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COMPLETE SPECIFICATION

Boron Nitride Thin Film Device and Process for Making Same

We, TEXAS INSTRUMENTS INCORPORATED, a Corporation organised according to the laws of the State of Delaware, United States of America, of 13500 North Central Expressway, Dallas, Texas, 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 depositing a boron nitride film on a substrate and also relates to articles, including electrical devices, in manufacture of which its process is used. Examples of such electrical devices are single and multi-layer insulated conductors and capacitors, in which the boron nitride film is used as a dielectric.

Pure and dense boron nitride has outstanding dielectric properties, is stable in most corrosive agents, is stable against oxidation even at high temperatures, and is not wetted by many molten materials. Therefore, boron nitride is a highly useful product, especially if it can be prepared as a thin film which is strongly adhered to the surface of an object, and is uniform, continuously dense and flexible. For example, useful applications of boron nitride films are in the field of dielectrics, either as insulation for a conductor, voltage protection device or as the dielectric in a capacitor.

It is well-known in the art that capacitance is directly proportional to the area of the opposed electrodes and inversely proportional to the thickness of the dielectric between the electrodes. The voltage at which the capacitor may be operated is determined by the breakdown voltage of the dielectric. Since it is desirable to have capacitors of minimum size,

but maximum capacitance and maximum breakdown voltage, attempts have been made to produce very thin dielectrics for use in capacitors having high insulation values.

Due to the outstanding dielectric properties of boron nitride, attempts have been made to construct capacitors using pure boron nitride as the dielectric. Substantially all of these attempts have involved what might be termed the "bulk" approach in that the dielectric layer is constructed by working a mass of boron nitride down to a thin sheet. For example, solid boron nitride has been successfully machined down to a thickness of about 25 mils and then placed between suitable electrodes such as metal films painted on the opposite surfaces of the thin sheet. Or powdered boron nitride has been combined with suitable binding material and subjected to high pressure and high temperature to form a relatively thin pressed dielectric sheet.

In the first instance, the minimum thickness of the machined boron nitride is limited by the machining process, except when using very costly machining techniques, to a minimum thickness of about 25 mils as compared with an optimum thickness of substantially less than one mil. In the second case, the intermixed binders and other additives appreciably decreased the insulation properties of the boron nitride. Further, the binders produce small zones in which no boron nitride is present. Therefore, as the sheet is pressed thinner, some areas between the electrodes do not have any boron nitride present and the capacitor shorts out or has a low breakdown voltage.

Other attempts to construct very thin film dielectrics for use in capacitors have entailed the production of a metal oxide film or other

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metal compound film on a metal substrate. While these capacitors are suitable for some purposes, metal ions must diffuse into the metal oxide dielectric being formed in order to carry out the oxidation reaction. This results in a metal ion gradient throughout the film which appreciably reduces the dielectric quality of the film.

More recently, it has been suggested that boron nitride can be deposited directly upon a metal substrate by the thermal decomposition of trichloroborazole and that the boron nitride deposited in this manner could be used for electrical capacitors. However, it has been found that boron nitride cannot be deposited directly upon a metal substrate to produce a thin, continuously dense film which is strongly adherent to the metal substrate so as to be used to manufacture electrical devices, and in particular, the quality and thickness of the film could not be sufficiently controlled for commercial application.

In accordance with the broader aspects of the present invention, a device is constructed by depositing a pure boron nitride film on to a metallic, graphite, silicon or other substrate and depositing an electrode film on to the boron nitride film. The film preferably is less than two mils in thickness although greater thicknesses can be used. The boron nitride film is bonded to the substrate material by an interlayer of material formed on the substrate and preferably is either a boride or a nitride of the substrate material. The deposited boron nitride film can be made thin, pure, dense, and strongly adherent to the metallic substrate such that very small capacitors having very high capacitance values can be constructed by use of this method.

In one specific embodiment of the invention, the interlayer is a boron compound of the substrate metal so that the interlayer has chemical elements common to both the substrate and the boron nitride film, and the substrate is taken from refractory metals in general, and specifically from the group consisting of molybdenum, tungsten, niobium, tantalum and base alloys of each, and ferrous base alloys.

This invention also contemplates a process for adherently applying a thin film of boron nitride to the surface of a metal other than those mentioned, and in particular to the surface of copper or copper alloys. The process is comprised of first depositing a thin film of a refractory metal on the surface of the substrate metal, forming an interlayer on the surface of the refractory metal by reacting a reagent with the metal, then depositing a thin film of boron nitride on the interlayer to produce a novel article of manufacture comprised of a conductive metal substrate, a first interlayer of refractory metal bonded to the substrate, a second interlayer bonded to the first metal interlayer, and a thin

film of boron nitride bonded to the interlayer. In accordance with a more specific aspect of the invention, a thin film of molybdenum is deposited on a copper surface, then the surface of the molybdenum film is bonded prior to the deposition of the thin film of boron nitride. The resulting article is a copper or copper alloy conductor having good electrical characteristics, coated by a thin film of boron nitride which is adherently bonded to the copper by first and second interlayers of molybdenum and molybdenum boride and which is a superior insulator, can be made flexible, and has outstanding mechanical, chemical and thermal stability at temperatures up to about 700°C.

The invention also contemplates several novel methods for constructing multilayer capacitors on an economical mass production basis. One such method entails the simultaneous deposition of boron nitride films on opposite sides of the substrate, then deposition of the metallic film electrodes on each of the boron nitride films. This sequence of steps can be repeated as desired because an interlayer compounded from the metallic film material can be formed to securely bond subsequent boron nitride films to each metallic film electrode.

Copper and many of its alloys are generally considered to be the best and most economical electrical conductors. In nearly all cases where copper is used as an electrical conductor, suitable insulation must be applied over the surface of the copper to prevent shorting. Many different organic and inorganic materials have been used as insulation for copper conductors. In general, the organic materials are mechanically unsound and deteriorate at relatively low temperatures, particularly if only thin coats are used. The inorganic insulations tend to crack on bending, are usually difficult to prepare without pinholes and, therefore, usually must be coated with a second material to protect against moisture and to reduce the deleterious effects of cracking. Sometimes other metals are clad over copper to prevent oxidation of the copper and then the conventional insulation materials applied. Another common technique consists of coating the copper with a slurry comprised of an organic enamel and ceramic or glass particles. The coating is then fired to sinter the particles into a continuous insulating film and drive off the organic portion of the slurry. Then an organic coating, such as "Teflon" (Registered Trade Mark) is applied as an overcoat. Another common technique is to coat the copper with aluminium, then anodize the aluminium to form a thin insulating film of alumina around the copper.

It is often desirable to use electrical conductors at temperatures substantially above 200°C., but prolonged use of most conductors at these temperatures results in damage

molybdenum



to the insulation or oxidation of the copper. It is desirable for the insulating coats to be thin so as to save space, particularly when using the conductors for motor and transformer windings, or the like. Thin boron nitride films have excellent dielectric, thermal, mechanical and chemical properties for use as an electrical insulator and, if adherently applied to a flexible substrate, protect the substrate from oxidation and are flexible. However, it is extremely difficult to adherently apply a continuous, pin-hole-free film of dense boron nitride to a copper substrate because of inherent incompatibilities in the lattice structures and coefficients of thermal expansion, and various other reasons.

In general, a process of the present invention comprises the steps of forming an interlayer on the surface of a substrate and then depositing the boron nitride film on the interlayer in such a manner that the interlayer adheres, and preferably chemically bonds, the boron nitride film to the substrate.

In accordance with another aspect of the invention, a plurality of boron nitride films of different thicknesses are deposited between metallic film electrodes to produce a highly versatile capacitor.

As mentioned, very thin boron nitride films can be formed such that extremely small capacitors having high capacitance values can be constructed in accordance with the present invention. In order to overcome the problem of connecting electrical leads to the appropriate electrodes, processes using selective etching, masking and abrasive etching can be used to make such connections to the capacitor electrodes, and in particular to the electrodes of multilayer capacitors.

Specifically, the electrical connections can be made after using selective etching techniques on the boron nitride and the metallic substrate and electrodes. In this connection, boron nitride has heretofore been considered as substantially stable in all acids and bases and mixtures thereof. However, we have discovered that boron nitride can be etched by hot phosphoric acid, such that a novel selective etching process can be employed as hereafter described in greater detail; this method of etching is the subject of copending Application No. 4695/67 (Serial No. 1083523).

A process embodying the invention can be used to manufacture a micro-circuit comprised of a resistor and capacitor connected in series and comprised of a thin metal film, an interlayer, a thin boron nitride dielectric film and a counterelectrode. The thin metal film can be tantalum and serves as both a resistor and an electrode for the capacitor.

By way of example, embodiments of the invention will be described in greater detail with reference to the accompanying drawings, wherein:—

Fig. 1 is a schematic drawing of an appar-

atus which may be used to practise the method of the present invention,

Fig. 2 is an enlarged, schematic, partial sectional view of an article of manufacture constructed in accordance with this invention which also serves to illustrate the method of the present invention,

Fig. 3 is an enlarged, partial sectional view of a capacitor constructed in accordance with the present invention,

Fig. 4 is a somewhat schematic plan view which serves to illustrate the manner in which the results of the method of the present invention were tested,

Fig. 5 is a graph illustrating an operating characteristic of three capacitors constructed in accordance with the present invention,

Fig. 6 is a graph illustrating another operating characteristic of a capacitor constructed in accordance with the present invention,

Fig. 7 is a graph illustrating still another operating characteristic of five capacitors constructed in accordance with the present invention,

Fig. 8 is a graph illustrating yet another operating characteristic of the five capacitors constructed in accordance with the present invention,

Fig. 9 is an enlarged partial sectional view of still another capacitor constructed in accordance with the present invention,

Fig. 10 is an enlarged partial sectional view of still another capacitor constructed in accordance with the present invention,

Fig. 11 is a broken, enlarged sectional view illustrating the manner in which electrical connections can be made to the electrodes of the capacitor shown in Fig. 9,

Fig. 12 is a broken, enlarged sectional view of another manner in which electrical connections can be made to the electrodes of the capacitor shown in Fig. 9, and

Fig. 13 is an enlarged, somewhat schematic sectional view of still another capacitor constructed in accordance with the present invention.

In accordance with the broader aspects of the present invention, an interlayer is used to adhere a thin film of boron nitride to a substrate. The interlayer can be formed by reacting a reagent with the substrate to form a boride, nitride, oxide or other compound of the substrate which will chemically bond with a boron nitride film subsequently deposited on the interlayer. The novel process is believed to be applicable to a wide variety of substrate materials and in particular to substantially all refractory metals which will withstand the temperatures used in the process, and is specifically applicable to molybdenum, niobium, tantalum, tungsten and to alloys comprised primarily of these metals, and to certain ferrous base alloys.

In a specific embodiment of the invention, boron is reacted with the metal substrate to



also



produce a metal boride interlayer. The boron may be supplied by reacting boron trichloride vapour with the surface of a heated substrate.

5 The boron nitride film may be formed by the reaction of boron and nitrogen from any suitable source reagents on a heated substrate upon which an interlayer has been formed. In a specific embodiment, however, the boron
10 nitride film is deposited by the thermal decomposition of beta-trichloroborazole on a heated substrate. Or the boron and nitrogen may be supplied by boron trichloride and ammonia.

15 The formation of the interlayer and the deposition of the boron nitride film are preferably accomplished in separate steps so that a uniform interlayer is assured over the entire surface to be coated. A uniform boron nitride
20 layer can then be deposited and the thickness of the film rather precisely controlled. However, the two steps can be accomplished simultaneously by supplying a mixture of boron trichloride and trichloroborazole vapours
25 at the surface of a heated substrate.

A suitable apparatus for performing the process of the present invention is indicated generally by the reference numeral 10 in Fig. 1. The apparatus 10 comprises a reaction
30 chamber 12 formed by a bell jar 14 and a base 16. The reaction chamber 12 can be evacuated by a suitable pump 18. A valve 20 is provided for sealing the reaction chamber from the pump when desired. A metal or other
35 substrate 22 upon which the boron nitride film is to be deposited is held by suitable clamps 24 through which an electrical current can be passed to heat the substrate. A valve 26 controls the introduction of boron trichloride vapours into the reaction chamber 12
40 from a suitable boron trichloride source 28. A similar valve 30 controls the introduction of trichloroborazole vapours to the reaction chamber 12 from a trichloroborazole source 32 which may conveniently comprise a
45 vacuum container in which trichloroborazole crystals can be heated and vaporised. In the event boron trichloride and ammonia are used for the deposition of the boron nitride film, the valve 30 can be used to control the introduction of the ammonia or the vapours of the
50 addition compound ammonia-boron trichloride which has been previously formed by a reaction between boron trichloride and ammonia to the reaction chamber 12.

55 When using the apparatus 10 to practise the process of the present invention, the substrate 22 is preferably degreased by a suitable solvent prior to placement in the reaction chamber 12. Next the reaction chamber 12 is evacuated by the pump 18 to a very low
60 pressure, preferably less than about one micron of mercury. The substrate 22 may then be heated in the vacuum to sublime all volatile impurities which are purged from

the system by the vacuum pump 18. Next the reaction chamber 12 is backfilled with boron trichloride from the source 28 to the desired pressure, which is preferably between about 5 and about 500 microns of mercury. The
70 substrate 22 is then resistively heated to a temperature in the range from about 700°C to about 1700°C for a short period of time, usually from about 15 to about 60 seconds. During this period the boride interlayer is formed upon the surface of the substrate 22 by the interaction of the metal and the boron from the boron trichloride vapours.

The reaction chamber 12 is then evacuated to a low pressure of about one micron of
80 mercury in order to remove the remaining boron trichloride vapours and the freed chlorine. The reaction chamber 12 is then backfilled with beta-trichloroborazole vapours to a pressure between about 10 and 20 millimeters of mercury. Next the substrate 22 is heated to a temperature between about 700°C and about 1700°C until a film of boron nitride of the desired thickness is achieved. A period from about 1 to about 5 minutes is normal. The thickness of the film can be rather precisely determined by controlling the various parameters of pressure, temperature and contact time between the vapours and the substrate. Boron nitride films from 0.2 microns to 5 microns have been prepared. The film can be made so thin and of such uniform thickness as to be substantially one colour of the substrate is uniformly heated.

Using the above described process, boron
100 nitride films of various thicknesses were deposited upon molybdenum wire having a diameter of 10 mils. The adherence of the film to the wire substrate was determined by simple bending tests. Although the precise thicknesses of the films were not measured, the thicknesses of the films are indicated by the DC breakdown voltage determined by using a ball-shaped contact to apply the voltage to the boron nitride film. The permissible bend diameters and breakdown voltages are tabulated below in Table 1. As the thickness of the boron nitride film increases, flexibility diminishes and the minimum permissible bend diameter and breakdown voltage increase.

TABLE 1.
Permissible Bend Diameter VS. Breakdown Voltage.

1/8" bend diameter	150 volts	120
1/4" bend diameter	250 volts	
1/2" bend diameter	1100 volts	
1" bend diameter	1400 volts	

The boron nitride films are chemically stable in a wide variety of corrosive media. Specifically, the boron nitride films are insoluble in H₂O, HCl (dilute and concentrate), HNO₃ (dilute and concentrate), H₂SO₄ (dilute and concentrate), aqua regia, NaOH,
125

trichloride



KOH (dilute and concentrate), cryolite mixtures, and HF (dilute and concentrate). The boron nitride films are stable in air up to 700°C, but are unstable above 800°C after 30 minutes. Negligible loss of boron nitride by evaporation occurred when the film was held at 900°C in a vacuum of 0.01 microns of mercury. From the above data relating to the flexibility, insulative properties and chemical stability at elevated temperatures, it will be evident that the strongly adherent, thin boron nitride films are highly useful as insulation in various adverse environments. The boron nitride films also exhibit the property of not being wetted by some molten metals including silver, gold, zinc, and some molten glasses including borosilicates. Accordingly, the boron nitride films prepared by the above process should be useful in protecting vessels and other equipment used in handling these molten materials.

However, we have discovered that the boron nitride films are subject to rapid attack by H_3PO_4 at about 295°C. This unique feature permits selective etching of the boron nitride to facilitate the construction of a capacitor as will hereafter be described in greater detail. In a specific example, a strip of molybdenum coated with a boron nitride film deposited in accordance with the present invention and a second weighed strip of molybdenum were placed in a solution of H_3PO_4 that had been boiled until bubbles had quit coming up and which was at a temperature of approximately 295°C. The strips were held in the H_3PO_4 solution for about five minutes before being removed and washed. The boron nitride film had been removed from the molybdenum strip and electrical conductance by point contact to the strip was good. The other weighed strip of molybdenum experienced no weight loss indicating that molybdenum is stable in the hot H_3PO_4 .

In accordance with another aspect of the present invention, a novel and highly useful electrical capacitor is manufactured by depositing a very thin boron nitride film on a metal substrate using the interlayer to chemically bond the film to the substrate as above described, and then depositing a metallic counterelectrode on the dielectric boron nitride film.

In order to test the continuity and uniformity of a boron nitride film and to construct a capacitor, a molybdenum foil substrate 40 (Fig. 3) was placed in the reaction chamber 12. A molybdenum boride interlayer 42 and a boron nitride film 44 were then deposited on the molybdenum substrate using the process described above. A series of randomly-placed aluminium electrodes 46 of progressively increasing diameters as illustrated in Fig. 4 were then vacuum-evaporated on to the surface of the boron nitride film using conventional techniques. The aluminium

film electrodes 46 had successively increasing areas up to 1.208 square inches. The breakdown voltage of the boron nitride film between each of the electrodes 46 and a metal substrate was uniformly about 500 volts DC. This indicates that the boron nitride is very uniform and continuously dense over the entire substrate because any defect in the boron nitride film under any electrode would result in a decrease in the breakdown voltage.

Further tests of capacitors constructed in accordance with the present invention indicated that a 0.5 micron thick boron nitride film has a dielectric strength of 5000 DC volts per mil (2×10^6 DC volts per centimeter) and a dielectric constant of 4.4. Thus a boron nitride film one micron thick can be expected to have a breakdown voltage of 200 DC volts and a capacitance of 25,000 micro micro farads per square inch. The DC voltage breakdown tests referred to above correspond to Method 301 of the procedures outlined in Milstd-202 of the United States Government and represent the ability of the boron nitride film to withstand an impressed DC voltage over a period in excess of one minute. By utilizing the breakdown characteristic of this device, a voltage overload protection circuit arrangement can be maintained.

The variations in breakdown voltage for three separate capacitors constructed in accordance with the present invention are represented by the curves 50, 52 and 54 on the graph of Fig. 5. The boron nitride film of the capacitor represented by the curve 52 was thicker than the boron nitride coating of the capacitor represented by the curve 50, and the boron nitride film of the capacitor represented by the curve 54 was still thicker. The voltage measurements were made in a dry nitrogen ambient atmosphere by making a point contact of the aluminium film electrode deposited on the boron nitride film. Considering some inaccuracies in the breakdown voltage measurements, it will be evident that no large changes in the rate of degradation of the breakdown voltages with temperature occurs with decreasing film thicknesses up to about 150°C where the breakdown voltage of the capacitor having the thinnest boron nitride film represented by curve 50 begins to decrease at a greater rate. In other words, the slopes of the curves 50, 52 and 54 are substantially the same constant value except for the curve 50 above 150°C. Considering some inaccuracies in the test measurement, this indicates that the rate of degradation for the thinnest boron nitride film might increase more rapidly above 150°C, whereas no change is apparent in the thicker boron nitride films represented by the curves 52 and 54.

Referring now to Fig. 6, the curve 60 represents the percentage change in capacitance with respect to temperature of five



randomly-selected capacitor assemblies selected from a group constructed by encapsulating a sandwich of molybdenum substrate, metal boride interlayer, boron nitride film and aluminium film electrode in transistor cans or in glass in conventional manner. The assemblies rather uniformly had capacitance values of 320 micro micro farads and 200 volts breakdown. The temperature coefficients calculated from the curve 60 are $-25 \text{ ppm}/^\circ\text{C}$ at -55°C , $+17 \text{ ppm}/^\circ\text{C}$ at $+85^\circ\text{C}$, $+10 \text{ ppm}/^\circ\text{C}$ at $+125^\circ\text{C}$, and $+16 \text{ ppm}/^\circ\text{C}$ at $+250^\circ\text{C}$. The overall accuracy of the capacitance measurements are approximately ± 0.2 micro micro farads or $\pm 5-10 \text{ ppm}/^\circ\text{C}$. No change in capacitance was detectable between $+200$ and $+250^\circ\text{C}$. From the above data, it will be evident to those skilled in the art that capacitors or other devices constructed in accordance with the present invention have an exceptional temperature stability.

The dissipation factors of a random group of 13 capacitor assemblies were measured to be in the range of 0.01% at 1 kc/s. The boron nitride capacitors which were carefully encapsulated in glass envelopes did not exhibit any change in the dissipation factor with temperature in the range measured, which was up to 175°C . Other capacitors encapsulated in transistor cans exhibited a slight increase in the dissipation factor, but even these compared very favourably with electrostatic precision units presently on the market.

Five capacitors constructed in accordance with the present invention were tested over extended periods of time to determine the percentage change in capacitance of each and the percentage change in the dissipation factor of each. The changes in the capacitance of each of the units are presented by one of the curves indicated collectively by the reference numeral 70 in the graph of Fig. 7. The changes in the dissipation factors of the corresponding capacitors are represented by the curves indicated collectively by the reference numeral 80 in the graph of Fig. 8. The graphs include only data obtained over 4500 hours, but the units exhibited no further change in capacitance over the period tested which was in excess of 1000 hours. It will be noted that the average capacitance change is approximately the same at 0 volts DC as at 75 volts DC, which indicates that no deterioration is caused by voltage stress. It will be noted in Fig. 8 that an appreciable change in the dissipation factor occurred during the first 24 hours, but a definite tendency towards stabilisation was subsequently exhibited. It is believed that this initial effect was caused primarily by small quantities of moisture remaining in the encapsulation ambient which subsequently dissipated, or may have been caused by electrode deterioration.

Another important aspect of the present

invention is illustrated by the novel capacitor construction indicated generally by the reference numeral 90 in Fig. 9. A metal foil substrate 91 is placed in a reaction chamber such as the chamber 12, and suitable interlayers 92 and 94 are simultaneously formed on the opposite surfaces of the foil using the process heretofore described. In the particular embodiment illustrated, the substrate 91 is molybdenum and the bonding interlayers are molybdenum boride. Boron nitride films 96 and 98 are then simultaneously deposited upon the metal boride interlayers 92 and 94, respectively, using the process heretofore described. Metallic film electrodes 100 and 102 are then deposited on the boron nitride films by any suitable technique, but preferably by vapour condensation, to produce the multilayer capacitor 90. The metallic films are preferably of a metal different from the substrate 91, such as gold, so that the two metals can be selectively etched as well hereafter be described. Electrical contact can be made with the electrodes individually and thereby produce two separate capacitors, or the metal film electrodes 100 and 102 can be electrically interconnected to provide a single capacitor having twice the capacitance for a given area of substrate.

It will be appreciated that the capacitor construction 90 is paper thin and that making separate electrical contact with the electrodes creates a considerable problem. The electrical connections to the multilayer capacitor 90 can be made by either of two methods, the first of which is illustrated in Fig. 11. The metal foil substrate 91 is cut up into small pieces having the desired area. This leaves a sandwich construction having relatively square peripheral edges. As previously mentioned, when the etching technique is to be employed, the metal film electrodes 100 and 102 will usually be a metal different from the metal foil substrate 91. For example, the substrate 91 may be molybdenum and the metal film electrodes 100 and 102 gold so that the two metals will not be attacked by the same etchants. Then the edge 104, for example, of the sandwich construction is dipped in a suitable etchant such as a solution of $\text{HCl}-\text{HNO}_3$ having a high concentration of HCl . The relatively thin gold film electrodes 100 and 102 will be rapidly etched away relative to the rate at which the edge of the molybdenum substrate 91 will be attacked. The gold film electrodes will be etched back to the points 106 and 108 for example. The boron nitride films 96 and 98 may then be etched back to the points 110 and 112, for example, by a solution of hot H_3PO_4 as previously described. A clip 114 can then be connected to the exposed edge of the substrate 91 by conventional welding techniques.

Another edge of the sandwich is then immersed in a suitable etchant which will selec-

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will

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5 tively attack the molybdenum substrate 91 but will not affect the boron nitride films 96 or 98 or the gold film electrodes 100 and 102 so that the substrate 91 is removed back to point 116. For example, a solution of HCl-HNO₃ having a very low concentration of HCl will attack the molybdenum at a much greater rate than the gold and will not attack the boron nitride. The electrodes 100 and 102 will tend to hold the otherwise fragile boron nitride films 96 and 98 intact and the free edges of the films will tend to come together as illustrated in Fig. 10 to cover the edge of the substrate. Then a clip 118 can be crimped over the edge of the sandwich and preferably welded to the metal films 100 and 102. The boron nitride covering the edge of the substrate 91 ensures that the clip 118 does not contact the substrate. The capacitor can then be encapsulated in a suitable insulating material.

20 An alternative technique for making contact with the electrodes of the multilayer capacitor construction 90 is illustrated in Fig. 12. When using this technique, an aperture indicated generally by the reference numeral 120 is punched in the metal foil substrate 91 prior to deposition of the various layers. The metal boride interlayers 92 and 94, the boron nitride films 96 and 98 will come together and cover the edge of the substrate 91 around the edge of the aperture 120. Then when the metal film electrodes 100 and 102 are deposited, a film 122 will also coat the edge of the aperture and provide electrical contact between the two electrodes 100 and 102. A suitable metal tack 124 may then be inserted through the aperture 120 and welded by conventional techniques to the metal film electrode 100. If for some reason the metal film around the periphery of the aperture 120 does not provide sufficient electrical contact between the two electrodes 100 and 102, the other end 126 of the tack 124 can also be welded or otherwise connected to the metal film electrode 102. A suitable lead wire 128 can then be welded to the tack 124.

50 Electrical connection is made to the substrate 91 by means of a second tack 130. The metal film electrodes 100 and 102 are either etched away in the areas 132 and 134 or the areas are masked prior to deposition of the electrodes to ensure that the tack 130 does not make contact with either. Then the tack 130 is merely coated with suitable weld material, pressed through the metal foil substrate in the boron nitride films 96 and 98, and the device is heated to fuse the weld material and weld the tack 130 to the substrate 91. A suitable lead wire 136 can then be welded to the tack 130.

65 Another multilayer capacitor constructed in accordance with the present invention is indicated generally by the reference numeral 140 in Fig. 10. The capacitor 140 is manufactured

by placing a metal foil substrate 141, such as molybdenum, in the reaction chamber and successively depositing a metal boride interlayer 142 and a boron nitride film 144 on the substrate using the process steps heretofore described. A metal foil electrode 146 is then deposited on the surface of the boron nitride film 144 preferably by conventional vacuum-evaporation and condensation techniques. The metal film electrode 146 should be chosen so that boron will react with the metal to form a metal boride interlayer by the above described techniques. Molybdenum may be used for the electrode film. Then a second metal boride interlayer 148, a second boron nitride film 150 and a second metal film electrode 152 are successively deposited upon the metal film electrode 146. This sequence of steps may be repeated any number of times to produce additional dielectric and electrode films such as a third metal boride interlayer 154, a third boron nitride film 156 and a third metal film electrode 158. The second metal film electrode 152 may also be molybdenum, as illustrated, in which case the interlayer 154 would be molybdenum boride. However, it will be appreciated that any one of the refractory metals heretofore specified can be used in accordance with the broader aspects of the invention.

An important aspect of the capacitor 140 is that the boron nitride dielectrics 144, 150 and 156 can each be made very thin yet can be made of different thicknesses so as to provide a variety of capacitances in the same device. For example, the boron nitride film 144 might have the least thickness, the boron nitride film 150 a greater thickness, and the boron nitride film 156 the greatest thickness. The thicknesses of the boron nitride films can be controlled with considerable accuracy as previously mentioned, and the total thickness of the films deposited on the substrate might be less than one mil.

In accordance with another aspect of the present invention, a thin film of dense, pin-hole-free boron nitride is adherently bonded to the surface of a substrate metal to which it otherwise could not be bonded by direct application. This is accomplished by first depositing a thin interlayer of a refractory metal as heretofore described, but preferably molybdenum, tungsten, niobium, or tantalum, forming a second interlayer by reacting a reagent with the first metal interlayer as heretofore described so as to provide a means for bonding the boron nitride to the refractory metal.

More specifically, the substrate may be copper or substantially any alloy of copper particularly suited for high temperature application as an electrical conductor, of which there are many. The first interlayer is preferably molybdenum applied to the substrate by any suitable conventional technique.

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The second interlayer is preferably molybdenum boride formed by reacting boron with the molybdenum interlayer, and boron nitride is preferably deposited by pyrolysis of a boron and nitrogen bearing compound or compounds on the heated substrate, as heretofore described.

The thin film of refractory metal may be deposited on the surface of a copper or copper alloy substrate using any suitable conventional technique. For example, a molybdenum film may be deposited on the substrate by conventional and well-known evaporation techniques wherein the substrate is positioned in a vacuum chamber and the molybdenum heated until vaporized into the chamber. The substrate is maintained at a relatively low temperature such that the molybdenum vapour will condense on the substrate and form a uniform, dense, thin film of molybdenum. The film of molybdenum should be relatively thin and preferably less than about 2.0 microns in thickness, and more particularly may be as thin as from 100 to 200 angstroms. It is believed that a thin film is desirable because the coefficients of thermal expansion of molybdenum and copper are not particularly well matched and a thick film would be more inclined to rupture during thermal cycling.

The interlayer film of molybdenum may also be deposited on the metal substrate by a suitable conventional chemical deposition technique such as, for example, the hydrogen reduction of molybdenum chloride or other halide or metal organic compound vapour. The molybdenum film may also be applied by conventional sputtering or electrochemical deposition techniques.

The second interlayer between the first metal interlayer film and the boron nitride is formed by reacting a reagent with the metal film to form a boride, nitride, oxide or other compound of the metal which will chemically bond with the boron nitride film which is to be subsequently deposited thereon, and more specifically may be formed by reacting boron with the metal film to produce a metal boride interlayer. The metal boride may be formed by heating the substrate in the presence of boron trichloride vapour as heretofore described. The boron nitride film may be formed by the reaction of boron-nitrogen from suitable source reagents on a heated substrate upon which the first and second interlayers have been formed using the process heretofore described. For example, the boron nitride film may be deposited by the thermal deposition of beta-trichloroborazole on a heated substrate. Or the boron and nitrogen may be formed from boron trichloride and ammonia.

The process of forming the second interlayer on the first metal interlayer and depositing the boron nitride film on the second interlayer can be carried out in a conventional vacuum reaction chamber of the type generally illus-

trated in Fig. 1. However, since the substrate is copper, the temperature must be rather closely controlled so as not to exceed the temperature limits of the copper or copper alloy. A temperature from about 700°C to about 1050°C is preferred because pure copper melts at 1083°C.

The novel article manufactured by the process is comprised of a body of electrically-conductive metal, preferably copper or a copper alloy, the surface of which is coated by a very thin film of refractory metal, preferably molybdenum, to which a thin film of boron nitride is bonded by an interlayer, preferably a metal boride. The novel article may be fabricated from copper which is recognised as the best electrical conductor for general use because of its high conductivity, abundance and relatively low cost among other reasons. Certain copper alloys have been developed, and are well-known, which may be used at temperatures substantially above the maximum useful temperature of pure copper because of higher strength, yet have conductivities approaching that of pure copper. These include dispersion-hardened forms of copper and copper alloys.

Electrical contact can be made with the electrodes of the device 140 in the manner illustrated in the transverse cross section of Fig. 13 by using either masking or selective etching techniques. When using the masking technique, a relatively long strip of metal foil 141 may be used as the substrate placed in the reaction chamber for deposition of the first interlayer 142, the first boron nitride film 144 and the first metal film electrode 146. Then the area 160 is covered by a suitable mask extending along the entire length of the substrate 141. Then the second interlayer 148, the second boron nitride film 150 and the second metal film electrode 152 are deposited. The area 162 is then covered by additional masking before the third interlayer 154, the third boron nitride film 156 and the third metal film electrode 158 are deposited. Then the masking can be removed and the elongated strip of foil 141 cut transversely into the desired number of capacitor sandwich units. The conductors 164, 166, 168 and 179 can then be welded to the substrate 141 and the first, second, and third metal film electrodes 146, 152 and 158 respectively. The edges of the capacitor can be cleared by suitable etching material to remove metals which have wiped over the cut edges and would otherwise tend to short out the capacitor. The capacitor can then be encapsulated in a suitable insulating material in a conventional manner, if desired.

The alternative process for attaching the leads to the various electrodes of the capacitor 140 involves the successive and selective etching of the various layers. When using such a technique, the metal film electrodes are



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preferably of a metal, such as molybdenum, that will not be attacked by the H_3PO_4 etchant for boron nitride, but which will be attacked by an etchant in which the boron nitride is stable, such as a solution of $HCl-HNO_3$.

The third metal film electrode 158 is first etched away by $HCl-HNO_3$ to expose the third boron nitride film 156 in both areas 160 and 162. During this step the third boron nitride layer 154 will protect the second metal film electrode 152. Next the third boron nitride film 156 in the areas 160 and 162 is etched away by hot H_3PO_4 . Then the third metal boride interlayer 154 is etched away in the areas 160 and 162 to expose the second metal film electrode 152 over both areas. The second metal film electrode 152 and the second boron nitride film 150 can then be successively etched away in the area 160 to expose the first metal film electrode 146. The leads 164, 166, 168 and 170 can then be connected by some conventional technique such as welding and the capacitor encapsulated if desired by a suitable insulating material.

Another important aspect of the invention is that a micro-circuit comprised of a resistor and a capacitor connected in series can be constructed in accordance with the present invention merely by controlling the thickness and properties of the metallic film electrode. For example, the electrode film 46 in Fig. 3 could be a high resistance metal such as tantalum rather than aluminium. The thickness of the metal film can be accurately controlled by controlling the parameters of the vapour phase deposition process so that a resistance of the desired value can be attained. The capacitor formed by the substrate 40, the boron nitride film dielectric 44 and the electrode film 46 is then connected in series with the resistor formed by the metal film.

From the above description, it will be evident to those skilled in the art that a novel and highly useful process for manufacturing electrical capacitors has been described. A novel capacitor not heretofore available has also been described which is comprised of a dense, continuous, pure and flexible dielectric layer which is strongly adherent to a metal foil substrate. The boron nitride is a material which has not heretofore been available in this form and in such thin films. Further, a novel process has been described for manufacturing multilayer capacitors of a size, quality, and character heretofore unobtainable. The boron nitride dielectric films of the novel capacitors of this invention ranged in thickness from 0.2 to 5 microns in thickness. The boron nitride films are very uniform and are continuously bonded to the substrate by the interlayer. Boron nitride films 0.5 micron thick deposited upon a 10 mil molybdenum and tantalum wire did not crack when bent at a

radius of 1/8 inch. The boron nitride films exhibited a dielectric strength of 200 volts DC per micron of thickness and 5000 volts DC per mil thickness at room temperature. A calculated capacitance of 50,000 micro micro farads per square inch for a 0.5 micron thick boron nitride film was exhibited. The boron nitride films are stable in air up to 800°C and can protect the substrate metal against oxidation. The boron nitride film is stable in most acids and alkalis including aqua regia, $HF-HNO_3$ and $NaOH$. Therefore, the novel capacitors can be used in high temperatures even in the presence or otherwise deleterious ambients. However, we have discovered that hot H_3PO_4 will attack the boron nitride film at a rapid rate such that novel selective etching techniques can be used in the construction of capacitors. Novel multilayer capacitors have also been described which are highly versatile and which permit very small devices to have very high capacitance values.

The boron nitride insulation films prepared by the above process have superior electrical characteristics, such as dielectric strength and resistivity, even at high temperature. The films are also strongly adherent to the substrate and are sufficiently flexible that coated wire may be used for substantially all conventional purposes. The substrate is chemically stable in a wide variety of corrosive media when coated by the boron nitride. Specifically, the boron nitride films are insoluble in and protect the substrate in the presence of H_2O , HCl (dilute and concentrate), HNO_3 (dilute and concentrate), H_2SO_4 (dilute and concentrate), aqua regia, $NaOH$, KOH (dilute and concentrate), *crystallite* mixtures, and HF (dilute and concentrate). The boron nitride films are stable in air up to about 700°C and protect the copper substrate from oxidation, but are unstable above about 800°C after 30 minutes. Negligible loss of boron nitride by evaporation occurs when the film is held at 900°C in a vacuum of 0.01 microns of mercury. From the above data relating to the flexibility, insulative properties and chemical stability at elevated temperatures, it will be evident that the strongly adherent, thin boron nitride films are highly useful in insulation in various adverse environments, and the thin insulation films result in significant savings in the space required for windings in motors, transformers and the like.

WHAT WE CLAIM IS:—

1. A process for manufacturing an electrical device including the steps of depositing a pure boron nitride film on a substrate and adhering it thereto by an interlayer of material formed on the substrate and depositing an electrode film on the boron nitride film.



preferably of a metal, such as molybdenum, that will not be attacked by the H_3PO_4 etchant for boron nitride, but which will be attacked by an etchant in which the boron nitride is stable, such as a solution of $HCl-HNO_3$.

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WHAT WE CLAIM IS:—

1. A process for manufacturing an electrical device including the steps of depositing a pure boron nitride film on a substrate and adhering it thereto by an interlayer of material formed on the substrate and depositing an electrode film on the boron nitride film.



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2. A process for manufacturing an electrical capacitor including the steps of forming a metal boride interlayer on a metal electrode by reacting boron with the metal electrode, depositing a boron nitride film on the interlayer, and depositing an electrode film on the boron nitride film.

3. A process for manufacturing an electrical capacitor including the steps defined in claim 2, wherein the metal boride interlayer is formed by heating the metal to a temperature in the range of about 700—1700°C in the presence of a boron halide, the boron nitride film is deposited by heating the metal to a temperature in the range of about 700—1700°C in the presence of reagents containing boron and nitrogen, and the electrode film is deposited by vapour phase condensation.

4. A process for manufacturing an electrical capacitor including the steps of, masking an area of a metal electrode, forming a metal boride interlayer on the unmasked area of the metal electrode by reacting boron with the metal electrode, depositing a boron nitride film on the interlayer, depositing a metallic electrode film on the boron nitride film, and removing the masking to make electrical contact with the metal electrode.

5. A process for manufacturing an electrical capacitor including the steps of, chemically bonding a boron nitride film to the surface of a metal foil by an interlayer, removing a portion of the boron nitride by applying hot phosphoric acid to permit electrical contact to be made with the metal foil, and depositing an electrode film on the boron nitride film.

6. A process for manufacturing an electrical capacitor including the steps of forming a first interlayer on a first metal electrode by reacting a reagent with the metal, adherently depositing a first boron nitride film on the first interlayer, adherently depositing a second metal electrode film on the first boron nitride film, forming a second interlayer on the second metal electrode film by reacting a reagent with the metal of the electrode film, adherently depositing a second boron nitride film on the second interlayer, and depositing a third metal electrode film on the second boron nitride film.

7. A process for manufacturing a multilayer electrical capacitor including the steps of, forming an interlayer on both sides of a metal foil substrate by reacting a reagent with the metal at a high temperature, depositing a boron nitride film on each of the interlayers, depositing metallic electrode films on each of the boron nitride films, selectively removing a portion of the edge of the metal foil such that the edges of the boron nitride films extend beyond the edges of the metal foil, selectively removing a portion of the edges of the boron nitride and metal electrode film to expose a portion of the edge of the metal foil, and attaching an electrical lead to the metal foil

and an electrical lead to the metallic electrode films.

8. A process for manufacturing a multilayer electrical capacitor including the steps defined in claim 7 wherein the metal foil is molybdenum, and the boron nitride films are removed by hot phosphoric acid.

9. An electrical device having a metal electrode, a boron nitride film chemically bonded to the metal electrode by a metal boride interlayer, and a metal film electrode attached to the boron nitride film.

10. An electrical device including at least a substrate, an interlayer and an electrode bonded together, wherein the electrode is comprised of a refractory metal base foil and the interlayer is essentially a refractory metal boride.

11. A process for depositing a strongly adherent, dense boron nitride film on a substrate including the steps of, producing an interlayer on the surface of the substrate by reacting a reagent with the substrate, depositing a film of boron nitride on the interlayer whereby the interlayer bonds the boron nitride film to the substrate.

12. A process for depositing a strongly adherent, dense boron nitride film on a substrate as claimed in claim 11 wherein the substrate includes a refractory metal and the interlayer includes a refractory metal boride.

13. A process for depositing a strongly adherent, dense boron nitride film on a substrate as claimed in claim 11 wherein the substrate includes molybdenum and the interlayer includes a boride of molybdenum.

14. A process for depositing a strongly adherent, dense boron nitride film on a metal substrate as claimed in claim 11 wherein the metal substrate is a ferrous base alloy and the interlayer is a boride of at least one of the constituents of the alloy.

15. A process for depositing a strongly adherent, dense boron nitride film on a metal substrate including the steps of: producing an interlayer on the surface of the metal substrate by reacting boron with the metal to produce a metal boride interlayer, and depositing a film of boron nitride on the interlayer by vapour phase deposition whereby the interlayer bonds the boron nitride to the metal substrate.

16. A process for depositing a strongly adherent, dense boron nitride film on a metal substrate including the steps of: forming a metal boride interlayer on the metal by heating the metal substrate in a low pressure atmosphere in the presence of boron trichloride, and forming a boron nitride film on the interlayer by heating the metal substrate in a low pressure atmosphere in the presence of beta-trichloroborazole.

17. A process for depositing a strongly adherent, dense boron nitride film on a metal substrate including the steps of: placing the



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metal substrate in a reaction chamber and evacuating the chamber to a low pressure on the order of one micron of mercury, filling the chamber with a boron halide vapour to a pressure in the range from about 5 microns to about 500 microns of mercury and heating the substrate to a temperature in the range from about 700°C to about 1700°C for a short period of time to form a metal boride interlayer, evacuating the chamber to a low pressure of about one micron of mercury, filling the chamber with beta-trichloroborazole vapours to a pressure in the range from about 10 microns to about 20 millimeteres of mercury and heating the substrate to a temperature in the range from about 700°C to about 1700°C until a film of boron nitride of the desired thickness is deposited on the interlayer.

18. An article of manufacture including a metal article having a film of dense boron nitride bonded to a selected portion of the surface of the metal article by an interlayer of metal boride.

19. An article of manufacture including a metal article having a film of dense boron nitride bonded to a selected portion of the surface of the metal article by an interlayer of a compound of said metal.

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