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(54) A METHOD FOR MANUFACTURING A COMPOSITE SINTERED STRUCTURE

(71) We, HITACHI LTD., of 1-5-1 Marunouchi, Chiyoda-ku, Tokyo, Japan, a Japanese Company, 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 method for manufacturing a composite sintered structure. More particularly, it relates to a method for manufacturing a composite sintered structure having a plurality of layers and for use in, e.g., an integrated semiconductor circuit device.

The manufacture of a composite sintered structure as stated above, has been generally performed as follows. Referring to Figure 1 of the accompanying drawings, conductor layers 20, 20' and 20'' of desired patterns are printed on the surfaces of substrates formed separately and made of a dielectric material, for example, green ceramic sheets 10, 10' and 10'', respectively. Holes 30 and 30' are formed at desired interconnection locations of the respective substrates and the holes filled with a conducting material. Subsequently, the substrates 10, 10' and 10'' are stacked one on the other into a laminated body so that the conducting layers 20, 20' and 20'' may have the desired interconnections.

Thereafter, the lamination or stack of substrates is heated at a temperature high enough to sinter the substrates and for a fixed period of time. Thus, a composite sintered structure such as a multi-layer interconnection substrate or a multi-layer interconnection package is completed.

With this known method, however, problems have arisen especially in the interconnections between the respective substrates. More specifically, when the conducting material is filled into the holes 30 and 30' which are provided in the desired portions

of the substrates 10, 10' and 10'' having the conducting layers, the holes may not be perfectly filled with the conductor material in some cases since they are very small. For this reason, disconnection etc. can occur due to an imperfect interconnection. The structure may therefore be of poor reliability. Although there is a technique by which, in order to eliminate the disadvantage, the conductor material is vacuum-absorbed into the holes, this procedure increases the number of working steps and may not be well suited to mass production.

Furthermore, with such a method, substrates equal in number to the multi-interconnection layers are required. In addition, a punch step for punching each substrate into a predetermined shape is included, which adds to the number of working steps. Also required is the step of hot-pressing the laminated substrates. In the hot-pressing step, unless the lamination is perfect, effects leading to non-standard articles, such as leakage due to inferior airtightness and unnecessary distortions of the substrates, both being attributable to instability of the lamination (insecurity of adhesion) are prone to occur. Besides, in the burning or sintering step, the ceramic sheet can undergo warping due to a distortion caused by the difference in the coefficient of shrinkage between the green ceramic sheet and the conducting layer. Furthermore, the bonding strength between the metallized conducting layer and the ceramic sheet can be reduced, leading for example to exfoliation. Accordingly, the process is comparatively complicated, and the yield is low. The cost is therefore high.

According to the present invention there is provided a method of making a composite sintered structure wherein a green ceramic insulating paste and a green

upon a green ceramic sheet, each paste forming at least one layer, and the sheet and pastes are sintered to form a unitary body, the green ceramic insulating paste 5 and the green ceramic sheet consisting of substantially the same powdered inorganic ceramic material and binder in substantially the same proportions and having substantially the same coefficient of shrinkage 10 upon sintering.

Suitably the paste layers are deposited by a printing process in the desired pattern. A layer of the green ceramic insulating paste will usually be deposited adjacent the green 15 ceramic sheet, preferably covering a major part of the sheet. Preferably each green paste has at least one area of contact with the sheet.

It may not be necessary for the shrinkage coefficient on sintering of the green conductor paste to be identical to that of the green sheet and green insulating paste. Preferably, the green ceramic conductor paste consists of powdered inorganic 20 ceramic material, conducting material in powder form and binder, the ceramic material and binder being substantially the same as those of the green ceramic insulating paste and the green ceramic sheet and 25 being in substantially the same proportions.

The coefficients of shrinkage on sintering of the green ceramic sheet and the printed paste layers are determined by their materials and mixing proportions. In consequence, if slip formed with the same 30 materials and mixing ratios and, furthermore, by the same mixing process, is used for the sheet and the pastes, control is facilitated and substantially equal coefficients of shrinkage are exhibited at the 35 sintering step at least in the case of the sheet and the insulating paste. By this means an excellent composite sintered structure may be provided, in which exfoliation, disconnection and other flaws due to difference in shrinkage are absent or 40 minimized. Multi-layer interconnections are facilitated and the manufacturing process can have high reliability.

Particular embodiments of the invention will now be described by way of example only with reference to the accompanying 45 drawings in which:—

Fig. 1 is a perspective exploded view of the respective sheets of the prior-art method 50 which has been described above;

Fig. 2 is a sectional view of a finished structure produced by a method within the 55 present invention; and

Figs. 3 and 4 are manufacturing process diagrams of respective embodiments of the 60 present invention.

The composite sintered structure or body of Fig. 2 consists of a ceramic sheet 1, a 65 plurality of insulating layers 4, 4', 4'',

4''', and a plurality of conductor layers 2, 2', 2'', the layers being applied on top of one another in patterns that provide for the desired interconnections between layers. It will be seen that the lowermost insulating layer 4 and the lowermost conducting layer 2 both contact the sheet 1. The sheet 1 is of generally greater thickness than 70 each layer.

In Fig. 3 the various blocks each signifying a step in the manufacture will be herein-after explained in detail: 75

(1) As an inorganic ceramic material, a mixture is prepared which consists of alumina (Al_2O_3) as the principal constituent 80 and mineralizers in powder form such as silica (SiO_2) and magnesia (MgO). The proportions are, for example, 91 weight % of Al_2O_3 , 6.8 weight % of SiO_2 and 2.2 weight % of MgO . As a binder to impart 85 a binding property to the mixture of inorganic ceramic material, Butvar (Registered mark of Monstano Co. for polyvinyl butyral) is added. The sintering temperature can be changed if desired by 90 varying the amounts of the mineralizing agents used. Generally, the amount of alumina may vary from 88 to 95% by weight of the inorganic ceramic material.

(2) The resulting mixture is agitated in a ball mill for about 30 minutes, thereby to obtain a powdered alumina mixture. 95

(3) As a solvent for Butvar, there is used a solvent adapted readily to aid the formation of the mixture into a sheet (i.e. a low-boiling solvent, for example, an azeotropic mixture consisting of 60 weight % of trichloro-ethylene, 23 weight % of butyl alcohol and 17 weight % of perchloro-ethylene). As a plasticizer for the green 105 ceramic material, there is used butylphthalyl butylglycolate. These materials are added and mixed, along with Butvar, into the alumina powder mixture in the proportions of 6 grams of Butvar, 38 grams of the low-boiling solvent and 2.8 grams of the plasticizer per 100 grams of ceramic 110 material (alumina + mineralizers).

(4) The resulting viscous mixture is sufficiently agitated in a ball mill for 3 115 hours, to obtain an alumina slip.

(5) The alumina slip is cast onto a film of a resin for example, a polyester known as Lumirror (Registered Trade Mark of Toyo-Rayon Co.) onto a film of Tetron (Regd. Trade Mark) or onto exfoliation paper. Thus, a slip sheet of a constant thickness (e.g. approximately 1.0 mm) and the desired shape is formed. Subsequently, the sheet-shaped slip is heated to volatilize the 125 low-boiling solvent, and to be dried into a green ceramic sheet 1.

The blocks (3') (4') (5') and (5'') of Fig. 3 signify the steps used in the production of the green ceramic insulating paste 130

Torr) to move the low-boiling solvent. Thus, a paste is obtained.

The paste produced by step (3') can be used as the insulating paste in that condition.

(3'') In order to produce the conductor paste, a powdery material of at least one refractory metal such as tungsten, molybdenum or titanium, is added and mixed into the above paste. The resistance of the conductor material is determined by the quantity of the metal additive or additives. Generally from 50 to 70% by weight of the conductor paste is made of the metal additives.

The insulating paste and the conductor paste are printed on the green ceramic sheet in the form of each single layer, or in the form of alternately laminated layers by, for example, the silk screen process. After the respective printing steps, the pastes are dried at 80°C.

The final laminated structure of the green ceramic sheet and the pastes is heated to between 1,450 to 1,650°C. in a reducing atmosphere of, for example, H₂ gas. The green lamination is sintered, and at the same time, the conducting paste is metalized.

In the composite sintered structure thus obtained (comprising the ceramic sheet and the insulating layer or layers and the metal layer or layers), the respective layers have been made of materials from the same pulverization batch, and hence, especially, the degrees of mixing are equal. In consequence, there is no major variation in sintering temperature of the materials. The coefficients of shrinkage are the same at least for the green sheet and the insulating layers and products with almost no distortion and high in bonding strength between the conductor and the substrate may be obtained.

In the above-described embodiments, the inter-connections of the wirings of the respective layers can be performed very easily, by the printing steps. In addition, the respective layers are formed by the printing of the ceramic paste and the conductor paste, and the thicknesses of the layers can be controlled to be sufficiently thin. The thickness of the composite sintered structure of the multi-layer inter-connections can therefore be made significantly smaller than the structures obtained with the prior-art method.

Furthermore, as described, the materials are selected and the mixing proportions are set so that no difference may occur in the shrinkage of the green ceramic sheet and at least the insulating layer at the sintering, the insulating paste being identical in coefficient of shrinkage with the green sheet. An excellent composite sintered structure

free from exfoliation, disconnection and warping due to the different shrinkage can therefore be obtained.

The method for manufacturing a composite sintered structure described may provide a saving in the labour required, and the structure may be made extremely thin, thereby eliminating waste of material. The resultant small-sized composite sintered structure can have a sealed construction which may be free from leakage due to imperfect airtightness, unnecessary distortions of substrates, etc. and which has a comparatively high endurance.

WHAT WE CLAIM IS:—

1. A method of making a composite sintered structure wherein a green ceramic insulating paste and a green ceramic conductor paste are deposited upon a green ceramic sheet, each paste forming at least one layer, and the sheet and pastes are sintered to form a unitary body, the green ceramic insulating paste and the green ceramic sheet consisting of substantially the same powdered inorganic ceramic material and binder in substantially the same proportions and having substantially the same coefficient of shrinkage upon sintering.
2. A method according to claim 1 wherein the green sheet generally has substantially greater thickness than each of said layers.
3. A method according to claim 1 or claim 2 wherein each green paste has at least one area of contact with the sheet.
4. A method according to any one of claims 1 to 3 wherein the green ceramic conductor paste consists of powdered inorganic ceramic material, conducting material in powder form and binder, the ceramic material and binder being substantially the same as those of the green ceramic insulating paste and the green ceramic sheet and being in substantially the same proportions.
5. A method according to claim 4 wherein the green ceramic sheet and both the said pastes are made from the same mixing batch of inorganic ceramic material and binder.
6. A method according to any of the preceding claims wherein the inorganic ceramic material of at least the green sheet and the insulating paste contains alumina as the principal ingredient and mineralizers.
7. A method according to claim 6 wherein the said inorganic ceramic material contains from 88 to 95 weight percent of alumina, the balance consisting of mineralizers.
8. A method according to claim 7 wherein the said inorganic ceramic material contains 91 weight percent Al₂O₃, 6.8 weight percent of SiO₂, and 2.2 weight per-



as well as the conductor paste.

(3') Into the powdered alumina mixture produced at the step (2), there are added a solvent which makes the resultant paste easy to print i.e. a high-boiling one, for example, butyl carbitol acetate as a solvent for Butvar, and a plasticizer for the green ceramic material which is the same as used in step (3). The mixing proportions are 2.8 grams of the plasticizer and 38 grams of the high-boiling solvent per 106 grams of the alumina powder mixture (which contains 6 grams of Butvar).

(4') The resulting viscous mixture is sufficiently agitated in a ball mill for 3 hours, thereby to produce an alumina slip. The slip is divided into two parts.

(5') One of the alumina slip parts is made into a green ceramic paste for the insulating layers 4.

(5'') Conducting powder, for example, a powdery material composed of at least one refractory metal such as tungsten molybdenum or titanium, is added and mixed into the other alumina slip part. In this manner, a conductor paste is produced. At this stage, the resistance of the conductor material can be determined by controlling the quantity of the metal additive or additives.

The conductor paste and the insulating paste are printed on the green ceramic sheet each in the form of a single layer, or in the form of alternately laminated layers by, for example, the silk screen process. After each printing step, the paste is dried at 80°C.

The lamination consisting of the green ceramic sheet and the printed pastes is heated to the range 1,450 to 1,650°C. in a reducing atmosphere of, e.g. a gaseous mixture of $N_2 + H_2$ or in an inert atmosphere of, e.g. N_2 gas so that the green lamination is sintered and the conductor paste is metallized.

In the embodiment of Fig. 3, when forming the green ceramic sheet, a solvent adapted to be easily sheeted or spread out (the low-boiling solvent) is added into the alumina mixture. The reason for the use of the low-boiling solvent is that it volatilizes at the normal temperature, which is convenient for the sheeting step where suitable a high-boiling solvent may alternatively be employed. The plasticizer is simultaneously added in this embodiment in order to facilitate handling of the sheet. When using the high-boiling solvent, however, the separate addition of plasticizer may be omitted if the high-boiling solvent, being difficult to volatilize away at normal temperature, partially remains and acts as the plasticizer.

When forming the pastes, a solvent adapted to be readily printed (the high-

boiling solvent) is added to the alumina mixture. This is because the pasty state is held by the presence of the high-boiling solvent, and so clogging of the screen of a screen printing device during printing is reduced or prevented. Accordingly, if improved printing means which avoids the problem is employed, a low-boiling solvent may alternatively be used.

Another embodiment will now be described with reference to the steps illustrated by the boxes of Fig. 4.

(1) As an inorganic ceramic material, there is prepared a mixture which consists of alumina (Al_2O_3) as the principal constituent and powdery mineralizers such as silica (SiO_2) and magnesio (MgO), the mixing proportions being for example, 91 weight % of Al_2O_3 , 6.8 weight % of SiO_2 and 2.2 weight % of MgO . The sintering temperature can be suitably changed by varying the amounts of the mineralizers.

Butvar is used as a binder. A low-boiling solvent for example, an azeotropic mixture consisting of 60 weight % of trichloroethylene, 23 weight % of butyl alcohol and 17 weight % of perchloro-ethylene) is prepared as a solvent for Butvar. Butylphthalyl butylglycolate is used as a plasticizer for the green ceramic material. 6 grams of Butvar, 38 grams of the low-boiling solvents and 2.8 grams of the plastizer are added and mixed into 100 grams of a ceramic material (alumina + mineralizers).

(2) The resulting mixture is sufficiently agitated in a ball mill for 3 hours, to obtain an alumina slip.

(3) The alumina slip is cast onto a film of a resin, for example, Lumirror or onto exfoliation paper, to form a green ceramic sheet having a constant thickness (about 1.0 mm) and a desired shape. The green ceramic sheet is dried by heating to volatilize away the low-boiling solvent.

(3') When using the alumina slip for the pastes, if it is not modified, the low-boiling solvent evaporates at the normal temperature and rapidly solidifies. As a result, clogging of the screen occurs when printing, and cleaning of the screen after printing is difficult. Therefore, the low-boiling solvent is in a sense replaced by a high-boiling solvent, i.e. the low-boiling solvent is used to prepare the slip for the sheet and the higher boiling point solvent is added to the slip containing the low-boiling point solvent. For example, 120 grams of butyl carbitol acetate and 0.2 grams of silicone oil as a deforming agent (Toray Silicone SH 5520, trade name of Toray Co.) are added to 500 grams of the alumina slip. The alumina slip with the additives is subjected to vacuum heating (at a temperature of 80-90°C. and under a pressure of 10^{-3}



Torr) to move the low-boiling solvent. Thus, a paste is obtained.

The paste produced by step (3') can be used as the insulating paste in that condition.

(3'') In order to produce the conductor paste, a powdery material of at least one refractory metal such as tungsten, molybdenum or titanium, is added and mixed into the above paste. The resistance of the conductor material is determined by the quantity of the metal additive or additives. Generally from 50 to 70% by weight of the conductor paste is made of the metal additives.

The insulating paste and the conductor paste are printed on the green ceramic sheet in the form of each single layer, or in the form of alternately laminated layers by, for example, the silk screen process. After the respective printing steps, the pastes are dried at 80°C.

The final laminated structure of the green ceramic sheet and the pastes is heated to between 1,450 to 1,650°C. in a reducing atmosphere of, for example, H₂ gas. The green lamination is sintered, and at the same time, the conducting paste is metalized.

In the composite sintered structure thus obtained (comprising the ceramic sheet and the insulating layer or layers and the metal layer or layers), the respective layers have been made of materials from the same pulverization batch, and hence, especially, the degrees of mixing are equal. In consequence, there is no major variation in sintering temperature of the materials. The coefficients of shrinkage are the same at least for the green sheet and the insulating layers and products with almost no distortion and high in bonding strength between the conductor and the substrate may be obtained.

In the above-described embodiments, the inter-connections of the wirings of the respective layers can be performed very easily, by the printing steps. In addition, the respective layers are formed by the printing of the ceramic paste and the conductor paste, and the thicknesses of the layers can be controlled to be sufficiently thin. The thickness of the composite sintered structure of the multi-layer inter-connections can therefore be made significantly smaller than the structures obtained with the prior-art method.

Furthermore, as described, the materials are selected and the mixing proportions are set so that no difference may occur in the shrinkage of the green ceramic sheet and at least the insulating layer at the sintering, the insulating paste being identical in coefficient of shrinkage with the green sheet.

An excellent composite sintered structure

free from exfoliation, disconnection and warping due to the different shrinkage can therefore be obtained.

The method for manufacturing a composite sintered structure described may provide a saving in the labour required, and the structure may be made extremely thin, thereby eliminating waste of material. The resultant small-sized composite sintered structure can have a sealed construction which may be free from leakage due to imperfect airtightness, unnecessary distortions of substrates, etc. and which has a comparatively high endurance.

WHAT WE CLAIM IS:—

1. A method of making a composite sintered structure wherein a green ceramic insulating paste and a green ceramic conductor paste are deposited upon a green ceramic sheet, each paste forming at least one layer, and the sheet and pastes are sintered to form a unitary body, the green ceramic insulating paste and the green ceramic sheet consisting of substantially the same powdered inorganic ceramic material and binder in substantially the same proportions and having substantially the same coefficient of shrinkage upon sintering.

2. A method according to claim 1 wherein the green sheet generally has substantially greater thickness than each of said layers.

3. A method according to claim 1 or claim 2 wherein each green paste has at least one area of contact with the sheet.

4. A method according to any one of claims 1 to 3 wherein the green ceramic conductor paste consists of powdered inorganic ceramic material, conducting material in powder form and binder, the ceramic material and binder being substantially the same as those of the green ceramic insulating paste and the green ceramic sheet and being in substantially the same proportions.

5. A method according to claim 4 wherein the green ceramic sheet and both the said pastes are made from the same mixing batch of inorganic ceramic material and binder.

6. A method according to any of the preceding claims wherein the inorganic ceramic material of at least the green sheet and the insulating paste contains alumina as the principal ingredient and mineralizers.

7. A method according to claim 6 wherein the said inorganic ceramic material contains from 88 to 95 weight percent of alumina, the balance consisting of mineralizers.

8. A method according to claim 7 wherein the said inorganic ceramic material contains 91 weight percent Al₂O₃, 6.8 weight percent of SiO₂, and 2.2 weight per-



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cent of MgO.

9. A method according to any one of the preceding claims wherein the binder is polyvinyl butyral.
10. A method according to any one of the preceding claims wherein the green sheet and pastes are formed from mixtures also containing a solvent for the binder and a plasticizer.
11. A method according to claim 10 wherein the solvent in at least the mixture for the green sheet is a low-boiling solvent.
12. A method according to any one of the preceding claims wherein the mixtures used to produce the green pastes contain a high-boiling solvent for the binder.
13. A method according to any one of the preceding claims wherein the conductor paste contains a conducting powder.
14. A method according to claim 13 wherein the conducting powder is at least one refractory metal in powdered form.
15. A method according to claim 14 wherein the metal is one or more of tungsten, molybdenum and titanium.
16. A method according to any one of

claims 13 to 15 wherein the conductor paste contains from 50 to 70 weight percent of the conducting powder.

17. A method according to any one of the preceding claims wherein the green ceramic sheet and the pastes are sintered in the range 1,450°C to 1,650°C in a reducing or an inert atmosphere.

18. A method for manufacturing a composite sintered structure substantially as herein described with reference to and as illustrated in any one of Figs. 2 to 4 of the accompanying drawings.

19. A composite sintered structure whenever prepared by a method according to any one of claims 1 to 18.

20. A composite sintered structure according to claim 19 wherein there are a plurality of conducting layers and at least one area of contact between different conducting layers.

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