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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Processes for Etching Boron Nitride

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:—

This invention relates to processes for etching boron nitrides and in particular to a method of selectively etching a boron nitride film overlying a substrate.

The specification of copending Application No. 50621/64 (Serial No. 1083522) describes a process for bonding thin boron nitride films to substrates in a strongly adherent manner. Such films are chemically stable in a wide variety of corrosive media. Specifically, boron nitride films are insoluble in H_2O, HCl (dilute and concentrate), HNO_3 (dilute and concentrate), H_2SO_4 (dilute and concentrate), aqua regia, NaOH, KOH (dilute and concentrate), cryolite mixtures, and HF (dilute and concentrate). Such 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 such a film was held at 900°C in a vacuum of 0.01 microns of mercury. Further, such boron nitride films have been found to be flexible, possess desirable electrically insulating properties and being chemically stable at elevated temperatures are very useful as insulation in various adverse environments. However in certain applications as in the manufacture of electrical components, e.g. microcircuits and capacitors, employing boron nitride films bonded to a substrate, it is desirable to be able to remove selected regions of the boron nitride film.

The present invention is based upon the discovery that despite the chemical stability of boron nitride in various corrosive media, as outlined above, it can be etched away using hot phosphoric acid. In a particular application of the invention to etching a boron nitride film overlying a substrate, hot phosphoric acid is applied to selected portions of the film to remove those portions of the film and expose selected portions of the substrate.

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

Figs. 1 and 3 are enlarged partial sections of capacitors incorporating boron nitride films, and

Figs. 2 and 4 are schematic sectional views illustrating the use of the present invention in making electrical connections to the electrodes of the capacitors illustrated in Figs. 1 and 3 respectively.

Despite the chemical stability of boron nitride in a range of corrosive media, we have discovered that it is subject to rapid attack by hot phosphoric acid. In a particular example, a first strip of molybdenum coated with a boron nitride film and a second, weighed, strip of uncoated molybdenum were placed in a solution of orthophosphoric acid (H_3PO_4) which had been boiled until bubbles ceased to come up, and which was at a temperature of approximately 295°C. The two strips were held in the H_3PO_4 solution for about five minutes and then removed and washed. The boron nitride film was removed from the first molybdenum strip and electrical conductance by point contact to the strip was good. The second, weighed, strip of uncoated molybdenum experienced no loss in weight indicating that molybdenum is stable in hot H_3PO_4.

[Price 4s. 6d.]

This selective etching of boron nitride by hot phosphoric acid can be usefully employed in the manufacture of electrical devices, e.g. capacitors, as will be described.

Fig. 1 shows a capacitor construction 10 having a metal, e.g. molybdenum, foil substrate 11 on opposite faces of which are formed molybdenum boride interlayers 12 and 14, boron nitride films 16 and 18 being deposited on the interlayers 12 and 14, respectively, which serve to strongly adhere the boron nitride films 16 and 18 to the substrate 11. This process is described in greater detail in the specification of copending Application No. 50621/64 (Serial No. 1083522). Metallic, e.g. gold film electrodes 20 and 22 are deposited, as by vapour condensation, on the boron nitride films to form the multilayer capacitor 10.

It will be appreciated that the capacitor construction 10 is paper thin and that making separate electrical contact with the electrodes creates a considerable problem, the solution of which can be assisted by use of the present invention, as will be described with reference to Fig. 2 which shows the capacitor with electrodes attached thereto. The capacitor shown in Fig. 2 includes a small piece of the composite material described with reference to Fig. 1 (like references being used in Fig. 2) cut to have a desired area and relatively square peripheral edges. One edge, 24 for example, is then dipped into a suitable etchant having a high concentration of HCl. The relatively thin gold film electrodes 20 and 22 are rapidly etched away relative to the rate at which the edge of the molybdenum substrate is attacked and are etched back to the points 26 and 28. The HCl content does not attack the boron nitride films 16 and 18 which are selectively etched back to points 30 and 32 using a solution of hot phosphoric acid prepared as previously described. A clip 34 is then connected to the exposed edge of the substrate 11 as by welding.

Another edge of the sandwich is then immersed in a suitable etchant which selectively attacks the molybdenum substrate 13 but does not affect the boron nitride films 16 or 18 or the gold film electrodes 20 and 22 so that the substrate 13 is removed back to point 36. For example, a solution of $HCl—HNO_3$ 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 20 and 22 will tend to hold the otherwise fragile boron nitride films 16 and 18 intact and the free edges of the films will tend to come together as illustrated in Fig. 2 to cover the edge of the substrate. Then a clip 38 can be crimped over the edge of the sandwich and preferably welded to the metal films 20 and 22. The boron nitride covering the edge of the substrate 13 ensures that the clip 38 does not contact the substrate. The capacitor can then be encapsulated in a suitable insulating material.

Another multilayer capacitor in the construction of which the present invention is utilised is indicated generally by the reference numeral 40 in Fig. 3. The capacitor 40 is manufactured by placing a metal, e.g. molybdenum, foil substrate 41, in a reaction chamber and successively depositing a metal boride interlayer 42 and a boron nitride film 44 on the substrate, as described in the specification of copending Application No. 50621/64 (Serial No. 1083522). A metal film electrode 46 is then deposited on the surface of the boron nitride film 44 preferably by conventional vacuum-evaporation and condensation techniques. The metal film electrode 46 should be so chosen that boron will react with the metal to form a metal boride interlayer; suitably molybdenum may be used for the electrode film. Then a second metal boride interlayer 48, a second boron nitride film 50 and a second metal film electrode 52 are successively deposited upon the metal film electrode 46. 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 54, a third boron nitride film 56 and a third metal film electrode 58. The second metal film electrode 52 may also be molybdenum, as illustrated, in which case the interlayer 54 would be molybdenum boride. However, it will be appreciated that other suitable refractory metals can be used.

Electrical contact can be made with the electrodes of the device 40 in the manner illustrated in the transverse cross-section of Fig. 4 by using selective etching techniques and utilising the present invention. The metal film electrodes are made 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 58 is first etched away by $HCl—HNO_3$ to expose the third boron nitride film 56 in both areas 60 and 62. During this step the third boron nitride layer 54 will protect the second metal film electrode 52. Next, the third boron nitride film 56 in the areas 60 and 62 is etched away using hot H_3PO_4 prepared in the manner previously described. Then the third metal boride interlayer 54 is etched away in the areas 60 and 62 to expose the second metal film electrode 52 over both areas. The second metal film electrode 52 and the second boron nitride film 50 can then be successively etched away in the area

60 to expose the first metal film electrode 46. The leads 64, 66, 68 and 70 can then be connected by some conventional technique such as welding and the capacitor encapsulated if desired by a suitable insulating material.

WHAT WE CLAIM IS:—

1. A method of etching boron nitride by applying hot phosphoric acid to the boron nitride.

2. A method of selectively etching boron nitride by applying hot phosphoric acid to selected portions of a boron nitride film overlying a substrate selectively to remove those portions of the film and expose the underlying portions of the substrate.

3. A method according to claim 1 or claim 2, in which the temperature of the phosphoric acid is about 295°C.

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