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(54) Title: THICK FILM CONDUCTOR COMPOSITIONS FOR USE ON ALUMINUM NITRIDE SUBSTRATES

(57) Abstract: The invention is directed to a conductive thick film composition for use on an aluminum nitride substrate that utilizes a boron containing reactant and a metal oxide to promote adhesion.

TITLE OF INVENTION

THICK FILM CONDUCTOR COMPOSITIONS FOR USE ON ALUMINUM NITRIDE SUBSTRATES

FIELD OF THE INVENTION

The invention is directed to a thick film composition for use on an aluminum nitride substrate. The composition includes a boron containing reactant and a metal oxide that promotes adhesion to the substrate.

BACKGROUND OF THE INVENTION

In recent years aluminum nitride substrates for circuit boards have been employed for use in high-temperature environments because of their high heat conduction coefficient. However, in order to adhere metal conductors to aluminum nitride substrates, it becomes necessary to use thick film compositions that are capable of providing a thin reactive layer (oxide film) formed between the metal found in the composition and the substrate by introducing the metal in atomic form to the surface of the substrate. The metal, which is extremely active, chemically bonds with excess oxygen that exists on the surface of the substrate. US Patent Number 6,103,146 to Okamoto describes such a composition for use on an aluminum nitride substrate wherein a conductive powder and a metal boride are dispersed in an organic medium. The present invention improves the adhesion performance of the existing compositions.

SUMMARY OF THE INVENTION

The invention is directed to a thick film composition comprising:

a) electrically conductive powder;

b) boron containing reactant selected from boron oxide, elemental boron, metal boride and mixtures thereof; and

c) metal oxide;

wherein a through c are dispersed in organic medium.

DETAILED DESCRIPTION OF INVENTION

The invention is a thick film composition for use on an aluminum nitride substrate. Thick film technology, which includes compositions thereof, is an established method in the electronic industry to efficiently manufacture hybrid electronic circuitry. The main components of the thick film conductor composition described herein are a conductor powder, a boron containing reactant, and a metal oxide dispersed in an organic medium. The components are discussed below.

A. Conductor Powder

Generally, a thick film composition comprises a functional phase that imparts appropriate electrically functional properties to the composition. The functional phase comprises electrically functional powders dispersed in an organic medium that acts as a carrier for the functional phase. The composition is fired to burn out the organics and to impart the electrically functional properties. Prior to firing, a processing requirement may include an optional heat treatment such as drying, curing, reflow, and others known to those skilled in the art of thick film technology. "Organics" comprise polymer or resin components of a thick film composition.

The electrically functional powders in the present thick film composition are conductor powders and may comprise a single type of metal powder, mixtures of metal powders, alloys, or compounds of several elements. The particle diameter and shape of the metal powder is not particularly important as long as it is appropriate to the application method. Some examples of such powders include: gold, silver, copper, nickel, aluminum, platinum, palladium, molybdenum, tungsten, tantalum, tin, indium, lanthanum, gadolinium, boron, ruthenium, cobalt, titanium, yttrium, europium, gallium, sulfur, zinc, silicon, magnesium, barium, cerium, strontium, lead, antimony, conductive carbon, and combinations thereof and others common in the art of thick film compositions.

B. Boron Containing Reactant

The boron containing reactant is selected from: combinations of boron and a metallic element which include binary, ternary and higher compounds of boron and a metallic element (called metal borides); boron oxide and sources that produce boron oxide under firing conditions (e.g. boric acid, B_20_3, and borate glass); elemental boron (hydrated or anhydrous) and a mixture of the listed reactants. In addition, included are compounds that generate B_2O_3 upon heating in the temperature range of 600-1000°C and all ranges contained therein in air. Some examples of metal borides includes TiB_2, ZrB_2, HfB_2, UB_2, NbB_2, TaB_2, CrB_2, CoB, MoB_2, W_2B_5, CaB_6, SrB_6, BaB_6, LaB_6, CeB_6, PrB_6, NdB_6, SmB_6, EuB_6, Ni_3B_6, and Ni_2B_6.

The level of the boride reactant added to the composition is determined by the extent that it does not cause poor solder wetting as a result of the B_2O_3 formed from boron in the firing process that becomes vitrified and covers the conductor surface. The unwanted decreased

solder wetting effect of the B_2O_3 is related to the type and form of noble metal used, that is, whether pure or alloy; the metal oxide additive; and the density of the thick film after firing. Consequently, through selection of combinations, it is possible to inhibit formation of vitreous B_2O_3 on or migration of vitreous B_2O_3 to the thick film surface.

The amount of boron containing reactant contained in the composition should be no more than 1.6 parts by weight per 100 parts by weight based on total composition in order to apply the thick film conductor composition on an aluminum nitride substrate without causing poor solder wetting.

C. Metal Oxide

The metal oxide may be one type of metal oxide powder or a mixture of different metal oxide powders. Some examples of metal oxides include Co_3O_4, Fe_2O_3, ZnO, SnO_2, TiO_2, ZrO_2 and mixtures thereof. The metal oxide (1) reacts with the aluminum nitride substrate in the presence of the boron containing reactant to form ternary metal aluminate compounds or quaternary metal boroaluminate compounds forming an adhesive bond and/or; (2) modifies the vitrification (glass formation) of the boron containing reactant upon its oxidation thereby improving the solder wettability of the composition.

Also, a metal oxide forming moiety can replace the metal oxide powders or partially replace some of the powders. The metal oxide can be produced several ways; such as, oxidation of metals, decomposition of metal carbonates, conversion from metal sulfides, sulfates, phosphates, nitriates, nitrides, borides, halides, etc., under firing conditions for processing the compositions.

The metal oxide in the composition is no more than 2 parts by weight per 100 parts by weight based on the total composition. The boron containing reactant and metal oxide in combination are no more than 3 parts by weight per 100 parts by weight of the total composition. The metal oxide and the boron containing reactant react with the aluminum nitride substrate during the firing process, producing an oxidation reaction product ($2Al_2O_3.B_2O_3$), which contributes to adhesion between the conductor and the substrate. For example, the combination of TiO_2 with anhydrous boron reacts with AlN in air to form B_2O_3, $2Al_2O_3.B_2O_3$, and a TiO_2 modified B_2O_3 glass. The TiO_2 inhibits the formation and flow of the B_2O_3 glass thus improving solder wettability of the metallic conductor thick film composition.

In another example, the addition of Co_3O_4 to TiB_2 reacts with the AlN to form both $2Al_2O_3.B_2O_3$ and $CoAl_2O_4$ interfacial (conductor – substrate interface) bond phases. The Co_3O_4 also inhibits the formation and flow of the B_2O_3 glass thus improving solder wettability.

D. Optional Components

The powders described hereinabove are finely dispersed in an organic medium and are optionally accompanied by inorganic binders, ceramics, and fillers, such as other powders or solids. The function of an inorganic binder in a thick film composition is binding the particles to one another and to the substrate after firing. Examples of inorganic binders include glass binders (frits), metal oxides, and ceramics. Glass binders useful in the thick film composition are conventional in the art. Some examples include borosilicates and aluminosilicates glasses. Examples further include combinations of oxides, such as: B_2O_3, SiO_2, Al_2O_3, Bi_2O_3, CuO, CdO, CaO, BaO, ZnO, SiO_2, Na_2O, PbO, and ZrO which may be used independently or in combination to form glass binders. In addition, the thick film composition can also include other metal particles and inorganic binder particles to enhance various properties of the composition, such as adhesion, sintering, processing, brazeability, solderability, reliability, etc., during processing.

E. Organic Medium

The powders are typically mixed with an organic medium (vehicle) by mechanical mixing to form a pastelike composition called "pastes", having suitable consistency and rheology for printing. A wide variety of inert liquids can be used as organic medium. The organic medium must be one in which the solids are dispersible with an adequate degree of stability. The rheological properties of the medium must be such that they lend good application properties to the composition. Such properties include: dispersion of solids with an adequate degree of stability, good application of composition, appropriate viscosity, thixotropic, appropriate wettability of the substrate and the solids, a good drying rate, good firing properties, and a dried film strength sufficient to withstand rough handling. The organic medium is conventional in the art and is typically a solution of polymer in solvent(s). The most frequently used resin for this purpose is ethyl cellulose. Other examples of resins include ethylhydroxyethyl

cellulose, wood rosin, mixtures of ethyl cellulose and phenolic resins, polymethacrylates of lower alcohols, and monobutyl ether of ethylene glycol monoacetate can also be used. The most widely used solvents found in thick film compositions are ethyl acetate and terpenes such as alpha- or beta-terpineol or mixtures thereof with other solvents such as kerosene, dibutylphthalate, butyl carbitol, butyl carbitol acetate, hexylene glycol and high boiling alcohols and alcohol esters. In addition, volatile liquids for promoting rapid hardening after application on the substrate can be included in the vehicle. The preferred mediums are based on ethylcellulose and β-terpineol. Various combinations of these and other solvents are formulated to obtain the viscosity and volatility requirements desired.

The solids are mixed with an essentially inert liquid medium (vehicle) by mechanical mixing using a planetary mixer, then dispersed on a three roll mill to form a paste-like composition having suitable consistency and rheology for screen printing. The latter is printed as a "thick film" paste on an aluminum nitride substrate in the conventional manner as known to those in the art of thick film technology.

The ratio of organic medium in the thick film composition to the inorganic solids in the dispersion is dependent on the method of applying the paste and the kind of organic medium used. Normally to achieve good coverage, the dispersions will contain complementarily 50-91% wt. inorganic solids and 50-9% wt. vehicle, as described above. The compositions of the present invention may, of course, be modified by the addition of other materials, which do not affect its beneficial characteristics. Such formulations are well within the state of the art.

The pastes are conveniently prepared on a three-roll mill. The viscosity of the pastes is typically within the following ranges when measured on a Brookfield HBT viscometer at low, moderate, and high shear rates:

Shear Rate (sec^{-1})	Viscosity (Pa *s)	
0.2	100-5000	
	300-2000	Preferred
	600-1500	Most Preferred
4	40-400	
	100-250	Preferred
	120-200	Most Preferred
40	10-150	
	25-120	Preferred
	50-100	Most Preferred

Test Procedure used in Examples

Aged Adhesion

Printed parts are dried 5-15 minutes at 80-150°C. They are then fired three times in a belt furnace which has a 10 minute peak temperature cycle at 850°C; and a 30 minute descending temperature ramp back down from 850°C to ambient.

After firing three times, the parts have wires attached as follows. Wires are clipped onto the substrate so that they each run down the center of three pads. Then the wires/fired parts are dipped into Alpha 611 solder flux. The parts are then prewarmed on the solder bath and dipped for 10 seconds, and allowed to cool. Residual solder flux is cleaned from the soldered wire parts with a CH_2CL_2/methanol mixture. Parts are placed in an oven at 150°C for 48 hours, then removed and cooled.

The aged parts are placed in an apparatus for measuring the force necessary to separate the wire from the substrate. The force necessary is recorded. Also, the type of separation is noted, i.e., whether separation involves the wires pulling out of the solder pulls off the substrate. Over 15 Newtons is good adhesion. Over 20 Newtons is excellent adhesion. Adhesion of 12-14 Newtons is marginal and below 12 is unacceptable.

EXAMPLES

This invention is described in further detail with practical examples (Examples 6 and 8-12) and comparative examples (Examples 1-5 and 7). In the examples, the mixing ratio of conductive powder, boride containing reactant, metal boride and organic medium (vehicle) is shown in Table 1 as percent by weight (wt. %) based on total composition. A typical test pattern with a conductor resistance test pattern and pads (2 x 2 mm) was prepared, and a thick film paste composition as given in Table 1 was

screen printed using the typical adhesion test pattern on an aluminum nitride substrate measuring 1"x1"x0.25", dried, and fired at 850°C/30 minutes in a belt furnace in air atmosphere and repeated three times so that the thickness of the conductor after firing was about 11 μm-12 μm. Tests were preformed as described above. Table 2 shows results of the test method.

The examples show the following:

Example 1: It is demonstrated that only silver powder in the composition results in an inadequate bond of the composition to the AlN substrate.

Example 2: Boron added to the silver composition produces an inadequate bond of the composition to the AlN substrate.

Example 3: TiO_2 added to the silver composition results in inadequate bonding of the composition to the AlN substrate.

Example 4: Co_3O_4 added to silver composition produces an inadequate bond of the composition to the AlN substrate.

Example 5: This composition has a combination of Co_3O_4 and TiO2. The resulting composition is unable to bond to the AlN substrate.

Example 6: This composition has a combination of B and Co_3O_4. The composition is able to provide reasonable bonding strength to the AlN substrates. Compared to Examples 2 and 4, it suggests that both B and a metal oxide like Co_3O_4 are needed to promote adhesion.

Example 7: TiB_2 added to a silver composition produces an acceptable bond of lower strength than that formed with both TiB_2+ Co_3O_4 (or Fe_2O_3) additions (Examples 8 to 10). The TiB_2 additive produces a lower quality solder fillet (poor wetting).

Examples 8-12 show the added adhesion through use of the claimed invention.

Table 1

	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8	Ex 9	Ex 10	Ex 11	Ex 12
Ag	78.5	78.15	77.2	77.82	76.52	77.47	77.2	76.5	76.5	77.0	76.85	76.17
TiB_2							1.3	1.3	1.3	1.0		
B		0.35				0.35					0.35	0.35
Co_3O_4				0.68	0.68	0.68		0.7		0.5		0.68
TiO_2			1.3		1.3						1.3	1.3
Fe_2O_3									0.7			
Vehicle	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5

* Vehicle - Texanol ® solvent and ethyl cellulose resin

Table 2

	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8	Ex 9	Ex 10	Ex 11	Ex 12
Resistivity +	2.1	2.5	3.4	2.4	4.9	3.0	3.0	3.4	3.1	2.6	3.4	3.9
Aged Adhesion (N)	<5	8	<5	<5	<1	17	22	31	32	28	21	29

+ (mohm/square at 12 microns thickness)

CLAIMS

What is claimed is:

1. A thick film composition comprising:
   a) electrically conductive powder;
   b) boron containing reactant selected from boron oxide, elemental boron, metal boride and mixtures thereof; and
   c) metal oxide; and
   wherein a through c are dispersed in organic medium.

2. The composition of Claim 1 wherein the metal boride is selected from TiB_2, ZrB_2, HfB_2, UB_2, NbB_2, TaB_2, CrB_2, CoB, MoB_2, W_2B_5, CaB_6, SrB_6, BaB_6, LaB_6, CeB_6, PrB_6, NdB_6, SmB_6, EuB_6, Ni_3B_6, N_2B_6 and mixtures thereof.

3. The composition of Claim 1 wherein the metal oxide is selected from TiO_2, Co_3O_4, ZnO, SnO_2, Fe_2O_3, CuO, Cu_2O, ZrO_2, Cr_2O_3, RuO_2, RhO_2, NiO, PbO, Bi_2O_3, Ga_2O_3, In_2O_3, GeO_2, and mixtures thereof.

4. The composition of Claim 1 wherein the conductive powder is selected from gold, silver, platinum, palladium, rhodium, mixtures and alloys thereof.

5. The composition of Claim 1 further comprising inorganic binder.

6. The composition of Claim 1 wherein the boron containing reactant is no more than 1.6 parts by weight per 100 parts by weight based on the total composition.

7. The composition of Claim 1 wherein the metal oxide is no more than 2 parts by weight per 100 parts by weight based on the total composition.

8. The composition of Claim 1 wherein the boron containing reactant and metal oxide in combination are no more than 3 parts by weight per 100 parts by weight based on the total composition.

9. The composition of Claim 1 wherein the composition is air-fireable.

10. The composition of Claim 1 further comprising a metal oxide forming moiety.

11. An article comprising the composition of Claim 1 wherein the organic medium has been volatilized.