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THE DIRECT BONDING OF METALS TO CERAMICS AND APPLICATIONS IN ELECTRONICS

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THE DIRECT BONDING OF METALS TO CERAMICS AND APPLICATIONS IN ELECTRONICS

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Abstract

The direct bonding of metals to ceramics is possible utilizing a gas metal eutectic. The mechanism of direct bonding of copper foil to ceramics in a slightly oxidizing atmosphere is presented. It involves the formation of eutectic melt between copper and oxygen at a temperature slightly below the melting point of copper, which serves to bring the foil into intimate contact with the substrate. Metals to which this technique is applicable include Cu, Fe, Ni, Co, Ag, Cr, Mo and Al. A brief review of other metal-ceramic bonding techniques is given for comparison.

The process for fabricating direct bonded copper structures is given, and properties of the bond are discussed. The use of the direct bonding process in a number of electronic applications such as hybrid packages and power device heat sinks is indicated.

Introduction

Strong bonding of metals to ceramics generally does not take place unless an intermediary layer is present, or forms due to diffusion or reaction. The adhesion of the metal to this intermediary is better than to the ceramic directly. However, an intermediary layer is undesirable in many applications. This is true, for instance, where high heat conductivity is required.

The presence of an intermediary layer generally reduces heat conductivity, especially if the layer is non-metallic. Further, in high frequency applications, where the current flows in a thin skin at the metal-ceramic boundary, intermediary layers are undesirable because they are generally more resistive than the metal to be bonded. Finally, intermediary layers are often less corrosion resistant and lead to premature failure.

Unfortunately, strong direct metal to ceramic bonds are not common, either because the bond is inherently weak, or because of the difficulty of bringing the metal into intimate contact with the ceramic. In this paper, a new method of direct bonding of metals to ceramics will be given. For a better perspective, a short summary of the mechanisms of presently used metal-ceramic bonding techniques is given below.

Bonding Mechanisms Involving Intermediary Layers

Some of the more pertinent literature in this area has been reviewed by C. I. Helgesson,⁽¹⁾ and a short review was recently given by Loasby et. al.⁽²⁾ Commonly used intermediary layers are glass layers, where the glass is intentionally added or is originally present in the ceramic itself, or polycrystalline semi-conducting compounds formed by the reaction between the metal or metal oxide and the ceramic itself.

1. Glassy Intermediary Layers

Glassy phases are usually present in the grain boundaries of impure (<99.8%) ceramics. Thus, Al_2O_3 or BeO ceramics usually contain glassy mixtures of MgO, SiO_2 and CaO concentrated in the

grain boundaries. When a metallizing mixture is applied to such a ceramic, and the temperature is raised to sintering temperatures, the glass from the ceramic penetrates into the (porous) metal layer and locks it to the ceramic after cooling by mechanical forces.

More commonly, glass is intentionally added to the metallizing mixture to form the intermediate layer. This is particularly true if the ceramic is pure. For example, to take advantage of the high thermal conductivity of BeO ceramic, glass must be kept out of the grain boundaries. Therefore, the common metallizing mixtures, such as Mo-Mn, when used on beryllia, contain up to 20% SiO₂. Thus the composition of a typical mixture is 71.5% Mo, 10.7% Mn, and 17.8% SiO₂, fired on BeO at 1300°C. The manganese diffuses into the glass.

Another commonly practiced method of bonding through an intermediary glass phase involves glass frit additions to the finely divided metal in the metallizing mixture. Thus, the majority of the so-called "thick film" conductor pastes contain a glass frit, generally chosen for low melting point and thermal expansion match, in addition to dispersed metal (normally noble metals) in an organic carrier. The glass frit melts and reacts with the ceramic (usually Al₂O₃), and it also forms a network within the metal conductor. Thus, the bond between the metal and the ceramic is due to mechanical locking by the reacted glass. It should be noted that the bond strength of glass frit compositions is best on alumina; for beryllia, cracking of the glass and spalling is generally observed.

2. Polycrystalline Intermediary Layers

Such layers are usually compounds formed between the metallizing mixture and the ceramic. In one method, the metal oxide is applied to the ceramic, and sintered with the ceramic to form a mixed oxide compound. For instance, such a compound is formed between copper oxide and alumina, possible CuAlO_2 , when they are sintered together at 1150°C in air. Subsequent reduction gives an adherent metal layer bonded on the mixed oxide phase. This method is also applicable to cobalt, nickel, iron and silver.

The widely used moly-manganese process also falls into this category. In this process, a mixture of molybdenum and manganese oxide is fired on alumina (not beryllia) at 1400°C in an atmosphere of wet hydrogen. The hydrogen reduces the molybdenum oxide to the metal, but not the manganese oxide, which reacts with the alumina to form the intermediate layer compound $\text{MnO} \cdot \text{Al}_2\text{O}_3$. The molybdenum, which is unable to diffuse deeply into pure Al_2O_3 , will diffuse readily into the manganese aluminate spinel. This leads to good adhesion of the Mo layer. When MoO_3 alone is used, some penetration of alumina by MoO_3 occurs, especially in hydrogen atmospheres at high humidities. A compound between Mo and Al_2O_3 , perhaps $\text{Al}_2(\text{MoO}_4)_3$,^(3,4) is formed to provide the intermediary bonding layer.

Direct Bonding

Direct bonding here implies the absence of a readily identifiable intermediate phase between the metal and the ceramic. It does not exclude, however, the presence of a transition layer one or two monolayers thick, such as perhaps oxygen bridges between the metal and ceramic.

A method of direct bonding which does not depend on any kind of intimate bond between metal and ceramic is that involving mechanical locking or keying.

In this process the metal is screened on the ceramic in the form of an organometallic paste. The paste decomposes on heating in air, with the result that metal particles are now locked in pores in the ceramic surface to give a mechanical bond. Films of noble metals, such as platinum, are typically applied in this way. However, poor adhesion is obtained in the mechanical locking process. Clearly, in order to get good adhesion by direct bonding it is required that

- the metal must be brought into intimate contact with the ceramic over the entire area on an atom to atom basis.
- the metal must form a strong bond with the ceramic, be it by Van der Waals or chemical bonding, without extensive reaction or diffusion of the two phases into each other.

To get intimate contact between metal and a ceramic surface, the metal could be brought into the liquid state by melting. The liquid will replicate the ceramic surface where it wets it, and if a strong bond is formed, good adhesion is obtained after cool-down. For instance, when copper is melted in hydrogen on an alumina substrate, a molten droplet is formed with a melting angle of approx. 120° , which after cool-down to room temperature adheres strongly to the ceramic. The problem with

simply melting the metal, of course, is that one or more droplets are formed, and the metal member to be bonded entirely loses its shape. This can be avoided by the gas metal eutectic method.

Direct Bonding by the Gas-Metal Eutectic Method

The basic idea here is to form a liquid skin around the metallic member to be bonded. The liquid must wet both the metallic member and the ceramic, and form a strong bond after cool-down. The melting point of this liquid should be near the melting point of the metal member itself, say within 50°C, so that the metal member becomes soft and pliant and conforms easily to the shape of the substrate surface. Further, the predominant constituent of this liquid should be the same element as makes up the metallic member, and any additional constituent should be present in only small amounts or be easily removable after bonding. The thickness of the molten skin must be kept small in comparison to the thickness of the member to be bonded.

Ideal for use as the skin material are eutectics formed by the flow gas in a bonding system with the metal member itself. Such a eutectic exists, for instance, between copper and oxygen, at 0.39% weight % oxygen.⁽⁵⁾ The melting point of this eutectic is 1065°C, as compared to 1083°C for pure copper. Thus, if the oxidizing conditions in the flow gas are chosen properly, one may have the molten copper-oxygen eutectic mixture and solid copper (containing a small amount of dissolved oxygen) coexist together, in the temperature interval $1065^{\circ} < T < 1083^{\circ} \text{C}$. It is this copper-oxygen eutectic skin which is in effect used as a glue to bond

the solid copper member to the ceramic, without the Cu member losing its shape. Thus, in order to bond copper foil to ceramic, the process is as follows:

The Cu foil is laid on top of the ceramic in a furnace containing a flow gas atmosphere consisting primarily of an inert gas, such as argon or nitrogen, with a small addition of oxygen, typically of the order of a few hundredths of a percent. Copper initially reacts during the heat-up period with the oxygen in the flow gas. A small amount of oxygen dissolves in the copper, but most of it reacts to form Cu_2O around the foil. When 1065°C or above is reached, a liquid phase of or near the eutectic composition forms a skin around the copper. The thickness of this molten skin depends on the O_2 partial pressure and the oxidation time. If the partial O_2 pressure in the flow gas is less than $1.5 \cdot 10^{-6}$ atm (the equilibrium partial pressure over Cu_2O at 1065°C), Cu_2O will not form and the eutectic phase also will not form. The formation of a molten layer between the Cu foil and the substrate serves to bring the copper in intimate contact with the ceramic, by wetting it over the entire interface. Once in intimate contact with the ceramic, copper forms a strong bond with it. The temperature must remain below 1083° , the melting point of copper, since otherwise the foil loses its structural integrity and liquid drops are formed. Similarly, if the partial pressure of oxygen is too high, all copper present is converted into eutectic melt. Thus, an intermediate O partial pressure is required where both phases are present simultaneously. On cool-down below 1065° , the eutectic segregates into Cu and

Cu_2O . Evidence of this is shown in Fig. 1, which is a micrograph through a section of bonded copper foil, and indicates the presence of a second phase. This oxide phase may now be reduced in hydrogen at low temperature, without loss of adhesion. The bonding process is schematically illustrated in Fig. 2.

Copper has been bonded successfully by the gas-metal eutectic methods on alumina, beryllia, silica, various other spinels, other metals and to itself. It does not bond, however, to boron nitride or carbon. The bond strength to oxygen-containing ceramics can be in excess of 20,000 psi. Removal of the copper by etching in nitric acid or ferric chloride solution leave no copper residue. Since the copper itself does not melt during bonding, pre-cut or stamped foils of copper of the desired shapes can be bonded. In addition, holes previously cut into ceramic substrates can be covered hermetically, and the copper can overhang the ceramic. Bonds between copper and other metals, and between two copper members, can also be made by this method. A photograph of various direct bonded copper structures prepared in this laboratory are shown in Fig. 3.

Properties of Direct Bonded Copper Structures

Some properties of direct bonded copper on ceramic structures are listed in Table I.

Table I

- o Electrical conductivity is at least within 5% of pure copper, in the as-bonded condition.
- o The hardness of the copper in the as-bonded condition is much higher than after hydrogen reduction, because of dispersion hardening due to precipitated Cu_2O from the eutectic.
- o The Cu-ceramic bond strength routinely exceeds 20,000 psi.
- o In spite of the expansion coefficient difference, repeated thermal cycling from 77°K to 600°K does not cause mechanical failure.
- o Brazing, soft and hard soldering, resistance and electron beam welding are possible to the bonded copper without causing bond failure.
- o Holes in the ceramic can be sealed hermetically by direct bonded copper.

Application of Direct Bonded Copper in Hybrid Packaging

The use of directly bonded Cu foil to ceramics for the construction of hybrid packages offers advantages because:

1. Foils from 1 to 250 mils thick or more thickness can be bonded on Al_2O_3 , BeO or metals without the use of an intermediary layer and without losing the structural integrity of the foil.
2. Several layers of Cu foil and ceramic can be bonded in one single firing step. This allows fabrication of conductor crossovers and interconnections among various conductor layers; the inclusion of a Cu backplate for heat sinking; and, external package leads in one single step.

3. Since the Cu-ceramic bond does not require an intermediate interfacial layer, better heat sinking is possible.

4. Thick film conductor screening and firing steps can be entirely eliminated.

5. The Cu-ceramic bond is exceptionally strong.

6. Fabrication costs are considerably below conventional methods because of process simplicity and lower materials cost.

Figure 4 illustrates the use and versatility of the copper foil bonding process in fabricating electronic packages, including heat sinking, conductor crossovers and interconnections, and top to bottom straps. Copper foil and ceramic pieces are previously cut to the desired dimensions and are appropriately located on the ceramic substrate before the furnace pass for one step bonding. Alternatively, the pattern can be etched after bonding. This latter technique is particularly suitable for fine and complex geometries.

Figure 5 gives a sequence of steps to fabricate a hermetic ceramic package. Pieces of copper and ceramic are cut to the appropriate size and are bonded directly to give a lead frame, conductor pattern, pellet bonding pad, conductor crossover, and heat sink. The window frame for lid attachment is fired on by means of a glass ceramic frit at $500 < T < 700^{\circ}\text{C}$. Pellet bonding and lid attachment complete the package.

When the direct bonded copper foil covers a hole previously cut into the ceramic, a hermetic seal is formed. This allows for the mounting of pins or tabs from the backside by soldering, welding, or plating on copper. Figure 6 illustrates a sequence of

steps to fabricate a package in this manner. After direct bonding of a copper foil to a pre-drilled ceramic substrate, the conductor pattern and window frame are photoetched. After nickel plating, the pins are mounted and the pellet is attached. Lid attachment completes the hermetic package. Figure 7 is a photograph of a hybrid circuit fabricated by this process.

Application to Other Metal-Ceramic Systems

For the direct bonding of metal by the gas-metal eutectic method, the following prerequisites must be fulfilled:

- a) a eutectic must exist between the metal and the flow gas,
- b) the percentage of the gas component in the eutectic must be low and/or easily removable after bonding,
- c) the eutectic temperature must be at least 10 degrees or so below the melting point of the metal to give a realistic temperature range for bonding,
- d) the metal must be pliant at the bonding temperature so that it conforms to the substrate shape.

Inspection of phase diagrams of metals with the more common gases reveals a number of possibilities. In particular, oxygen, sulfur, and phosphorous form eutectics with several metals. These are listed in Table II, in addition to the eutectic temperature, the melting point of the metal, and the percentage of the gas component in the eutectic.

Table II: Metal-Gas Eutectics for Direct Bonding

Eutectic	Eutectic Temp. °C	Weight % non-metal	Melting Point of metal
Copper-oxygen	1065	0.39	1083
Iron-oxygen	1523	0.16	1535
Nickel-oxygen	1438	0.24	1452
Cobalt-oxygen	1451	0.23	1480
Copper-sulfur	1067	0.77	1083
Silver-sulfur	906	1.8	960
Chromium-sulfur	1550	2.2	1615
Silver-phosphorous	878	1.0	960
Nickel-phosphorous	714	11.0	1452
Copper-phosphorous	714	8.4	1083
Molybdenum-silicon	2070	5.5	2625
Aluminum-silicon	577	11.7	660

The flow gas would contain small amounts of oxygen, hydrogen disulfide, phosphine, or silane, as appropriate, However, in some cases a constituent of the flow gas such as silicon may not be easily removable, and the bond in such a case could not, strictly speaking, be called "direct".

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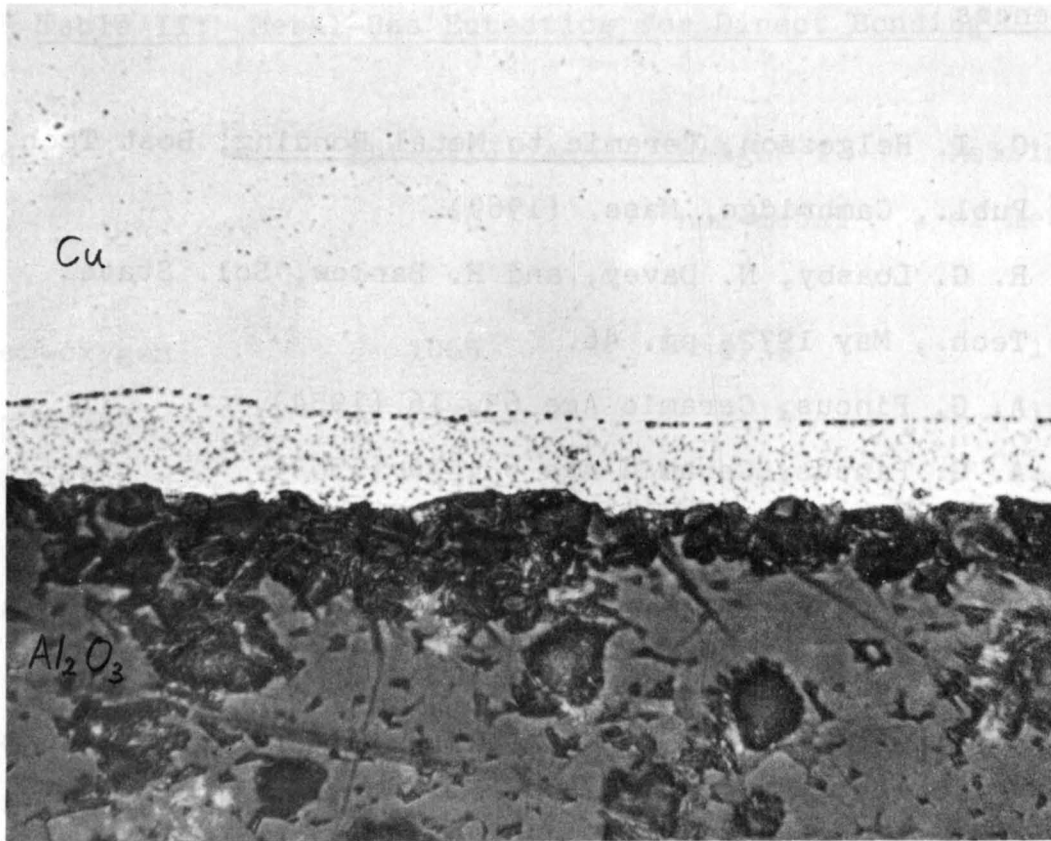


Fig. 1 Micrograph of section through direct copper bond to alumina, showing the precipitated Cu_2O from the eutectic.

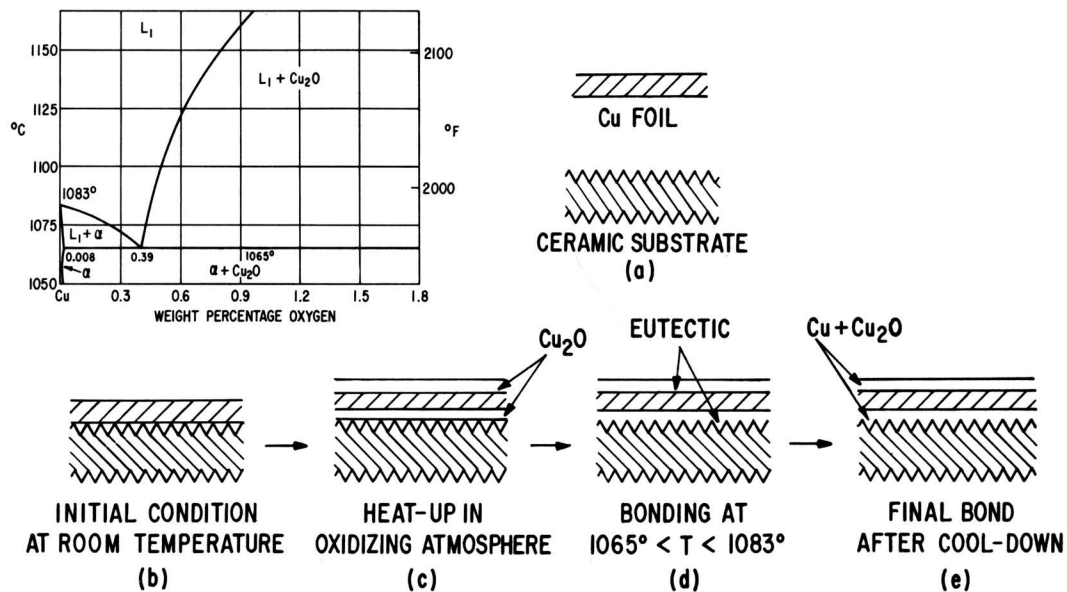


Fig. 2 Eutectic phase diagram and schematic of bonding process.

Fig. 3 Direct bonded copper structures.

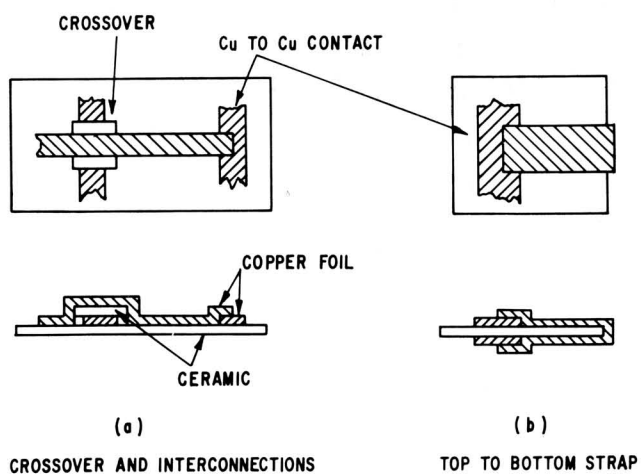
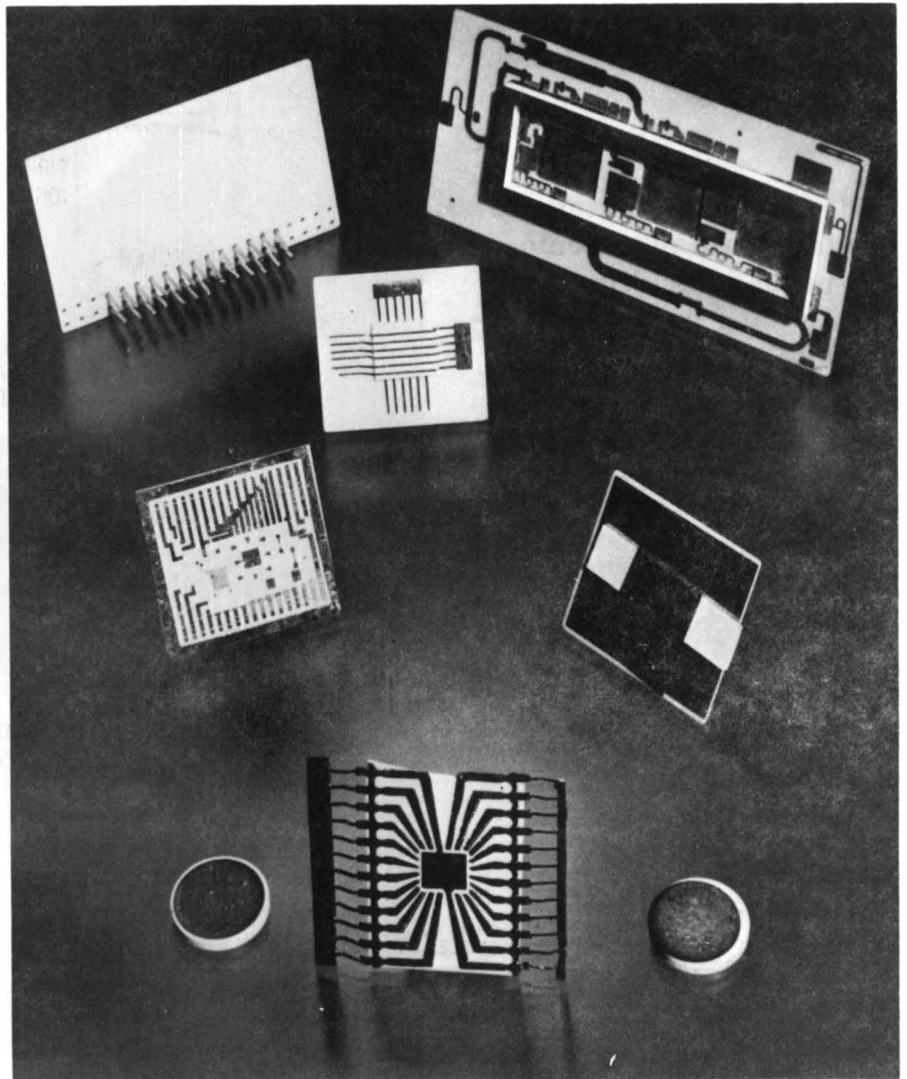


Fig. 4 Using direct bonded copper in constructing electronic packages.

Fig. 5 Process steps to fabricate electronic package by direct bonding process.

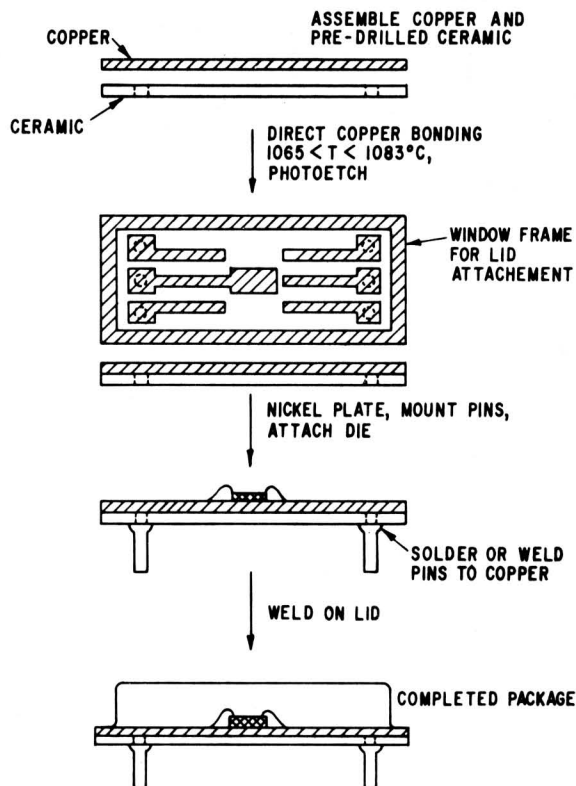
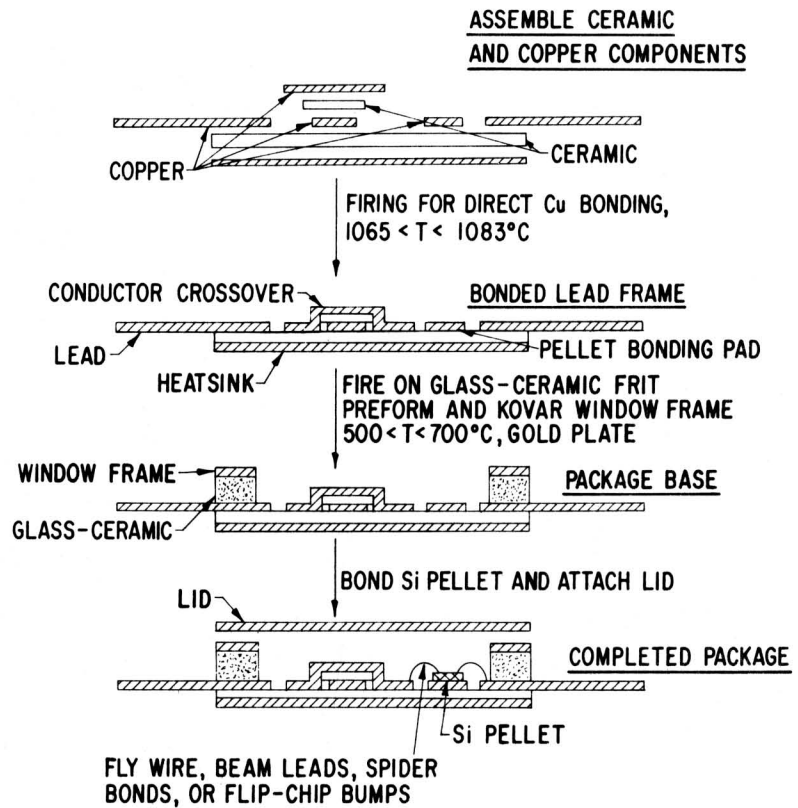


Fig. 6 Process steps to fabricate electronic package by direct copper bonding process.

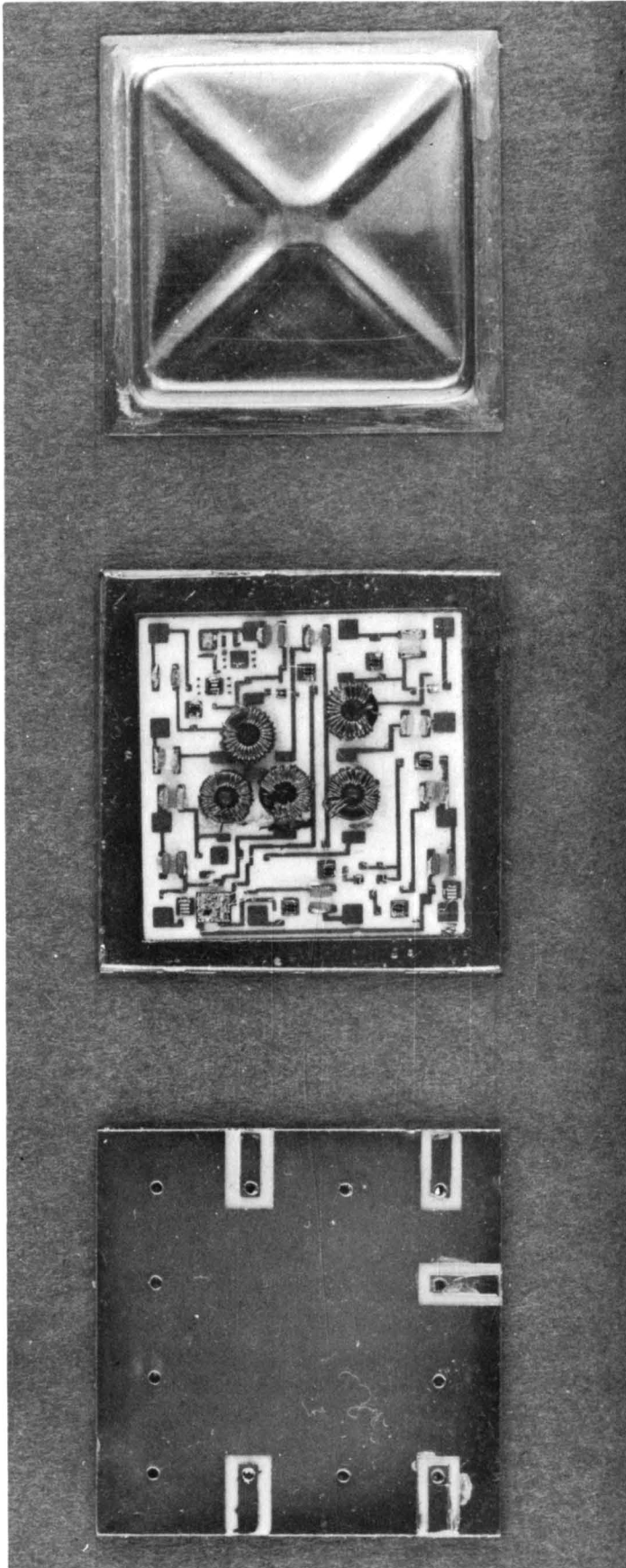


Fig. 7 Example of hybrid circuit fabricated by process illustrated in Fig. 6.

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