New Mixed Metal Transition Via-Fill Conductors for Cost Effective DuPont GreenTape™ 951 & 9K7 LTCC Circuits

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Abstract

LTCC (Low Temperature Co-fired Ceramic) technology provides an option for circuit designers that combines the benefits of HTCC and thick film technologies and is the technology of choice for many complex automotive, consumer, and military applications. For demanding and high reliability applications, LTCC circuits containing gold conductors for all ground planes, signal traces, and via fills are common. With the rise in gold cost from $400/TO in 2005 to a recent peak of over $1,200/TO in 2009, OEMs and circuit designers are forced to seek lower cost alternatives to all gold LTCC structures. The use of all silver conductors raises questions of reliability, especially for the external silver layers, and wire-bonding to silver is not possible.

The traditional method employed to address cost and reliability has been the use of mixed metallurgies, rather than using gold throughout the LTCC module. Silver based conductors for signal and ground are used internally, with gold conductors for wire bonding, brazing, or soldering on the external surfaces. Today there are two primary options to achieve this type of structure: 1) Ni/Au plating the top silver surface; or 2) Use of precious metal based transition via fill compositions that interconnect the silver to the gold conductors.

Traditional LTCC transition via fills compositions have consisted of Pd/Ag or Pd/Pt/Ag mixtures. However, such systems may be disposed to certain phenomena at the surface interface(s) between dissimilar metals. For example, the Kirkendall Effect has been found in various alloy systems and can impact the bonding between different materials. In particular, it has been studied and is used to describe voids that are produced in the boundary region at a bonding interface especially during high temperature processes such as metallic powder sintering.

This paper introduces two new mixed metal via-fill conductors that are compatible with the DuPont GreenTape™ 951 and 9K7 LTCC systems. Reliability and refire stability are described in detail.

Key Words: LTCC, Kirkendall effect, Kirkendall Void, Mixed metal system, GreenTape™ 9K7, GreenTape™ 951

Introduction:

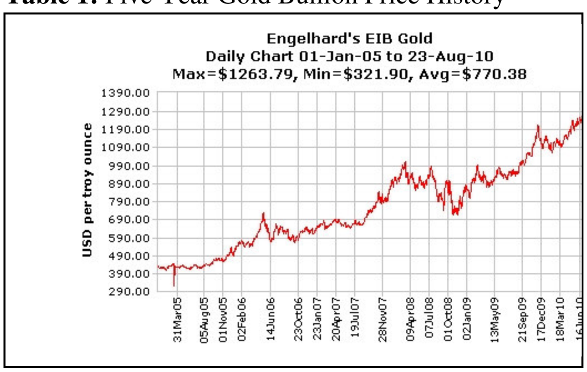
DuPont began development of GreenTape™ LTCC (Low Temperature Co-fired Ceramic) systems in the early 1980s, and remains the leading supplier of commercial LTCC materials systems. The glass-ceramic LTCC tape system combines the benefits of ceramic HTCC (High Temperature Co-fired Ceramic) tape and thick film hybrid technologies to provide the ideal material system for high frequency circuit designers. LTCC can use highly conductive metal traces – Gold, Silver, Copper – and LTCC provides the following desirable properties: consistent and reliable dielectric insulation between signal lines, high routing density, ability to add or embed passive functions (resistors, capacitors, inductors), stable dielectric properties over both frequency and temperature, uniform layer thickness, CTE match to typical MMIC semiconductor materials, high thermal conductivity compared to organic substrate materials, very low dielectric losses, and a relatively smooth surface finish. Moreover, the LTCC ceramic composite is highly hermetic by nature, and the LTCC system metal conductors are generally compatible with wire-bonding, soldering, and low temperature brazing.

There are two commercial DuPont GreenTape™ LTCC Systems - 951 and 9K7. Both of these DuPont GreenTape™ systems were designed to be compatible with either gold-based or silver-based co-fired conductor traces for use in automotive, consumer, aerospace, and military applications. . The DuPont GreenTape™ 951 System continues to be the industry standard of commercial LTCC systems, and it is used for many general purpose applications that operate below 20 GHz. The DuPont GreenTape™ 9K7 System was introduced in 2009 and is comprised of low loss glass-ceramic dielectric tape that is designed for applications operating at higher frequencies.

Escalating Cost of Gold

Until recently, the majority of "Hi-Rel" LTCC and hybrid microcircuit applications - Aerospace, Defense, National Security, Military – have utilized circuit construction consisting of gold conductors to achieve the benefits of gold's circuit performance and high reliability at a reasonable cost. This was true through the 1990s and early 2000s while the market price of gold remained relatively stable in the $275-400/T.O. range. However and as shown in Table 1, the steady rise of gold commodity prices - from $275/T.O. in early 2002, to the low $400s in 2004, $800s in 2008 and >$1,200 in 2010 - has forced many OEM system designers and program managers to seek lower cost alternatives to gold based circuitry. This is especially true for applications where the complex multilayer design for a single LTCC module might contain four or more grams of gold conductor in the via fill, inner layer, and outer layer circuit traces.

Table 1: Five Year Gold Bullion Price History[1]



In an effort to reduce system costs while maintaining the electrical performance advantages of LTCC, many end users have elected to pursue the use of silver conductors for the inner layer circuit traces. Silver as an internal layer has been proven to be reliable under high power RF conditions[2]. But to maintain top layer reliability, there is a need to use a metallurgical solution other than silver. One such option involves electroless Ni/Au plating of the exposed co-fired silver surface conductors. The electroless Ni/Au plating process and reliability have been discussed and proven[3]. Assuming a consistent high yield plating process, electroless Ni/Au plating is commonly viewed as the lowest cost, high reliability option for LTCC circuitry. However in cases where electroless Ni/Au plating to LTCC is not a desirable option, the system provider seeks alternate high performance and high reliability solutions that offer significant cost reductions.

Mixed Metal LTCC System:

Hi-Reliability applications targeting aerospace, military and other industries require the use of gold conductor materials due to their wire bonding, corrosion resistance and metallization migration resistance properties. The use of un-encapsulated surface silver conductors is typically not an option due to difficulty of wire-bonding directly to silver and the reduced reliability due to the oxidation of exposed silver conductors and the potential for silver migration. A mixed metal based system with buried silver conductors and exposed gold conductors should meet all requirements - high circuit reliability, wire-bondability and reduced cost – provided the silver-to-gold transition area remains defect free.

Complex multilayer electronic circuits require that the circuit be constructed of several layers of conductors separated by insulating dielectric layers. The conductive layers are interconnected between levels by electrically conductive pathways, called vias, through a dielectric layer. The conductors used in LTCC technology are typically screen printed thick film conductors. The conductive phase is ordinarily gold, silver, palladium, platinum or alloys, the choice of which depends both on the particular performance characteristics, and also the cost of the devices. While the use of all gold conductors may provide the highest reliability LTCC circuit modules, the continued increase in the cost of gold has caused some end users to seek alternate technologies. One of these alternatives involves the use of silver-based conductors inside the LTCC structure with gold-based conductors on the exposed outer layers. This approach can be called a Mixed Metal system, as it combines the low cost of silver internal layers with the high reliability of gold-based external layers. A major component in the mixed metal system is the transition via-fill conductor which connects the inner silver conductors to surface gold conductors. Present or past transition via-fill technologies have used Pd/Ag, Pd/Pt/Ag or Ru within the transition via compositions, but reliability uncertainties have prevented widespread adoption.

Historically, such mixed metal systems have been sensitive to the development of certain phenomenon known as the Kirkendall Effect, or Kirkendall voids, at the interface(s) between dissimilar metals . The Kirkendall voids have been found in various alloy systems[4-6] and are used to describe voids that are produced in the boundary region at a bonding interface of dissimilar metals especially during high temperature processes such as metallic powder sintering.

It is also considered that there may be EMF difference generated defects at the interface between different metals such as at an electrical connection in an LTCC device. Figure 1 shows examples of defects at the interfaces of DuPont GreenTape™ 9K7 and 951 after firing a mixed metal structure containing a Pd/Pt/Ag transition via-fill material.

Thick film conductors used in LTCC usually contain ceramic oxides and glasses as binders which bond with ceramics on firing, which can result in variations in the interface void formations, porosity distribution around the vias, and the bonding of the LTCC - via-fill conductor interface.

Possible Mechanism of Formation Kirkendall Voids Formation in LTCC:

The mechanism that leads to the formation of Kirkendall void defects when dissimilar metals or metal alloys are connected together and heated is still unclear, but it could be hypothesized by using the self diffusion and inter-diffusion coefficients differences of metal atoms. The thermal inter-diffusion of atoms is by a direct exchange of atoms controlled by the activation energy Q and the concentration gradient. In the case of conductor couples (layers of different metals in contact) with similar inter-diffusion activation energy Q, metal ion inter-diffusion and intra-diffusion between via-fill and line conductors is minimized and thus the materials transport is reduced and is unlikely to form an interface defect such as Kirkendall voids. Table 2 is a list of the approximate activation energy in Kcals/mole for self diffusion and interdiffusion for Au, Ag, Pd and Pt metal atoms used in LTCC via-fill conductors. Calculated Activation Energy for diffusion D of metal atoms using Arrhenius Equation: $D=A \exp(-Q/RT)$ where Q is the activation energy, A frequency factor, R gas constant and T absolute temperature[4]

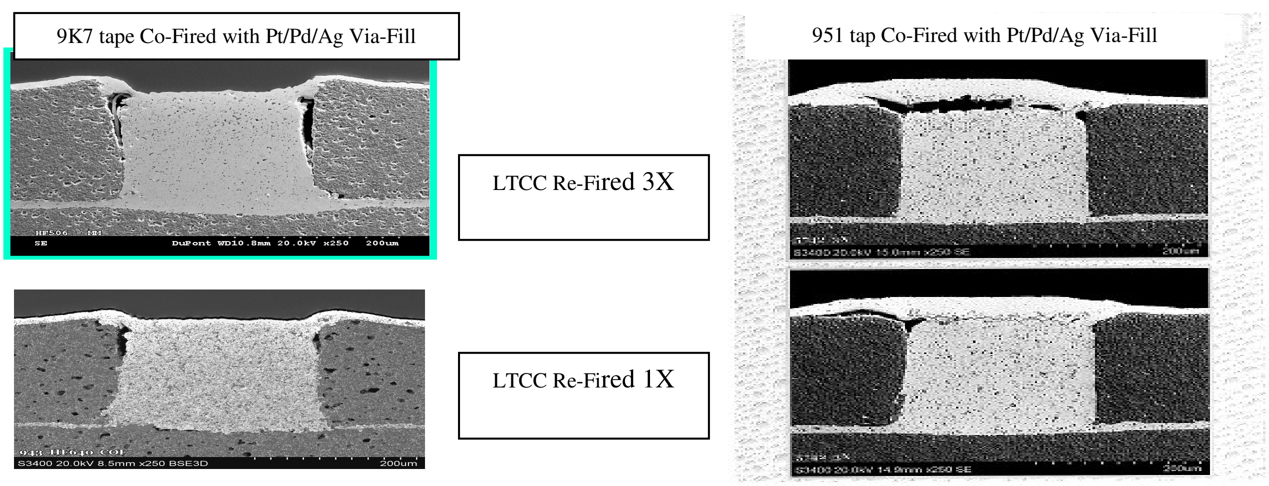


Figure 1: Kirkendall defect at the interfaces of two gold conductors and Pd/Ag/Pt Via-fill conductor after 1X and 3X firing of 9K7 and 951-based LTCC respectively

Table 2: Calculated Activation Energy (K Cals/mole) for Diffusion of Metal Atoms Used in Via-fill conductors[7]

Metal Ions	Approximate Activation Energy Q
Ag in Ag	45
Au in Au	42
Ag to Au	48
Au to Ag	41
Pd in Pd	64
Pt in Pt	68
Pd to Ag	57
Au to Pt	61

The activation energy needed for self diffusion and inter-diffusion between metal atoms present in the transition via-fill and signal line conductors are very close in the case of Ag/Au transition via-fill unlike Pd/Ag or Pd/Pt/Ag conductors. As mentioned earlier, major differences in the activation energy for diffusion could cause the unequal material transport across the via-fill and line conductor boundary which could create a void at the interface as shown in the hypothetical metal diffusion diagram in Fig 2.

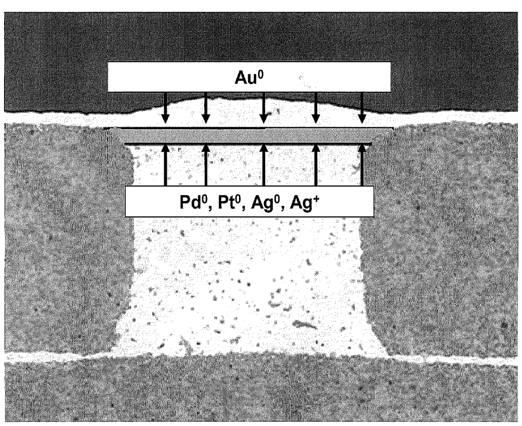


Figure 2: Hypothetical metal ion diffusion across the via-fill and surface conductor creating unequal material transport across the boundary results a void at the boundary

Metallurgy of the Ag/Au Transition Via-fill Conductor

In order to minimize the formation of the interface voids between transition via-fill and signal line conductors, Au and Ag metal powders are used because the close value of the activation energy for diffusion for these two metal ions. The atom ratios of the metal powders in the formulation are kept as close to each other as possible, in order to minimize

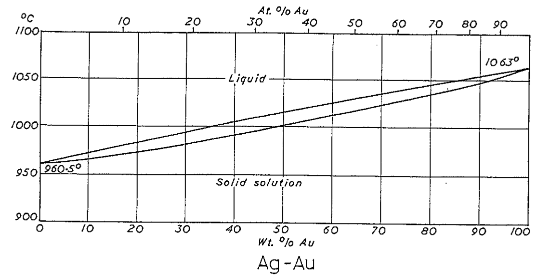


Figure 3: Gold-Silver Phase Diagram[8]

the concentration gradients across the system, Ag-Ag/Au-Au, specifically both boundaries (1) boundary between transition via and bottom silver line conductor and (2) transition via and surface gold conductor. Gold and silver form a continuous solid solution with established solidus and liquidus curves as shown in Figure 3. Unlike Pd/Ag transition via composition, there is no reduction oxidation reaction or volume change in the case of Au/Ag composition during the thermal processing of the LTCC.

Daisy Chain Test Pattern / Stacked Via Fill Integrity

To determine the compatibility and integrity of the LTCC tape, the transition via fill conductor and the conductor materials with one other, the compositions were evaluated in "daisy chain" test patterns and stacked via arrays. The daisy chain pattern consists of an array of 308 vias, each 0.010" in diameter, plus a 0.006" wide serpentine daisy chain trace that is 5133 squares in length. Following the via fill step, the conductor trace patterns are printed in such a manner that the via fills are alternately interconnected on the top and bottom surface of a single tape layer. Each printed sheet is then laminated to several blank tape layers and co-fired in the appropriate firing profiles for the DuPont GreenTape(TM) 951 and 9K7 LTCC Systems.

Following the initial co-fire and 6x subsequent 850°C/30 minute refires, circuit continuity and resistance were measured using a 4-point probe method. Sample parts are removed for cross-sectioning following the initial co-fire and predetermined refire intervals for SEM micro-structural analysis purposes. Separation of a single via from the conductor line or a single line break within the 5133 squares of signal lines will result in an infinite resistivity.

The GreenTape™ 951 System daisy chain test patterns were built using silver 6142D internal silver and 5742 top layer gold interconnected with the new TC701 transition via fill. The resistivity of 951 test circuits increased approximately 4% after 6x refires for 5742 surface. Similar resistivity variations have also been noted with other 951 top layer gold conductors, 5731 & TC502. Similarly, the GreenTape™ 9K7 System daisy chain test patterns were built with LL612 internal silver and LL507 top layer gold interconnected with the new LL701 transition via fill. The initial resistivity of ~2.6 milliohms per square increased to approximately 3.5 milliohms per sq. after 6x refires. These results are similar to the results for 9K7 silver system[9]. The gradual increase in resistivity after each refire is due to the combination of additional sintering, if any, and the increase in interactions of the conductor and tape ingredients.

Evaluation of additional via-fill formulations with minor changes to the metal ratio have been demonstrated to confirm there is no effect of slight changes in the atom ratio of gold and silver on defect formation.

conductor interface connections at the top and bottom signal line conductors are excellent.

Stacked via fill arrays are incorporated into LTCC structures as a method of shielding high frequency circuits from outside electrical interference and providing an avenue for the heat dissipation and thermal management of high power integrated circuits and other devices. Since LTCC designs often incorporate ten or more tape layers, it is important to have a via fill composition's Z-shrinkage that closely matches that of the surrounding tape layer. In doing so, the overall fired posting of a stacked via array must be minimized. Having a minimal amount of via posting or variations in the module's surface topography is desirable when applying post fired prints, attaching discrete components, seal rings or other devices. In these stacked via configurations, care must be taken at the interface of the underlying LL601 via-fill and the LL701 transition via-fill. Porosity can form between the LL601 stacks and LL701 due to the lack of binders in the via-fills. To compensate, the circuit design should include a LL612 silver line cap over the LL 601 via stacks to improve reliability. Figure 6 shows an example of LL601 Ag stacked via-fill array with top layer LL701 transition via-fill within the 9K7X tape, both with and without the LL612 silver cap.

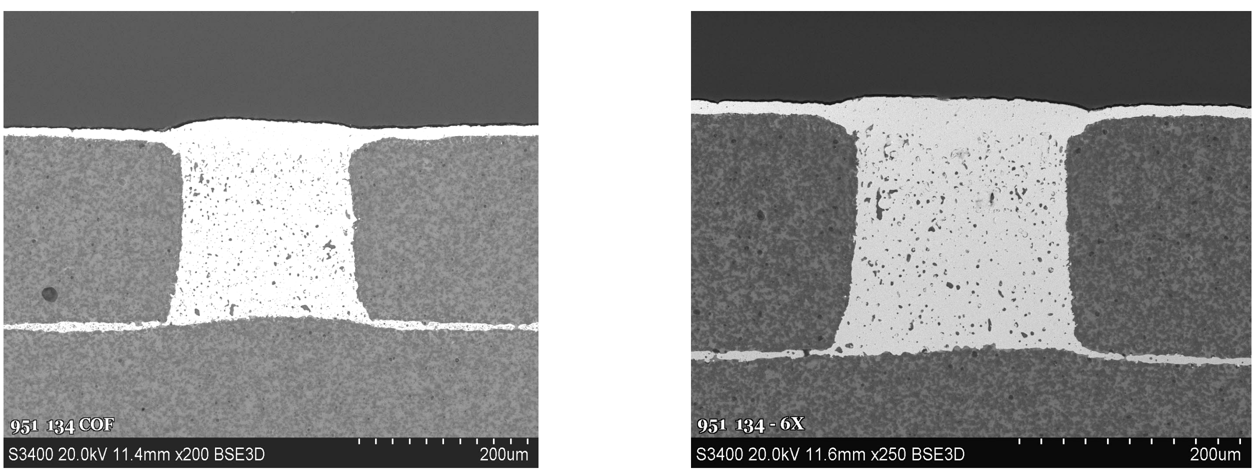


Figure 4: Microstructure of DuPont GreenTape™ 951 LTCC Mixed Metal System with TC701 transition via-fill after co-fire, and after 6x refire:

Microstructural Evaluations

The series of microstructures in Figures 4 and 5 show that even after 6 re-fires, the via-fill and dielectric remain well bonded, there are no via-fill - signal line interface defects, and the via-fill - line

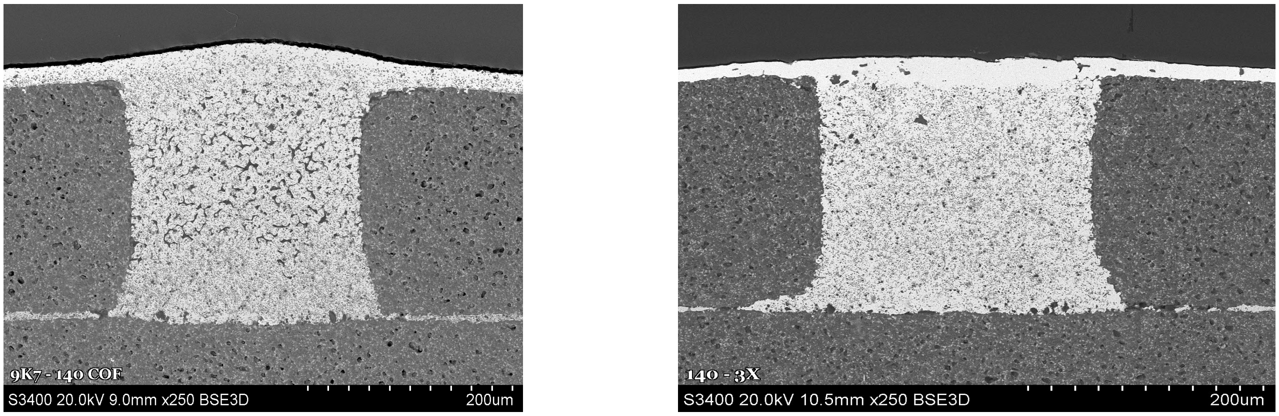


Figure 5: Microstructure of GreenTape™ 9K7 LTCC Mixed Metal System with LL701 transition via-fill after co-fire and 3x refire

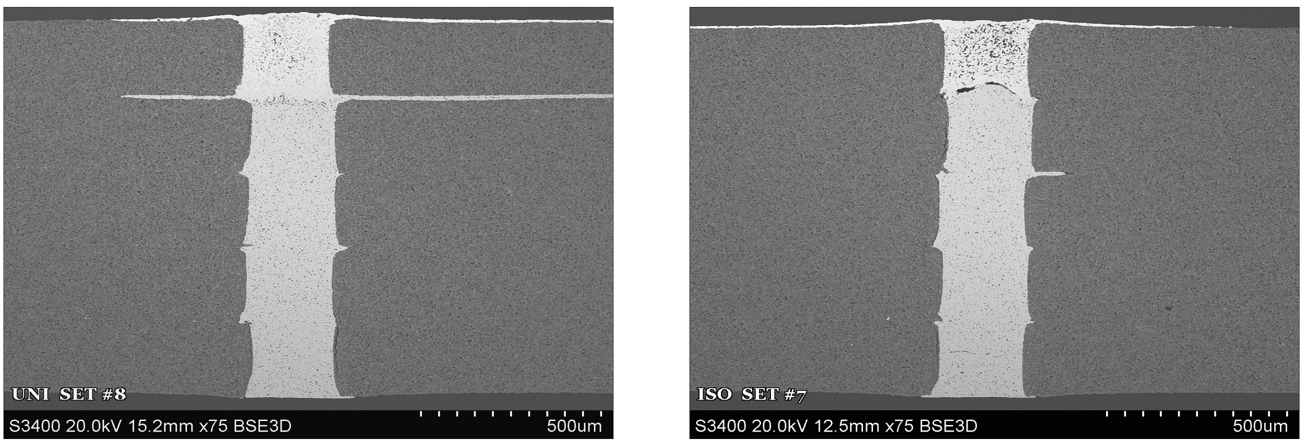


Figure 6: Transition via fill over Stacked LL601 thermal vias with a printing LL612 and without LL612

Conclusions

The developments of two new transition via-fill conductor compositions are shown to be free of Kirkendall void defects. System designers can now reduce the cost of high reliability electronic circuits by allowing the replacement of gold-based LTCC circuits with mixed-metal systems consisting of low cost silver internal conductors with high reliability and multi-functioning surface gold conductors. The cost savings will vary by circuit design, but the impact can be especially significant for complex LTCC modules containing four or more grams of precious metal conductors. This development will increase the utility of high performance LTCC in high frequency electronic circuit applications for the aerospace, telecom, military, and automotive markets. The TC701 and LL701 transition via-fill conductor compositions described in this paper are compatible with the commercially available DuPont

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