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(54) HIGH RESISTANCE CERMET FILM AND METHOD OF MAKING THE SAME

(71) We, RCA CORPORATION, a Corporation organized under the laws of the State of Delaware, United States of America, of 30 Rockefeller Plaza, City and State of New York, 10020, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a cermet film, and particularly to such a cermet film having a high resistivity and a low temperature coefficient of resistivity so as to be useful as a resistor. The cermet film also exhibits high electric field stability and high temperature stability.

Cermets are mixtures of ceramic and metal particles. When a ceramic insulator and a metal are co-sputtered, the resultant cermet film may consist of very small metal granules in an insulating matrix. Cermets have found extensive use as resistors in microelectronic devices, integrated semiconductor circuits and in hybrid thick film circuits. The use of cermet materials permits one skilled in the art to obtain a particular resistivity merely by choosing the proper kind and quantity of ingredients, i.e., ceramic and metal.

For some applications a high resistance, relatively low temperature coefficient of resistivity (TCR) film would be useful. For example, insulating substrates coated with cermet films would make excellent chip resistors for thick film hybrid circuits. High sheet resistivity could then be obtained without the need for mechanical, chemical or laser trimming to create long meander paths. Furthermore, for some applications, it may be necessary that the resistive films function at temperatures of 250° C to 300° C and under dc fields of up to 30,000 volts/cm.

The device of the present invention is a high resistance cermet film on a substrate capable of withstanding temperatures up to 1000° C. The cermet film is composed of metal particles having an average diameter

of 30 Å to 120 Å and a ceramic insulator. The film has a metal percent volume no greater than the metal percent volume at which the percolation threshold (as herein-after defined) appears. The metal is selected from the class consisting of molybdenum, tungsten, cobalt and nickel. The film is annealed, at a temperature preferably in the range from about 750° C to about 925° C, in a hydrogen or other reducing atmosphere.

FIGURE 1 is a cross-sectional view of a resistor which includes a high resistance cermet film produced in accordance with the present invention.

FIGURE 2 is a graph showing resistivity (ρ) of a tungsten-aluminum oxide cermet film of the present invention as a function of the volume fraction (x) of tungsten before and after annealing for the indicated temperature and time.

FIGURE 3 is a graph showing the temperature coefficient of resistivity (TCR) at room temperature of a tungsten-aluminum oxide cermet film of the present invention as a function of the volume fraction (x) of tungsten prior to being annealed and after being annealed.

FIGURE 4 is a graph showing resistivity (ρ) of a molybdenum-aluminum oxide cermet film of the present invention as a function of the volume fraction (x) of molybdenum before and after annealing for the indicated temperature and time.

FIGURE 5 is a graph showing resistivity (ρ) of a tungsten-silicon dioxide cermet film of the present invention as a function of the volume fraction (x) of tungsten before and after annealing for the indicated temperature and time.

FIGURE 6 is a graph showing the average tungsten particle diameter d_p as a function of the volume fraction (x) of tungsten in a tungsten-aluminum oxide cermet of the present invention before and after annealing for the indicated temperature and time.

FIGURE 7 is a cross-sectional view of a portion of a conventional sputtering system

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in which a plasma confining enclosure is disposed around the target so as to be useful in forming the cermet film of the present invention.

5 Referring initially to FIGURE 1, one form of a resistor of the present invention is generally designated as 10. The resistor 10 of the present invention comprises a refractory substrate 12 upon which is a high resistance cermet film 14. Suitable substrate materials are those which conform to the requirements imposed by the various process stages and the intended operation of the high resistance cermet film. The substrate 12 is of a material which is able to withstand temperatures as high as 1000° C. Refractory materials such as ceramics, quartz, and high melting point materials, e.g., aluminum oxide, meet these requirements.

20 The high resistance cermet film 14 is composed of a metal and a ceramic insulator in which the metal content is less than that at which the percolation threshold appears. The metal is selected from tungsten, molybdenum, cobalt, and nickel. Suitable insulators include inorganic materials such as aluminum oxide, silicon dioxide, zirconium oxide, and yttrium oxide. Generally, the insulators

include any stable oxide that won't become conductive after annealing, i.e., heating. As will be described, the cermet film 14 must be annealed in order to achieve the desired properties.

30 An annealed $W_x(Al_2O_3)_{1-x}$ cermet film of the present invention, where x = volume fraction of tungsten, can have a high resistivity (ρ) i.e., up to approximately 10^7 ohm-cm, as shown in FIGURE 2. The annealed $W_x(Al_2O_3)_{1-x}$ cermet film unexpectedly exhibits substantially the same temperature coefficient of resistivity (TCR), i.e., as low as -1000 ppm/°C, as the unannealed film, as shown in FIGURE 3. Other annealed cermet compositions of the present invention exhibit similar properties, i.e., $Mo_x(Al_2O_3)_{1-x}$ and $W_x(SiO_2)_{1-x}$, as shown in FIGURES 4 and 5, respectively.

50 In addition to exhibiting high resistivity (ρ) (i.e. 10^5 to 10^7 ohm-cm) and low temperature coefficient of resistivity (TCR), the cermet films of the present invention also exhibit temperature stability, i.e., to at least 300° C. Furthermore, the annealed cermet films of the present invention have been found to be stable in the presence of electric fields of up to 10^5 V/cm as shown in Table I below.

TABLE I

Tungsten-Aluminum Oxide Cermet Films
($x = 0.20$ vol fraction tungsten)

Time (min)	Volts (kV)	Current (μ A)	Resistance (ohms)	Power (m Watts)
0	20	2.2	0.91×10^{10}	44
10	20	2.4	0.83×10^{10}	48
20	20	2.4	0.83×10^{10}	48
40	20	2.4	0.83×10^{10}	48
50	20	2.4	0.83×10^{10}	48

60 X-ray measurements show that the resistivity, low temperature coefficients of resistivity cermet films of the present example, e.g., $W_x(Al_2O_3)_{1-x}$, consist of small isotropic crystalline tungsten particles and amorphous aluminum oxide, i.e., a granular film. The average diameter of the particles was determined from the widths of the diffraction lines, as is well known in the art. It was found that the annealed cermet films of the present invention which exhibit high resistivity and low temperature coefficient of resistivity are films which include metal particles having an average diameter d_p of from about 30Å to about 120Å, as shown in FIGURE 6 in

75 which the average particle diameter d_p of tungsten particles is shown as a function of the composition of a $W_x(Al_2O_3)_{1-x}$ cermet. We believe the x-ray measurements indicate that the increase in resistance of such a tungsten-aluminum oxide film due to annealing can be attributed to the grain growth of the tungsten particles.

80 In the fabrication of the high resistivity, low temperature coefficient of resistivity cermet films of the present invention, the substrate 12 selected is initially cleansed by means of any conventional cleaning techniques, the choice of a particular cleansing agent being dependent upon the composition of the

substrate itself. Thereafter, the substrate is placed in a sputtering apparatus suitable for the deposition of the desired cermet film. The conditions used in sputtering as employed herein are known. By employing a proper voltage, pressure and spacing of the various elements within the vacuum chamber, a cermet film of a desired composition can be deposited upon the substrate, e.g. a tungsten-aluminum oxide cermet film onto an aluminum oxide substrate. As will be explained, it is desirable to maintain low background pressure of gaseous impurities in the sputtering system so as to reproducibly and consistently produce films having the desired properties.

Specifically, the high resistance cermet film of the present invention can be obtained, for example, by co-sputtering from a tungsten-aluminum oxide target onto an aluminum oxide substrate. The films can be prepared by radio frequency (rf) sputtering at an argon pressure of about 5×10^{-3} torr in a conventional diode sputtering system. The sputtering target can consist of a large diameter tungsten disk upon which an aluminum oxide disk with an evenly spaced array of holes is located (not shown). The cermet film composition can be varied, as is well known in the art, for example, by using different diameter holes thereby changing the relative area fraction of aluminum oxide to tungsten. The composition of the sputtered cermet film can be determined from the sputtering rates of tungsten and aluminum oxide, and from electron beam microprobe measurements and chemical analysis, as is known in the art.

It is essential in the sputtering step in the preparation of the cermet films of the present invention to maintain low background pressure of gaseous impurities, e.g., O_2 , CO_2 , H_2O , and other condensable or reactive gases, so as to produce films with the desired properties. The low background pressure can be obtained

by fitting a plasma confining enclosure around the substrate and target so that getter sputtering occurs as shown in FIGURE 7 in which a portion 20 of a conventional sputtering system is shown. The portion 20 of the sputtering system includes a target 22, a water-cooled cathode 24 and a cathode shield 26. A water-cooled substrate 28 is disposed in spaced relation to the target 22. The portion 20 of the sputtering system includes a plasma confining enclosure 30 which is conducive to getter sputtering which is known to reduce the gaseous impurities in deposited films.

In addition to the use of the plasma confining enclosure 30 of FIGURE 7, it is also preferable that the sputtering system be pumped to initial pressures of less than 1×10^{-7} torr before the inert gas, e.g. argon, is admitted. Also it is desirable to have efficient substrate cooling during the sputtering, e.g., water cooling, so that the deposited film is not heated by the plasma. Furthermore, it is desirable to have a liquid nitrogen or similarly cooled trap to remove gaseous impurities during deposition, i.e., a Meissner trap, near the region of sputtering.

The cermet films are then removed from the sputtering system and annealed in a reducing atmosphere. For example, annealed in hydrogen at temperatures in excess of about $750^\circ C$, preferably for time periods in excess of one hour. It is essential that the films be annealed in a reducing atmosphere, e.g., in the presence of hydrogen, as can be observed in Table II below in which one part of a tungsten-aluminum oxide cermet film having a volume fraction (x) of tungsten of 0.30 was annealed in dry hydrogen at $850^\circ C$ for 6 hours and another part of the film was annealed in vacuum, i.e., $p = 6 \times 10^{-6}$ tr, also at $850^\circ C$ for 6 hours.

TABLE II

Annealing Method	Initial Resistivity (ohm-cm)	Final Resistivity (ohm-cm)
Dry Hydrogen	2.07×10^4	7.45×10^4
Vacuum	1.93×10^4	1.47×10^4

Following the sputtering step, the sputtered cermet film exhibits a conventional resistivity (ρ) and temperature coefficient of resistivity (TCR). For example, a cermet film having a volume fraction (x) of tungsten of approximately 0.30, i.e., 30 per cent by volume, exhibits a resistivity (ρ) of approximately 20 ohm-cm as shown in FIGURE 2. The same cermet film exhibits a temperature coefficient of resistivity (TCR) of approximately

$-4,000$ ppm/ $^\circ C$ as shown in FIGURE 3. It has been observed that when such a cermet film is subsequently annealed in accordance with the present invention its resistivity is substantially increased, e.g., by up to a factor of 10^2 wherein the resistivity (ρ) changes from approximately 10^{-1} ohm-cm to approximately 10^1 ohm-cm as shown in FIGURE 2 for films having a volume fraction (x) of tungsten within the range of from about 0.45 to

about 0.25. Thus, at any given cermet composition having a volume fraction (x) of tungsten less than about 0.46, an upward controlled adjustment of resistivity is possible through a suitable choice of the temperature and time of anneal, as shown in FIGURE 2.

Of great importance for various device applications of cermet films has been the unexpected result that the temperature coefficient of resistivity (TCR) of the cermet film of the present invention is substantially invariant with respect to the annealing process. After annealing it has been discovered that the temperature coefficient of resistivity (TCR) of the cermet film of the present invention is substantially the same as its initial value as shown in FIGURE 3. Thus, as shown in FIGURES 2 and 3, the resistivity (ρ) of cermet films of various compositions can be increased through an annealing step without any significant corresponding change in the temperature coefficient of resistivity (TCR). It is believed that within the range of interest for this invention the temperature coefficient of resistivity (TCR) of the cermet of the present invention is a function of the cermet composition only.

It is presently believed that the unexpected properties of the cermets of the present invention involves the presence of the classical percolation threshold in the cermet composition. The percolation threshold is defined as the cermet composition at which it first appears that substantially no continuous conduction channels exist, i.e., most of the metal grains do not touch each other, so that the resistivity increases sharply. Thus, at the percolation threshold, and at metal contents less than that at which the percolation threshold appears, tunneling of electrons is the only conduction process. We have found, for example, that by annealing granular $W_x(Al_2O_3)_{1-x}$ films in hydrogen at temperatures in excess of 750°C, an abrupt percolation threshold appears near $x \cong .46$, as can be observed from FIGURE 2.

The x-ray results, indicate that the appearance of the resistivity edge for $W_x(Al_2O_3)_{1-x}$ with annealing is due to grain growth. The decrease in resistivity with annealing for $x > .46$ is attributed to an increase of the electron mean free path in the metal continuum while the increase in resistivity for $x < .46$ is attributed to the decrease in the number density of the W grains. The sharp resistivity edge indicates a classical percolation threshold at $x \cong 0.46$. Such a percolation threshold has been predicted for a mixture of insulating and conducting phases by R. Landauer in *J. Appl. Phys.*, 23, 779 (1952) and by some of the more recent three dimensional percolation theories, e.g. V. K. S. Shante and Scott Kirkpatrick, *Advances in Physics*, 20, 325 (1971). The maxima and minima in the resistivity of the annealed films

in the curve of FIGURE 2 indicate that the change in the resistivity rate is most rapid in the vicinity of $x \cong .46$. This is to be expected since the particles in the vicinity of this composition touch or nearly touch and grain growth occurs by particle coalescence.

The percolation threshold for the molybdenum-aluminum oxide cermet occurs at a volume fraction of $x \cong .44$, as shown in FIGURE 4, which is less than the corresponding value for the tungsten-aluminum oxide cermet film shown in FIGURE 2. The percolation threshold for the tungsten-silicon dioxide cermet occurs at a volume fraction of $x \cong .39$, as shown in FIGURE 5. However, the important consideration is that all these systems exhibit the conduction percolation threshold at a particular composition. The large increase in resistance upon annealing occurs in all the systems at metal concentrations which are no greater than the percolation threshold concentration.

It should be noted that although cermet films of the present invention were described with tungsten or molybdenum metal and aluminum oxide and/or silicon dioxide insulators, many substitutions can be made for both the metal and the insulator. Thus, there is provided by the present invention a high resistance cermet film which also exhibits a low temperature coefficient of resistivity. In addition, the high resistance cermet film exhibits high electric field and high temperature stability.

WHAT WE CLAIM IS:—

1. An article of manufacture comprising a high resistance cermet film on a substrate capable of withstanding temperatures up to 1000°C, said cermet film being composed of metal particles having an average diameter of 30 Å to 120 Å, and a ceramic insulator, said film having been annealed in a reducing atmosphere and having a metal percent volume no greater than the metal percent volume at which the percolation threshold (as hereinbefore defined) appears, and said metal being selected from the class consisting of molybdenum, tungsten, cobalt and nickel.

2. An article of manufacture in accordance with Claim 1 in which said metal comprises tungsten.

3. An article of manufacture in accordance with Claim 1 in which said insulator comprises aluminum oxide.

4. An article of manufacture in accordance with Claims 2 and 3 in which said cermet film has a tungsten content of less than 46 percent by volume.

5. An article of manufacture in accordance with Claim 4 with said tungsten content in the range of from 45 to 25 percent volume.

6. An article of manufacture in accordance with Claim 1 in which said insulator comprises silicon dioxide.



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It should be noted that although cermet films of the present invention were described with tungsten or molybdenum metal and aluminum oxide and/or silicon dioxide insulators, many substitutions can be made for both the metal and the insulator. Thus, there is provided by the present invention a high resistance cermet film which also exhibits a low temperature coefficient of resistivity. In addition, the high resistance cermet film exhibits high electric field and high temperature stability.

WHAT WE CLAIM IS:—

1. An article of manufacture comprising a high resistance cermet film on a substrate capable of withstanding temperatures up to 1000°C, said cermet film being composed of metal particles having an average diameter of 30 Å to 120 Å, and a ceramic insulator, said film having been annealed in a reducing atmosphere and having a metal percent volume no greater than the metal percent volume at which the percolation threshold (as hereinbefore defined) appears, and said metal being selected from the class consisting of molybdenum, tungsten, cobalt and nickel.

2. An article of manufacture in accordance with Claim 1 in which said metal comprises tungsten.

3. An article of manufacture in accordance with Claim 1 in which said insulator comprises aluminum oxide.

4. An article of manufacture in accordance with Claims 2 and 3 in which said cermet film has a tungsten content of less than 46 percent by volume.

5. An article of manufacture in accordance with Claim 4 with said tungsten content in the range of from 45 to 25 percent volume.

6. An article of manufacture in accordance with Claim 1 in which said insulator comprises silicon dioxide.



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7. An article of manufacture in accordance with Claim 1 in which said metal comprises molybdenum.
- 5 8. An article of manufacture in accordance with Claims 6 and 7 in which the cermet film has a molybdenum content of less than 44 percent volume.
- 10 9. An article of manufacture in accordance with Claims 2 and 6 in which said cermet film has a tungsten content of less than 39 percent by volume.
- 15 10. A method of making a high resistance cermet film comprising the steps of:
sputtering a granular film of a metal selected from the class consisting of molybdenum, tungsten, cobalt and nickel, and a ceramic insulator, onto a substrate capable of withstanding temperatures up to 1000°C, said granular film having a metal percent volume
- 20 no greater than the metal percent volume at which the percolation threshold (as hereinbefore defined) appears, and annealing the deposited film at a temperature over 750° C in a hydrogen or other such reducing atmosphere.
- 25 11. A method in accordance with Claim 10 in which said annealing is done at temperatures in the range of from about 750° to about 925° C.
- 30 12. An article of manufacture comprising on a substrate a cermet film composed and characterised substantially as hereinbefore described with reference to Figures 1—6 of the accompanying drawings.

T. I. M. SMITH,
Chartered Patent Agent,
50 Curzon Street,
London W1Y 8EU,
Agent for the Applicants.

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