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TITLE OF THE INVENTION

Metal Thin Film having Excellent Transferability and
Method of Preparing the Same

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a metal thin film
which has excellent transferability, and a method of
preparing the same.

10 A metal thin film obtained according to the present
invention is so transferred that the same is applicable to
a circuit which is provided on a substrate; an electrode
for an electronic component, a display metallic foil or
the like, for example.

Description of the Background Art

15 Japanese Patent Laying-Open No. 1-42809 (1989)
discloses a transfer technique which is employed for
forming electrodes for an electronic component, more
specifically, internal electrodes for a multilayer ceramic
capacitor, for example. Such a transfer technique is
20 evaluated as a technique which is effective for forming
thin internal electrodes.

In more detail, a thin-film-forming method such as
vapour deposition or sputtering is known as a method of
forming thin internal electrodes, i.e., metal thin films.
25 While a plurality of unfired ceramic green sheets are

laminated in order to prepare a multilayer ceramic capacitor, internal electrodes, which are provided between adjacent ones of the ceramic green sheets, must be formed in advance of lamination. However, it is difficult to
5 directly form metal thin films on the ceramic green sheets, which are mechanically weak and hard to handle, by the aforementioned thin-film-forming method. In the first place, therefore, thin films for defining internal electrodes are formed on handleable films which are
10 different from ceramic green sheets, and then transferred onto ceramic green sheets, so that it is easy or possible to form the metal thin films on the ceramic green sheets.

Thus, the internal electrodes are formed by metal thin films through a transfer technique, so that it is
15 possible to reduce the dimensions, particularly the thickness, of the as-formed multilayer ceramic capacitor. In addition, it is also possible to further homogenize the thickness in the laminated state along the direction of extension of the ceramic green sheets. Due to the latter
20 property, it is possible to reduce a possibility of inconvenience such as delamination after firing of the laminated ceramic green sheets.

While the transfer technique enables formation of internal electrodes of metal thin films which provide some
25 advantages in relation to a multilayer ceramic capacitor,



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it is desirable that each metal thin film is completely transferred onto a target surface with excellent transferability, in order to carry out the transfer technique. If the metal thin film is not completely transferred with a desired pattern by the transfer technique which is employed for forming an internal electrode for a multilayer ceramic capacitor, for example, the as-formed multilayer ceramic capacitor is rendered defective, as a matter of course.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a metal thin film having excellent transferability and a method of preparing the same.

The metal thin film according to the present invention is provided with at least two layers, including a first metal layer which is formed on a film and a second metal layer which is formed above the first metal layer. The first metal layer is formed by vapour deposition, while the second metal layer is formed by wet plating such as electroplating or electroless plating.

Metals for forming the first and second metal layers may be different from or identical to each other.

The first metal layer is formed of nickel, copper or silver, for example. The second metal layer is formed of nickel, copper or palladium, for example.

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The film employed for forming the metal layers must have flexibility and heat resistance, as well as sufficient resistance against vapour deposition, wet plating and patterning with photolithography or the like. Such a film is prepared from a resin film of polyethylene terephthalate etc., or a metallic foil of nickel, copper aluminium or the like.

The metal thin film according to the present invention is prepared with excellent transferability, to be transferred onto a target of a ceramic green sheet, a ceramic material, a resin material, a metal or the like. As to transfer conditions, the metal thin film is first brought into contact with the target, and then transferred thereto under a pressure of 10 to 500 kg/cm² at a temperature of 60 to 95°C, for example by so-called hot stamping.

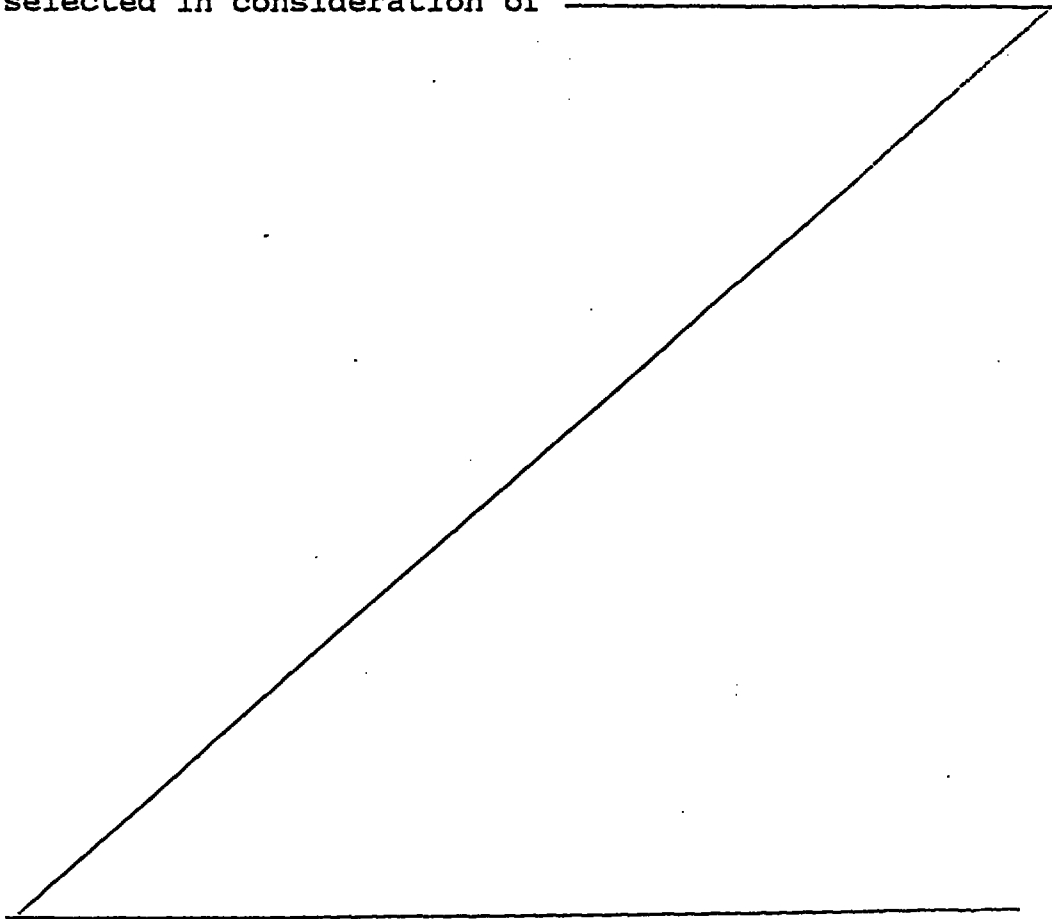
The present invention is based on the recognition that a metal thin film which is formed on a carrier film by vapour deposition generally has relatively weak adhesion with respect to the carrier film, i.e., it has excellent transferability.

However, easiness of vapour deposition for forming a metal thin film depends on the type of metal used. Further, transferability of a metal thin film which is formed by vapour deposition also depends on the type of metal used. In order to attain the object of the present invention, therefore, it is necessary to prepare the material for the thin film, which is formed on a carrier film by vapour deposition, from a metal which is excellent in transferability and easy to deposit. However, a metal selected in consideration of easiness in vapour deposition and transferability is not necessarily suitable as an electrode material for a target electronic component



or the like. When a metal layer is formed only by vapour deposition along its overall thickness, further, a peel surface of the film is thermally denatured in the vapour deposition process, to require
5 high peel strength or cause difficulty in peeling. Further, the film is warped by residual stress of the metal layer which is obtained by vapour deposition. In addition, a long time is required for forming the metal layer due to a low vapour deposition rate,
10 leading to increase in manufacturing cost.

According to the present invention, therefore, the first metal layer is formed of a metal which is selected in consideration of easiness in vapour deposition and transferability, while the second metal
15 layer is formed above the first metal layer to compensate for properties which are insufficient in the metal forming the first metal layer. The second metal layer can be formed of an optimum metal which is selected in consideration of _____





properties required for an electrode for a target electronic component or the like, since it is not necessary to consider easiness in vapour deposition and transferability. Further, the second metal layer also
5 compensates for the thickness of the first metal layer which is formed by vapor deposition in addition to compensating for insufficient properties of the first metal layer, to easily attain a thickness required for the overall metal thin film to be transferred. Therefore, the
10 first and second metal layers may be formed of either different or identical metals.

According to the present invention, further, the second metal layer is formed by wet plating such as electroplating or electroless plating. When the second
15 metal layer is formed above the first metal layer by wet plating, adhesion of the first metal layer with respect to the film is not increased as compared with a case of forming a metal layer only by vapour deposition along its overall thickness.

20 Thus, according to the present invention, the metal thin film is provided with at least two layers including first and second metal layers, so that the first metal layer is adapted to provide transferability while the second metal layer is adapted to provide properties which
25 are required for an electrode for a target electronic



component or the like. Therefore, it is easy to satisfy both transferability and other desired properties over the entire metal thin film. For example, a metal thin film having excellent transferability can be formed by a metal, which has not been suitable for transfer in general, to widen the range of metals that can be subjected to transfer, while it is also possible to widen the range of application of the transferable metal thin film.

Since it is easy to pattern a metal thin film which is formed on a film by photoetching, for example, a metal thin film according to the present invention can be advantageously applied as an electrode for an electronic component, an internal or external conductor for a multilayer substrate, a conductor which is provided on a circuit board, a display metallic foil, or the like.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view showing an embodiment of the present invention; and

Fig. 2 is a sectional view showing another embodiment of the present invention.

DESCRIPTION OF THE EMBODIMENTS

The following Experimental Examples were made according to the present invention:

Experimental Example 1

5 Experimental Example 1 was adapted to prepare a transfer metallic foil.

A film 1 was first prepared as shown in Fig. 1. This film 1 was prepared from polyethylene terephthalate, which is not deformed even under a temperature of about 100°C,
10 and coated with silicon in order to further improve the transferability of a metal thin film to be formed.

Then, a nickel deposition film 2 was formed on the film 1, as shown in Fig. 1. This nickel deposition film 2 was formed by electron beam heating with an acceleration
15 voltage of 10 kV under an atmosphere pressure of not more than 5×10^{-4} Torr. The as-formed nickel deposition film 2 was 0.1 μm in thickness (comparative sample 1).

Then, a nickel plating film 3 was formed on another nickel deposition film 2 by electroplating, as shown in
20 Fig. 1. The electroplating step was carried out with a current density of 1 A/dm² in a plating bath of sulfonamino acid, while setting the nickel deposition film 2 and a nickel plate on minus and plus sides respectively. Such plating was performed for 3 minutes, to obtain the
25 nickel plating film 3 of 1 μm in thickness (inventive



sample 1).

Then, a nickel plating film 3 was formed on still another nickel deposition film 2 by electroless plating, in place of the aforementioned electroplating, as shown in Fig. 1. The electroless plating step was carried out in an alkaline hydrazine bath at a liquid temperature of 80°C. Such plating was performed for 4 minutes, to obtain the nickel plating film 3 of 1 μ m in thickness (inventive sample 2).

The aforementioned comparative sample 1 and the inventive samples 1 and 2 were subjected to evaluation of transferability onto paper and plastic surfaces. First, the surfaces of the metal thin films, i.e., those of the nickel deposition film 2 in the comparative sample 1 and the nickel plating films 3 in the inventive samples 1 and 2, were coated with adhesive agents. Then, the metal thin films were transferred to the paper and plastic surfaces by hot stamping, with application of a pressure of 100 kg/cm² for 10 seconds.

According to the comparative sample 1, the metal thin film, i.e., the nickel deposition film 2, was transferred onto the paper and plastic surfaces when the hot stamping temperature was 100°C. In the inventive samples 1 and 2, on the other hand, it was possible to transfer the metal thin films, i.e., the nickel deposition films 2 and the



nickel plating films 3, onto the paper and plastic surfaces at a temperature of 80°C.

In the aforementioned Experimental Example 1, similar results were obtained also when gold, silver and copper
5 were employed in place of nickel. Further, similar results were obtained also when at least two layers were prepared from such metals.

Experimental Example 2

As shown in Fig. 2, a film 4 was first prepared from
10 the same material as the film 1 employed in Experimental Example 1.

Then, a copper deposition film 5 of 0.1 μm in thickness was formed on the film 4 by vapour deposition under the same conditions as Experimental Example 1
15 (comparative sample 2).

Then, a nickel plating film 6 of 1 μm in thickness was formed on another copper deposition film 5 by electroplating under the same conditions as Experimental Example 1 (inventive sample 3).

20 In addition, a nickel plating film 6 of 1 μm in thickness was formed on still another copper deposition film 5 by electroless plating, in place of the aforementioned electroplating, under the same conditions as Experimental Example 1 (inventive sample 4).

25 In order to evaluate transferability of the



comparative sample 2 and the inventive samples 3 and 4,
the following experiment was performed:

A slurry was prepared from a nonreducing dielectric
ceramic material which was mainly composed of barium
5 titanate. The surfaces of the metal films, i.e., those of
the copper deposition film 5 in the comparative sample 2
and the nickel plating films 6 in the inventive samples 3
and 4, were coated with this slurry and dried to form
ceramic green sheets 7, which were then peeled. In the
10 comparative sample 2, the copper deposition film 5 was not
in the least separated from the film 4, although the
ceramic green sheet 7 was peeled. In the inventive
samples 3 and 4, on the other hand, the copper deposition
films 5 and the nickel plating films 6 were separated from
15 the films 4 upon peeling of the ceramic green sheets 7.

Then, the nickel plating films 6 of the inventive
samples 3 and 4 were coated with photoresist films, and
thereafter the metal thin films, i.e., the copper
deposition films 5 and the nickel plating films 6, were
20 patterned to form internal electrodes for multilayer
ceramic capacitors by photoetching.

Then, ceramic green sheets 7 of 10 to 15 μm in
thickness were formed on the surfaces of the films 4,
which were provided with the metal thin films, by a doctor
25 blade coater. The ceramic green sheets 7 were formed of

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the aforementioned slurry of a nonreducing dielectric ceramic material.

Then, a plurality of such ceramic green sheets 7 were stacked with thermocompression bonding applied to every stack, and
5 the films 4 were peeled after every thermocompression bonding. In this case, the metal thin films were completely separated from the films 4.

Each of the as-formed laminates were cut in dimensions for defining a single multilayer ceramic
10 capacitor, fired and provided with external electrodes, thereby forming a multilayer ceramic capacitor.

The as-formed multilayer ceramic capacitor was smaller in thickness as compared with a conventional typical multilayer ceramic capacitor whose internal
15 electrodes were formed by screen printing of metal paste, and its thickness was further homogeneous along the direction of extension of the ceramic sheets. In addition, no deterioration of electric characteristics, such as reduction of capacitance, was observed since the
20 internal electrodes exhibited no defects such as pores.

Experimental Example 3

A film 1 was prepared in a similar manner to Experimental Example 1.

Then, a copper deposition film 2 of 1 μm in thickness
25 was formed on the film 1 by vapour deposition as shown in



Fig. 1, under the same conditions as Experimental Example 1 (comparative sample 3).

Also, a copper deposition film 2 of 0.1 μm in thickness was formed on another film 1 by vapour deposition as shown in Fig. 1, and a copper plating film 3 of 1 μm in thickness was formed on the copper deposition film 2 by electroplating under the same conditions as Experimental Example 1 (inventive sample 5).

Then, a copper plating film 3 of 1 μm in thickness was formed on still another copper deposition film 2 by electroless plating in place of the aforementioned electroplating, under the same conditions as Experimental Example 1 (inventive sample 6).

In order to evaluate transferability of the comparative sample 3 and the inventive samples 5 and 6, the following experiment was performed:

A pair of 2 cm-square plates were prepared to hold each of the comparative sample 3 and the inventive samples 5 and 6, and contact surfaces therebetween were fixed to each other with an adhesive agent. In this case, the plates were outwardly pulled to examine strength required for peeling the copper deposition film 2 from the film 1. The comparative sample 3 required peel strength of 3000 g, while the inventive samples 5 and 6 required 2000 g respectively.



Further, it was difficult to pattern the comparative sample 3 by photoetching, since the film 1 was extremely warped and it was difficult to obtain a flat surface.

Experimental Example 4

5 A film 1 was prepared in a similar manner to Experimental Example 1.

Then, a nickel deposition film 2 of 1 μ m in thickness was formed on the film 1 by vapour deposition as shown in Fig. 1, under the same conditions as Experimental Example
10 1 (comparative sample 4).

Also, a nickel deposition film 2 of 0.1 μ m in thickness was formed on another film 1 by vapour deposition as shown in Fig. 1, and a nickel plating film of 1 μ m in thickness was formed on the nickel deposition
15 film 2 by electroplating under the same conditions as Experimental Example 1 (inventive sample 7).

Then, a nickel plating film 3 of 1 μ m in thickness was formed on still another nickel deposition film 2 by electroless plating, in place of the aforementioned
20 electroplating, under the same conditions as Experimental Example 1 (inventive sample 8).

The comparative sample 4 and the inventive samples 7 and 8 were subjected to evaluation of transferability
25 similarly to Experimental Example 1. In the comparative

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sample 4, it was impossible to transfer the metal thin film even if hot stamping was performed at a temperature of 100°C. Further, it was difficult to pattern the comparative sample 4 by photoetching since the nickel deposition film 2 was extremely cracked and the film 1 was so warped that it was difficult to obtain a flat surface. In the inventive samples 7 and 8, on the other hand, it was possible to transfer the metal thin films, i.e., the nickel deposition films 2 and the nickel plating films 3, onto paper and plastic surfaces at a temperature of 80°C.

While the present invention has been described in relation to Experimental Examples 1 to 4, the first and second metal layers may be prepared from arbitrary metals.

The second metal layer may not necessarily be brought into contact with the first metal layer. For example, at least a single third metal layer may be provided between the first and second metal layers. In this case, the third metal layer may be formed by a method such as sputtering, electroplating, electroless plating or the like.

The film for forming the first metal layer, which is prepared from resin, for example, may not inevitably be subjected to treatment for improving transferability, such as the aforementioned silicon coating. When the film itself is formed of a material which essentially has small



adhesion with respect to a metal, it is not necessary to perform surface treatment for improving transferability.

In addition to the aforementioned Examples, it is possible to form the following substance by properly
5 selecting materials for the first and second metal layers:

A first metal layer which is prepared from copper and a second metal layer which is prepared from nickel are transferred onto a ceramic green sheet for a
semiconducting ceramic capacitor. A plurality of such
10 ceramic green sheets are laminated and then fired so that the same are vitrified. Thereafter re-oxidation treatment is performed to diffuse copper into the ceramic material and convert grain boundaries of the semiconducting ceramic material into insulator states, thereby obtaining an intergranular-
15 insulated multilayer ceramic capacitor.

Alternatively, a first metal layer of aluminium second metal layer of copper and a third metal layer of aluminium may be transferred onto a ceramic green sheet. A plurality of such ceramic green sheets are laminated and
20 then fired, so that the aluminium layers are converted to Al_2O_3 layers, thereby preventing diffusion of copper. Such a technique is so applied to preparation of a multilayer ceramic capacitor as to prevent the ceramic layers from diffusion of copper for forming internal electrodes.
25 Thus, it is possible to prepare a multilayer ceramic

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capacitor which has small dispersion of characteristics, particularly capacitance. In this case, the second metal layer may be formed of nickel in place of copper, to attain a similar effect.

5 The present invention is advantageously applicable to forming electrodes for an electronic component, more specifically, internal electrodes for a multilayer ceramic capacitor. For example, first, a capacitor can be obtained by the steps of transferring metal thin films
10 onto ceramic sheets, and stacking the ceramic sheets. Secondly, a capacitor can be obtained by the steps of transferring metal thin films onto a ceramic block of a plurality of stacked ceramic sheets, further stacking a ceramic sheet on the ceramic block, transferring metal
15 thin films onto the ceramic sheet, and repeating the last two steps. Thirdly, a capacitor can be obtained by the steps of forming a metal thin film on a film, forming a ceramic sheet on the surface of the film, which is provided with the metal thin film, peeling the ceramic
20 sheet together with the metal thin film from the film, and stacking such peeled ceramic sheets. Fourthly, a capacitor can be obtained by the steps of forming a metal thin film on a film, forming a first ceramic sheet on the surface of the film, which is provided with the metal thin
25 film, stacking the first ceramic sheet on a second ceramic

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sheet, and peeling the film from the first ceramic sheet.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not
5 to be taken by way of limitation, the scope of the present invention being limited only by the terms of the appended claims.



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CLAIMS:

1. A metal thin film having excellent transferability, said film comprising:
a first metal layer formed by vapour deposition;
5 and
a second metal layer formed on said first metal layer by wet plating.
2. A metal thin film in accordance with claim 1, wherein said wet plating is electroplating.
- 10 3. A metal thin film in accordance with claim 1, wherein said wet plating is electroless plating.
4. A metal thin film in accordance with claim 1 or 2 or 3, wherein said first and second metal layers are formed of different metals.
- 15 5. A metal thin film in accordance with claim 1 or 2 or 3 wherein said first and second metal layers are formed of the same type of metals.
6. A method of preparing a metal thin film having excellent transferability, said method comprising the
20 steps of:

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forming a first metal layer by vapour deposition;
and

forming a second metal layer on said first metal
layer by wet plating.

5 7. A method of preparing a metal thin film in
accordance with claim 6, wherein said wet plating is
electroplating.

8. A method of preparing a metal thin film in
accordance with claim 6, wherein said wet plating is
10 electroless plating.

9. A method of manufacturing a ceramic electronic
component comprising a ceramic sheet and an electrode
formed on said ceramic sheet, said method comprising:

forming a first metal layer on a carrier by
15 vapour deposition;

forming a second metal layer above said first
metal layer by wet plating; and

transferring said first and second metal layers
onto a ceramic sheet.

20 10. An electronic component including a metal thin
film as claimed in any of claims 1 to 5, or a metal
thin film manufactured by a method as claimed in any

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of claims 6 to 8.

11. An electronic component as claimed in claim 10
and comprising a ceramic sheet and one or more said
metal thin films.

5 12. An electronic component as claimed in claim 11
and comprising a ceramic capacitor.

13. An electronic component as claimed in claim 12
and comprising a multilayer ceramic capacitor
comprising a plurality of ceramic sheets and said thin
10 metal films.

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ABSTRACT OF THE DISCLOSURE

A metal thin film having excellent transferability is provided in order to facilitate formation of an internal electrode for a multilayer ceramic capacitor, for example, by a technique of transferring a metal thin film. A first metal layer (2) of nickel or copper is formed on a carrier film (1) by vapour deposition, and then a second metal layer (3) of nickel or copper is formed thereon by wet plating such as electroplating or electroless plating, thereby providing a metal thin film comprising the first and second metal layers (2 and 3) which can readily be transferred.

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FIG. 1.

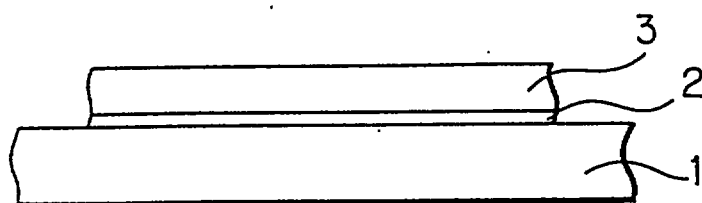
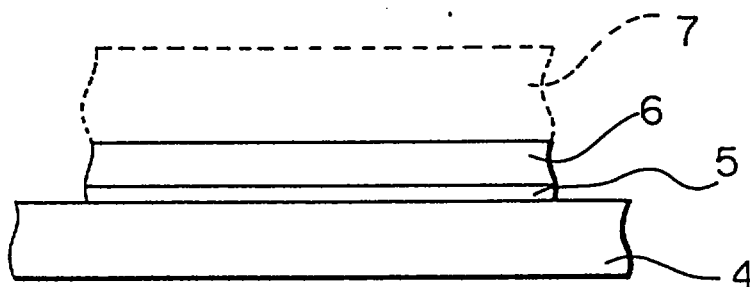


FIG. 2



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TITLE OF THE INVENTION

Metal Thin Film having Excellent Transferability and
Method of Preparing the Same

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a metal thin film which has excellent transferability, and a method of preparing the same.

A metal thin film obtained according to the present invention is so transferred that the same is applicable to a circuit which is provided on a substrate, an electrode for an electronic component, a display metallic foil or the like, for example.

Description of the Background Art

Japanese Patent Laying-Open No. 1-42809 (1989) discloses a transfer technique which is employed for forming electrodes for an electronic component, more specifically, internal electrodes for a multilayer ceramic capacitor, for example. Such a transfer technique is evaluated as a technique which is effective for forming thin internal electrodes.

In more detail, a thin-film-forming method such as vapour deposition or sputtering is known as a method of forming thin internal electrodes, i.e., metal thin films.

While a plurality of unfired ceramic green sheets are

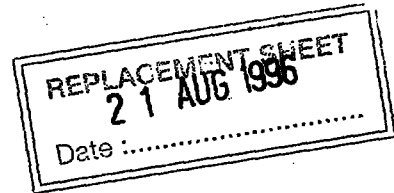
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laminated in order to prepare a multilayer ceramic capacitor, internal electrodes, which are provided between adjacent ones of the ceramic green sheets, must be formed in advance of lamination. However, it is difficult to directly form metal thin films on the ceramic green sheets, which are mechanically weak and hard to handle, by the aforementioned thin-film-forming method. In the first place, therefore, thin films for defining internal electrodes are formed on handleable films which are different from ceramic green sheets, and then transferred onto ceramic green sheets, so that it is easy or possible to form the metal thin films on the ceramic green sheets.

Thus, the internal electrodes are formed by metal thin films through a transfer technique, so that it is possible to reduce the dimensions, particularly the thickness, of the as-formed multilayer ceramic capacitor. In addition, it is also possible to further homogenize the thickness in the laminated state along the direction of extension of the ceramic green sheets. Due to the latter property, it is possible to reduce a possibility of inconvenience such as delamination after firing of the laminated ceramic green sheets.

While the transfer technique enables formation of internal electrodes of metal thin films which provide some advantages in relation to a multilayer ceramic capacitor,



it is desirable that each metal thin film is completely transferred onto a target surface with excellent transferability, in order to carry out the transfer technique. If the metal thin film is not completely transferred with a desired pattern by the transfer technique which is employed for forming an internal electrode for a multilayer ceramic capacitor, for example, the as-formed multilayer ceramic capacitor is rendered defective, as a matter of course.

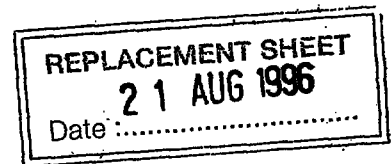
SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a metal thin film having excellent transferability and a method of preparing the same.

The metal thin film according to the present invention is provided with at least two layers, including a first metal layer which is formed on a film and a second metal layer which is formed above the first metal layer. The first metal layer is formed by vapour deposition, while the second metal layer is formed by wet plating such as electroplating or electroless plating.

Metals for forming the first and second metal layers may be different from or identical to each other.

The first metal layer is formed of nickel, copper or silver, for example. The second metal layer is formed of nickel, copper or palladium, for example.



The film employed for forming the metal layers must have flexibility and heat resistance, as well as sufficient resistance against vapour deposition, wet plating and patterning with photolithography or the like. Such a film is prepared from a resin film of polyethylene terephthalate etc., or a metallic foil of nickel, copper aluminium or the like.

The metal thin film according to the present invention is prepared with excellent transferability, to be transferred onto a target of a ceramic green sheet, a ceramic material, a resin material, a metal or the like. As to transfer conditions, the metal thin film is first brought into contact with the target, and then transferred thereto under a pressure of 10 to 500 kg/cm² at a temperature of 60 to 95°C, for example by so-called hot stamping.

The present invention is based on the recognition that a metal thin film which is formed on a carrier film by vapour deposition generally has relatively weak adhesion with respect to the carrier film, i.e., it has excellent transferability.

However, easiness of vapour deposition for forming a metal thin film depends on the type of metal used. Further, transferability of a metal thin film which is formed by vapour deposition also depends on the type of metal used. In order to attain the object of the present invention, therefore, it is necessary to prepare the material for the thin film, which is formed on a carrier film by vapour deposition, from a metal which is excellent in transferability and easy to deposit. However, a metal selected in consideration of easiness in vapour deposition and transferability is not necessarily suitable as an electrode material for a target electronic component

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or the like. When a metal layer is formed only by vapour deposition along its overall thickness, further, a peel surface of the film is thermally denatured in the vapour deposition process, to require high peel strength or cause difficulty in peeling. Further, the film is warped by residual stress of the metal layer which is obtained by vapour deposition. In addition, a long time is required for forming the metal layer due to a low vapour deposition rate, leading to increase in manufacturing cost.

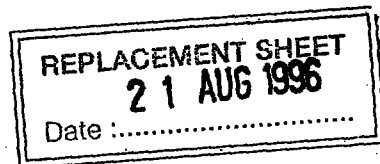
According to the present invention, therefore, the first metal layer is formed of a metal which is selected in consideration of easiness in vapour deposition and transferability, while the second metal layer is formed above the first metal layer to compensate for properties which are insufficient in the metal forming the first metal layer. The second metal layer can be formed of an optimum metal which is selected in consideration of



properties required for an electrode for a target electronic component or the like, since it is not necessary to consider easiness in vapour deposition and transferability. Further, the second metal layer also compensates for the thickness of the first metal layer which is formed by vapor deposition in addition to compensating for insufficient properties of the first metal layer, to easily attain a thickness required for the overall metal thin film to be transferred. Therefore, the first and second metal layers may be formed of either different or identical metals.

According to the present invention, further, the second metal layer is formed by wet plating such as electroplating or electroless plating. When the second metal layer is formed above the first metal layer by wet plating, adhesion of the first metal layer with respect to the film is not increased as compared with a case of forming a metal layer only by vapour deposition along its overall thickness.

Thus, according to the present invention, the metal thin film is provided with at least two layers including first and second metal layers, so that the first metal layer is adapted to provide transferability while the second metal layer is adapted to provide properties which are required for an electrode for a target electronic



component or the like. Therefore, it is easy to satisfy both transferability and other desired properties over the entire metal thin film. For example, a metal thin film having excellent transferability can be formed by a metal, which has not been suitable for transfer in general, to widen the range of metals that can be subjected to transfer, while it is also possible to widen the range of application of the transferable metal thin film.

Since it is easy to pattern a metal thin film which is formed on a film by photoetching, for example, a metal thin film according to the present invention can be advantageously applied as an electrode for an electronic component, an internal or external conductor for a multilayer substrate, a conductor which is provided on a circuit board, a display metallic foil, or the like.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

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DESCRIPTION OF THE EMBODIMENTS

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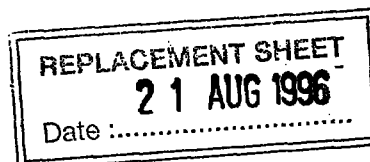
Experimental Example 1

Experimental Example 1 was adapted to prepare a transfer metallic foil.

A film 1 was first prepared as shown in Fig. 1. This film 1 was prepared from polyethylene terephthalate, which is not deformed even under a temperature of about 100°C, and coated with silicon in order to further improve the transferability of a metal thin film to be formed.

Then, a nickel deposition film 2 was formed on the film 1, as shown in Fig. 1. This nickel deposition film 2 was formed by electron beam heating with an acceleration voltage of 10 kV under an atmosphere pressure of not more than 5×10^{-4} Torr. The as-formed nickel deposition film 2 was 0.1 μm in thickness (comparative sample 1).

Then, a nickel plating film 3 was formed on another nickel deposition film 2 by electroplating, as shown in Fig. 1. The electroplating step was carried out with a current density of 1 A/dm² in a plating bath of sulfonamino acid, while setting the nickel deposition film 2 and a nickel plate on minus and plus sides respectively. Such plating was performed for 3 minutes, to obtain the nickel plating film 3 of 1 μm in thickness (inventive

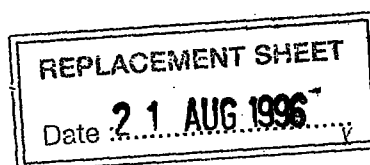


sample 1).

Then, a nickel plating film 3 was formed on still another nickel deposition film 2 by electroless plating, in place of the aforementioned electroplating, as shown in Fig. 1. The electroless plating step was carried out in an alkaline hydrazine bath at a liquid temperature of 80°C. Such plating was performed for 4 minutes, to obtain the nickel plating film 3 of 1 μm in thickness (inventive sample 2).

The aforementioned comparative sample 1 and the inventive samples 1 and 2 were subjected to evaluation of transferability onto paper and plastic surfaces. First, the surfaces of the metal thin films, i.e., those of the nickel deposition film 2 in the comparative sample 1 and the nickel plating films 3 in the inventive samples 1 and 2, were coated with adhesive agents. Then, the metal thin films were transferred to the paper and plastic surfaces by hot stamping, with application of a pressure of 100 kg/cm^2 for 10 seconds.

According to the comparative sample 1, the metal thin film, i.e., the nickel deposition film 2, was transferred onto the paper and plastic surfaces when the hot stamping temperature was 100°C. In the inventive samples 1 and 2, on the other hand, it was possible to transfer the metal thin films, i.e., the nickel deposition films 2 and the



nickel plating films 3, onto the paper and plastic surfaces at a temperature of 80°C.

In the aforementioned Experimental Example 1, similar results were obtained also when gold, silver and copper were employed in place of nickel. Further, similar results were obtained also when at least two layers were prepared from such metals.

Experimental Example 2

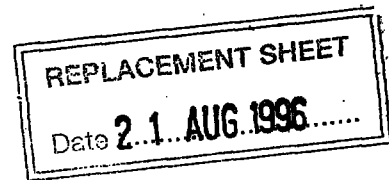
As shown in Fig. 2, a film 4 was first prepared from the same material as the film 1 employed in Experimental Example 1.

Then, a copper deposition film 5 of 0.1 μm in thickness was formed on the film 4 by vapour deposition under the same conditions as Experimental Example 1 (comparative sample 2).

Then, a nickel plating film 6 of 1 μm in thickness was formed on another copper deposition film 5 by electroplating under the same conditions as Experimental Example 1 (inventive sample 3).

In addition, a nickel plating film 6 of 1 μm in thickness was formed on still another copper deposition film 5 by electroless plating, in place of the aforementioned electroplating, under the same conditions as Experimental Example 1 (inventive sample 4).

In order to evaluate transferability of the

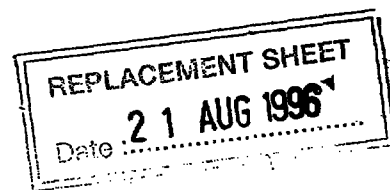


comparative sample 2 and the inventive samples 3 and 4, the following experiment was performed:

A slurry was prepared from a nonreducing dielectric ceramic material which was mainly composed of barium titanate. The surfaces of the metal films, i.e., those of the copper deposition film 5 in the comparative sample 2 and the nickel plating films 6 in the inventive samples 3 and 4, were coated with this slurry and dried to form ceramic green sheets 7, which were then peeled. In the comparative sample 2, the copper deposition film 5 was not in the least separated from the film 4, although the ceramic green sheet 7 was peeled. In the inventive samples 3 and 4, on the other hand, the copper deposition films 5 and the nickel plating films 6 were separated from the films 4 upon peeling of the ceramic green sheets 7.

Then, the nickel plating films 6 of the inventive samples 3 and 4 were coated with photoresist films, and thereafter the metal thin films, i.e., the copper deposition films 5 and the nickel plating films 6, were patterned to form internal electrodes for multilayer ceramic capacitors by photoetching.

Then, ceramic green sheets 7 of 10 to 15 μm in thickness were formed on the surfaces of the films 4, which were provided with the metal thin films, by a doctor blade coater. The ceramic green sheets 7 were formed of



the aforementioned slurry of a nonreducing dielectric ceramic material.

Then, a plurality of such ceramic green sheets 7 were stacked with thermocompression bonding applied to every stack, and the films 4 were peeled after every thermocompression bonding. In this case, the metal thin films were completely separated from the films 4.

Each of the as-formed laminates were cut in dimensions for defining a single multilayer ceramic capacitor, fired and provided with external electrodes, thereby forming a multilayer ceramic capacitor.

The as-formed multilayer ceramic capacitor was smaller in thickness as compared with a conventional typical multilayer ceramic capacitor whose internal electrodes were formed by screen printing of metal paste, and its thickness was further homogeneous along the direction of extension of the ceramic sheets. In addition, no deterioration of electric characteristics, such as reduction of capacitance, was observed since the internal electrodes exhibited no defects such as pores.

Experimental Example 3

A film 1 was prepared in a similar manner to Experimental Example 1.

Then, a copper deposition film 2 of 1 μm in thickness was formed on the film 1 by vapour deposition as shown in

Fig. 1, under the same conditions as Experimental Example 1 (comparative sample 3).

Also, a copper deposition film 2 of 0.1 μm in thickness was formed on another film 1 by vapour deposition as shown in Fig. 1, and a copper plating film 3 of 1 μm in thickness was formed on the copper deposition film 2 by electroplating under the same conditions as Experimental Example 1 (inventive sample 5).

Then, a copper plating film 3 of 1 μm in thickness was formed on still another copper deposition film 2 by electroless plating in place of the aforementioned electroplating, under the same conditions as Experimental Example 1 (inventive sample 6).

In order to evaluate transferability of the comparative sample 3 and the inventive samples 5 and 6, the following experiment was performed:

A pair of 2 cm-square plates were prepared to hold each of the comparative sample 3 and the inventive samples 5 and 6, and contact surfaces therebetween were fixed to each other with an adhesive agent. In this case, the plates were outwardly pulled to examine strength required for peeling the copper deposition film 2 from the film 1. The comparative sample 3 required peel strength of 3000 g, while the inventive samples 5 and 6 required 2000 g respectively.

Further, it was difficult to pattern the comparative sample 3 by photoetching, since the film 1 was extremely warped and it was difficult to obtain a flat surface.

Experimental Example 4

A film 1 was prepared in a similar manner to Experimental Example 1.

Then, a nickel deposition film 2 of 1 μm in thickness was formed on the film 1 by vapour deposition as shown in Fig. 1, under the same conditions as Experimental Example 1 (comparative sample 4).

Also, a nickel deposition film 2 of 0.1 μm in thickness was formed on another film 1 by vapour deposition as shown in Fig. 1, and a nickel plating film of 1 μm in thickness was formed on the nickel deposition film 2 by electroplating under the same conditions as Experimental Example 1 (inventive sample 7).

Then, a nickel plating film 3 of 1 μm in thickness was formed on still another nickel deposition film 2 by electroless plating, in place of the aforementioned electroplating, under the same conditions as Experimental Example 1 (inventive sample 8).

The comparative sample 4 and the inventive samples 7 and 8 were subjected to evaluation of transferability similarly to Experimental Example 1. In the comparative

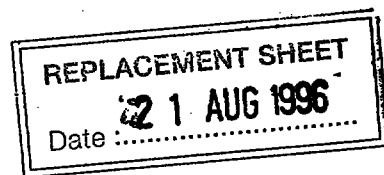


sample 4, it was impossible to transfer the metal thin film even if hot stamping was performed at a temperature of 100°C. Further, it was difficult to pattern the comparative sample 4 by photoetching since the nickel deposition film 2 was extremely cracked and the film 1 was so warped that it was difficult to obtain a flat surface. In the inventive samples 7 and 8, on the other hand, it was possible to transfer the metal thin films, i.e., the nickel deposition films 2 and the nickel plating films 3, onto paper and plastic surfaces at a temperature of 80°C.

While the present invention has been described in relation to Experimental Examples 1 to 4, the first and second metal layers may be prepared from arbitrary metals.

The second metal layer may not necessarily be brought into contact with the first metal layer. For example, at least a single third metal layer may be provided between the first and second metal layers. In this case, the third metal layer may be formed by a method such as sputtering, electroplating, electroless plating or the like.

The film for forming the first metal layer, which is prepared from resin, for example, may not inevitably be subjected to treatment for improving transferability, such as the aforementioned silicon coating. When the film itself is formed of a material which essentially has small

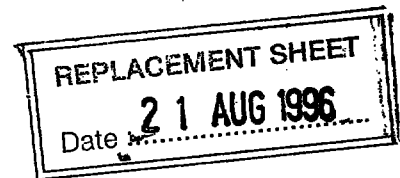


adhesion with respect to a metal, it is not necessary to perform surface treatment for improving transferability.

In addition to the aforementioned Examples, it is possible to form the following substance by properly selecting materials for the first and second metal layers:

A first metal layer which is prepared from copper and a second metal layer which is prepared from nickel are transferred onto a ceramic green sheet for a semiconducting ceramic capacitor. A plurality of such ceramic green sheets are laminated and then fired so that the same are vitrified. Thereafter re-oxidation treatment is performed to diffuse copper into the ceramic material and convert grain boundaries of the semiconducting ceramic material into insulator states, thereby obtaining an intergranular-insulated multilayer ceramic capacitor.

Alternatively, a first metal layer of aluminium second metal layer of copper and a third metal layer of aluminium may be transferred onto a ceramic green sheet. A plurality of such ceramic green sheets are laminated and then fired, so that the aluminium layers are converted to Al_2O_3 layers, thereby preventing diffusion of copper. Such a technique is so applied to preparation of a multilayer ceramic capacitor as to prevent the ceramic layers from diffusion of copper for forming internal electrodes. Thus, it is possible to prepare a multilayer ceramic



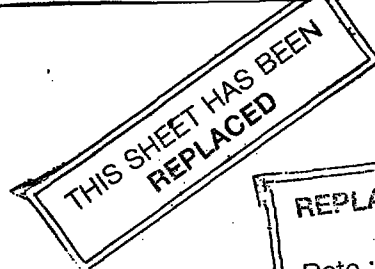
capacitor which has small dispersion of characteristics, particularly capacitance. In this case, the second metal layer may be formed of nickel in place of copper, to attain a similar effect.

The present invention is advantageously applicable to forming electrodes for an electronic component, more specifically, internal electrodes for a multilayer ceramic capacitor. For example, first, a capacitor can be obtained by the steps of transferring metal thin films onto ceramic sheets, and stacking the ceramic sheets. Secondly, a capacitor can be obtained by the steps of transferring metal thin films onto a ceramic block of a plurality of stacked ceramic sheets, further stacking a ceramic sheet on the ceramic block, transferring metal thin films onto the ceramic sheet, and repeating the last two steps. Thirdly, a capacitor can be obtained by the steps of forming a metal thin film on a film, forming a ceramic sheet on the surface of the film, which is provided with the metal thin film, peeling the ceramic sheet together with the metal thin film from the film, and stacking such peeled ceramic sheets. Fourthly, a capacitor can be obtained by the steps of forming a metal thin film on a film, forming a first ceramic sheet on the surface of the film, which is provided with the metal thin film, stacking the first ceramic sheet on a second ceramic



sheet, and peeling the film from the first ceramic sheet.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the scope of the present invention being limited only by the terms of the appended claims.



CLAIMS:

1. A metal thin film having excellent transferability, said film comprising:

a first metal layer formed by vapour deposition;
and

a second metal layer formed on said first metal layer by wet plating.

2. A metal thin film in accordance with claim 1, wherein said wet plating is electroplating.

3. A metal thin film in accordance with claim 1, wherein said wet plating is electroless plating.

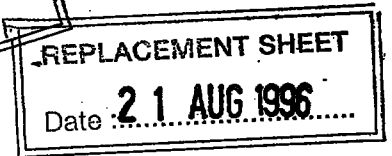
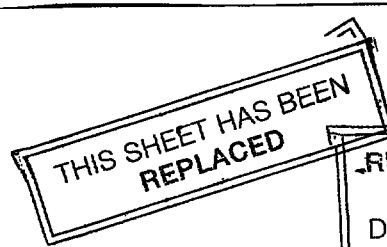
4. A metal thin film in accordance with claim 1 or 2 or 3, wherein said first and second metal layers are formed of different metals.

5. A metal thin film in accordance with claim 1 or 2 or 3 wherein said first and second metal layers are formed of the same type of metals.

6. A method of preparing a metal thin film having excellent transferability, said method comprising the steps of:

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forming a first metal layer by vapour deposition;
and

forming a second metal layer on said first metal
layer by wet plating.

7. A method of preparing a metal thin film in
accordance with claim 6, wherein said wet plating is
electroplating.

8. A method of preparing a metal thin film in
accordance with claim 6, wherein said wet plating is
electroless plating.

9. A method of manufacturing a ceramic electronic
component comprising a ceramic sheet and an electrode
formed on said ceramic sheet, said method comprising:

forming a first metal layer on a carrier by
vapour deposition;

forming a second metal layer above said first
metal layer by wet plating; and

transferring said first and second metal layers
onto a ceramic sheet.

10. An electronic component including a metal thin
film as claimed in any of claims 1 to 5, or a metal
thin film manufactured by a method as claimed in any





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of claims 6 to 8.

11. An electronic component as claimed in claim 10 and comprising a ceramic sheet and one or more said metal thin films.

12. An electronic component as claimed in claim 11 and comprising a ceramic capacitor.

13. An electronic component as claimed in claim 12 and comprising a multilayer ceramic capacitor comprising a plurality of ceramic sheets and said thin metal films.

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**METAL THIN FILM HAVING EXCELLENT TRANSFERABILITY
AND METHOD OF PREPARING THE SAME**

ABSTRACT OF THE DISCLOSURE

A metal thin film having excellent transferability is provided in order to facilitate formation of an internal electrode for a multilayer ceramic capacitor, for example, by a technique of transferring a metal thin film. A first metal layer (2) of nickel or copper is formed on a carrier film (1) by vapour deposition, and then a second metal layer (3) of nickel or copper is formed thereon by wet plating such as electroplating or electroless plating, thereby providing a metal thin film comprising the first and second metal layers (2 and 3) which can readily be transferred.

Figure 1.

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FIG. 1

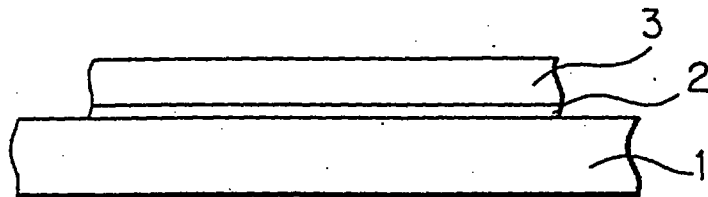
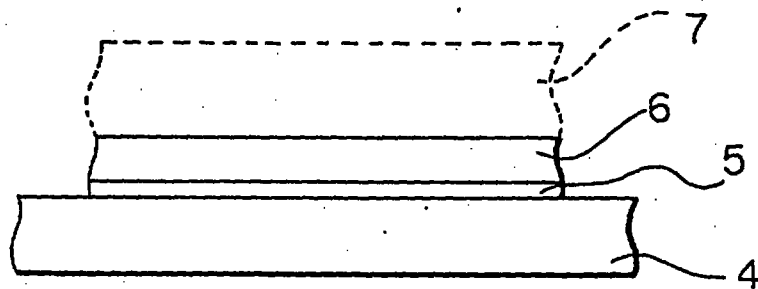
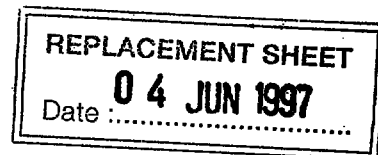


FIG. 2





Claims

1. A method of manufacturing a ceramic electronic component from a plurality of ceramic green sheets, the method comprising:

preparing each of said plurality of ceramic green sheets by forming a first metal layer on a carrier by vapour deposition,
forming a second metal layer on said first metal layer by wet plating,
patterning said metal layers, and
applying a ceramic slurry to said patterned metal layers thereby to form a ceramic green sheet including said patterned metal layers on said carrier;
forming a stack of ceramic green sheets by taking one of said plurality of ceramic green sheets and peeling said carrier therefrom so that said one green sheet serves as the first sheet in the stack and repeatedly laminating another one of said plurality of ceramic green sheets to the stack and peeling said carrier therefrom; and
firing said stack.
2. A method according to claim 1, further comprising preparing a film of polyethylene terephthalate coated with silicon as said carrier.
3. A method according to claim 1 or 2, wherein said wet plating comprises electroplating.
4. A method according to claim 1 or 2, wherein said wet plating comprises electroless plating.



5. A method according to any preceding claim, wherein said first and second metal layers are formed of different metals.
6. A method according to any of claims 1 to 4, wherein said first and second metal layers are formed of the same type of metals.
7. A method according to any preceding claim, wherein said metal layers are patterned by photoetching.
8. A method according to any preceding claim, wherein the ceramic slurry is applied to said patterned metal layers by a doctor blade coater.
9. A method according to any preceding claim, wherein said ceramic green sheets are laminated by thermocompression bonding each sheet to said stack.
10. A method according to any preceding claim, further comprising forming a third metal layer between said first and second metal layers by sputtering, electroplating or electroless plating.
11. A method according to any preceding claim, further comprising re-oxidizing said first metal layer to diffuse the metal into the ceramic green sheet and convert grain boundaries of the ceramic green sheet into insulator states.
12. A method according to any preceding claim, further comprising applying external electrodes to said first stack so as to complete the ceramic electronic component.
13. A method according to claim 12, wherein said external electrodes are connected to said metal layers to form a multilayer ceramic capacitor.