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(71) Applicant : GENERAL ELECTRIC COMPANY
1 River Road
Schenectady, NY 12345 (US)

(72) Inventor : Iacovangelo, Charles Dominic
1717 Dorwaldt Boulevard
Schenectady, New York 12309 (US)
Inventor : Jerabek, Elihu Calvin
504 Feura Bush Road
Glenmont, New York 12077 (US)

(74) Representative : Greenwood, John David et al
London Patent Operation,
General Electric Technical Services Company, Inc.,
Essex House,
12/13 Essex Street
London WC2R 3AA (GB)

(54) **Resistor coated on diamond substrate**

(57) A thin film resistance layer is deposited on a diamond substrate. A nickel-chromium-carbon alloy with improved adhesion of the metal to the diamond substrate and a desirably low temperature coefficient of resistance is created.

Jouve, 18, rue Saint-Denis, 75001 PARIS

This invention relstes to a metal coated diamond substrate for electronic applications, and more particularly to coatings on said diamond substrate for use as an electrical resistor.

Diamond is of high interest as a substrate material for use in integrated circuits and multi-chip modules. This is particularly true of synthetic diamond prepared by chemical vapor deposition (hereinafter "CVD diamond"); i.e., by activation of a mixture of gases including hydrogen and a hydrocarbon at low pressure, whereupon diamond is deposited on a substrate surface. By reason of its low electrical conductivity and dielectric constant, as well as its high thermal conductivity that makes it useful as a heat sink material, it is of particular interest for use in high density interconnect modules and circuits containing laser diodes, where the circuit elements are packed closely together and heat dissipation is essential.

The manufacture of such modules generally requires the deposition of connecting conductive and/or resistive metal traces on the diamond surface. Nickel-chromium alloys are of particular value for the deposition of traces of controlled resistance, chiefly by reason of their stability as well as the relatively low cost of both metals.

Resistors comprising patterned thin films of nickel-chromium alloy on a ceramic substrate have been in use for many years. A problem with such resistors that has been encountered and solved is that such alloys have a high temperature coefficient of resistance (hereinafter sometimes "TCR"); that is, their resistance changes substantially with changes in temperature. Since resistors with specific resistance levels are typically produced by varying the dimensions of a conductive trace of known resistivity, it has been necessary to lower the TCR of the nickel-chromium alloy, typically to values of at most about 5 ppm/°K. This is typically done in the case of materials employing ceramic substrates by incorporating elements such as oxygen or aluminum in the metal coating.

A further problem with nickel-chromium coatings on diamond is that adhesion to the substrate is generally poor. An adhesion of about 140-350 kg/cm^2 is generally required for electronics applications, and must survive high temperature processing operations performed in the creation of integrated circuits and the like.

Adhesion to diamond of many metals that readily form carbides can be improved by heat treatment at temperatures as high as 900-1000°C, often in a reducing atmosphere, which apparently causes the formation of a carbide bond coating. Chromium forms carbide; in fact, it can form three different carbides. However, the carbide preferentially formed under the aforementioned heat treatment conditions can be brittle and incapable of producing an adequate bond coating. Moreover, heating under such conditions in the presence of a large proportion of a ferrous metal such as nickel can cause graphitization of the diamond, as well as loss of any oxygen or aluminum introduced to control the TCR. Thus, the use of such alloys in combination with diamond substrates has heretofore been unsuccessful.

Tantalum nitride is also commonly used as a thin film resistor. It can be formed with a well controlled TCR, but only after passivation in air at temperatures in the range of 300-400°C. In attempts to use tantalum nitride in combination with diamond substrates, the passivation operation can convert the tantalum nitride (or tantalum carbide bond layer in contact with the diamond) to tantalum oxide, decreasing adhesion to the diamond.

Therefore, it would be desirable to create an improved metal layer, for example an alloy coating comprising nickel and chromium, on a diamond substrate. It would further be desirable to produce such coatings in the form of conductive metal traces suitable for the fabrication of thin film resistors. These goals are achieved by the present invention, namely a resistance element comprising :

a) a diamond substrate; and

b) a resistance layer comprising a deposited metal layer, which adheres to said diamond substrate, with carbon diffused into said metal layer,

wherein the resistance layer exhibits a temperature coefficient of resistance of less than 10 ppm/°K and adhesion to said diamond substrate of greater than 700 kg/cm^2.

Any diamond surface, single crystal or polycrystalline, may be coated with the resistance layer of this invention. However, it is most useful with polycrystalline diamond, and especially with CVD diamond. The CVD diamond may remain on the substrate on which it is deposited, but is more often removed therefrom as a sheet, which may be cut into units of the desired size and shape for use in integrated circuits.

Typically, the electrical surface resistance of uncontaminated diamond is greater than 15 MΩ/mm and its resistivity is on the order of 10^{13} Ω-cm. However, surface resistance may decrease substantially if the diamond is contaminated with other materials. Moreover, adhesion of metal traces thereto may be poor if there is carbon in graphitic form on the surface of the diamond. Therefore, it is advisable to thoroughly remove graphite and other contaminants prior to depositing the metal layer of the invention. This may be achieved by contacting the diamond at relatively high temperature with various strong acid mixtures. Contact with a boiling hydrochloric-hydrofluoric-nitric acid mixture to remove traces of metal, and with a boiling sulfuric-nitric acid mixture to- remove graphite, is conventional. Following cleaning, the diamond surface may be treated to promote adhesion of the metal layer, as by sputter etching or other plasma cleaning techniques.

The nickel-chromium alloys deposited to produce embodiments of the invention generally comrise about 60-90% (by weight) nickel, with the balance being chromium. The preferred alloys comprise about 75-85% nickel, with 80% being most preferred.

The nickel-chromium alloy may be deposited by conventional techniques. Sputtering is often preferred. The thickness of the alloy layer is typically about 100-5000 and preferably about 1000-5000 Å.

It is generally preferred to pattern the alloy coating, either simultaneously with the coating operation or subsequently. Simultaneous patterning by simple masking is generally employed.

Following deposition and (optionally) patterning of the alloy coating, the substrate containing said coating is heated in a non-oxidizing, non-nitride-forming atmosphere. Said atmosphere preferably contains at least one reducing gas, most often hydrogen, typically in the amount of up to about 10% by weight of total gases. Inert gases may be employed alone or in combination with said reducing gas. Illustrative inert gases are the noble gases helium, argon, neon and xenon, with argon generally being preferred by reason of its availability and relatively low cost. Nitrogen must be avoided since it will readily form nitrides with one or more of the metals under the conditions of heat treatment.

The temperature of the heat treatment is also critical for this embodiment. It must be in the range of about 750-900°C, preferably about 750-850°C and most desirably about 800°C. Employment of temperatures lower than about 750°C is ineffective, while at temperatures above about 900°C the nickel in the alloy can catalyze graphitization of the diamond surface, rendering it in part conductive and thus detracting from its effectiveness as a dielectric material.

The reasons for the effectiveness of heat treatment under the conditions of the present invention are not known with certainty. It has been found, however, that said heat treatment causes diffusion of carbon from the substrate into the metal alloy layer and of chromium toward the substrate, forming a nickel-chromium-carbon layer that bonds well to the substrate. It is also believed that chromium carbide formation and carbon dissolution in nickel, result in creation of a material having a low TCR.

An embodiment of the invention is illustrated by a procedure in which highly polished CVD diamond samples, about 12 mm square and 250 microns thick, were cleaned for 12 hours in a boiling mixture of equal volumes of hydrochloric, hydrofluoric and nitric acids to remove metal contaminants, and then for 4 hours in a boiling mixture of 4 volumes of sulfuric acid and 1 volume of nitric acid to remove graphitic carbon and other materials, from the surface. The surface resistance of each sample was determined after cleaning to be greater than 15 MΩ/mm, the upper limit of the resistance meter employed.

The surfaces of the samples were sputter etched for 6 minutes, after which a 3000 Å layer (as determined by weight gain and surface profilometry) of nickel-chromium alloy (80% nickel, 20% chromium) was sputtered onto the surface using a DC magnetron at 100 watts and a pressure of 8 millitorr of argon. Patterned sputtering was achieved using a Mylar polyester mask, to produce metal strips about 3.2 mm wide. As deposited, the nickel-chromium layer had an adhesion varying from about 7 to about 175 kg/cm^2 and a resistivity of about 1.2 x 10^{-4} ohm-cm. In many instances, the metal deposit would spall off the surface upon heating to 150-200°C.

The metallized substrates were heat treated at 800°C for 1 hour in contact with a gas mixture consisting of 5% (by weight) hydrogen and 95% argon, whereupon the adhesion increased to greater than 700 kg/cm^2. At the same time, the resistivity dropped to 6.6 x 10^{-5} ohm-cm. Auger analysis of the samples showed that carbon had diffused into the nickel-chromium alloy and that chromium had diffused toward the metal-diamond interface, creating conditions conducive to formation of a chromium carbide bond layer.

The samples were heated in air at 200-500°C for various periods to measure the thermal stability of the metal layer. The resistance of each sample was measured while the sample was at the elevated temperature. Those which had been heat-treated showed no loss in adhesion or change in resistivity after exposures to 450°C temperatures for periods up to 4 hours. At 500°C, an increase in resistivity was observed after 1 hour, which was shown by Auger analysis to be due to oxidation and loss of carbon from the alloy layer.

Claims

1. A resistance element comprising:

a) a diamond substrate; and

b) a resistance layer comprising a deposited metal layer, which adheres to said diamond substrate, with carbon diffused into said metal layer,

wherein the resistance layer exhibits a temperature coefficient of resistance of less than 10 ppm/°K and adhesion to said diamond substrate of greater than 700 kg/cm^2.

2. A resistance element according to claim 1 wherein said metal layer comprises about 60-90% by weight nickel and the balance chromium.

3. A resistance element according to claim 1 wherein said metal layer is patterned.

4. A resistance element according to claim 1 wherein said diamond substrate comprises polycrystalline diamond.

5. A resistance element according to claim 1 wherein said diamond substrate comprises chemical vapor deposited diamond.

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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 3424

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PROCEEDINGS OF IEEE 43RD ELECTRONIC COMPONENTS AND TECHNOLOGY CONFERENCE, 1 June 1993 - 4 June 1993 ORLANDO, FL, USA, pages 910-919, DAVID NORWOOD ET AL. 'Diamond - A New High Thermal Conductivity Substrate for Multichip Modules and Hybrid Circuits' * page 915, column 1, paragraph 5 - column 2, paragraph 3 *	1,4,5	H01C7/00
A	PROCEEDING OF 1993 INTERNATIONAL SYMPOSIUM ON MICROELECTRONIS, 9 November 1993 - 11 November 1993 DALLAS, TEXAS, pages 132-138, CD IACOVANGELO ET AL. 'Metallizing CVD Diamond for Electronic Applications'		
A	THIN SOLID FILMS, vol. 57, no. 2, 1979 LAUSANNE, pages 359-362, F. HEGNER 'The industrial production of High Quality Nickel-Chromium Resistors with Controlled Temperature Coefficient of Resistance'		TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 September 1995	Goossens, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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