0.5	<0.5

While other modifications of this invention and variations of method which may be employed within the scope of the invention have not been described, the invention is intended to include such that may be embraced within the following claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method of forming an electrical resistor which comprises positioning an electrically non-conductive substrate within a chamber, evacuating said chamber to a pressure range of 1×10^{-9} to 5×10^{-5} mm. of mercury, heating said substrate, evaporating silicon monoxide within said chamber and condensing a layer of silicon monoxide on said substrate, evaporating carbon within said chamber and condensing a layer of carbon on said silicon monoxide layer, evaporating an electrically conductive metal within said chamber and condensing said metal as a pair of spaced apart electrodes on said carbon layer, oxidizing a portion of said carbon layer and subsequently evaporating silicon monoxide within said chamber and condensing a second layer of silicon monoxide on said carbon layer.

2. A method of forming an electrical resistor which comprises positioning an electrically non-conductive substrate within a chamber, evacuating said chamber to a pressure range of 1×10^{-9} to 5×10^{-5} mm. of mercury, heating said substrate, evaporating silicon monoxide within said chamber and condensing a layer of silicon monoxide on said substrate, evaporating carbon within said chamber while simultaneously providing a boron vapor within the chamber to condense a layer of carbon having 2–10% boron content atop the silicon monoxide layer, evaporating an electrically conductive metal within said chamber and condensing said metal as a pair of spaced apart electrodes on said boron containing carbon layer, and evaporating silicon monoxide within said chamber and condensing a second layer of silicon monoxide on said boron containing carbon layer.

3. A method of forming an electrical resistor which comprises positioning an electrically non-conductive substrate within a chamber, evacuating said chamber to a pressure range of 1×10^{-9} to 5×10^{-5} mm. of mercury, heating said substrate, evaporating carbon within said chamber and condensing a layer of carbon on said substrate, evaporating an electrically conductive metal within said chamber and condensing said metal as a pair of spaced apart electrodes of said carbon layer, oxidizing a portion of said carbon layer, and subsequently evaporating silicon monoxide within said chamber and condensing a layer of silicon monoxide on said carbon layer.

4. A method of forming an electrical resistor which comprises positioning an electrically non-conductive substrate within a chamber, evacuating said chamber to a pressure range of 1×10^{-9} to 5×10^{-5} mm. of mercury, heating said substrate, evaporating carbon within said chamber while simultaneously providing a boron vapor within the chamber and condensing a layer of carbon having a 2–10% boron content atop said substrate, evaporating an electrically conductive metal within said chamber and condensing said metal as a pair of spaced apart electrodes on said boron containing carbon layer, and evaporating silicon monoxide within said chamber and condensing a layer of silicon monoxide on said boron containing carbon layer.

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RALPH S. KENDALL, *Primary Examiner.*

C. K. WEIFFENBACH, *Assistant Examiner.*

U.S. Cl. X.R.

117—106, 212, 216, 217, 62