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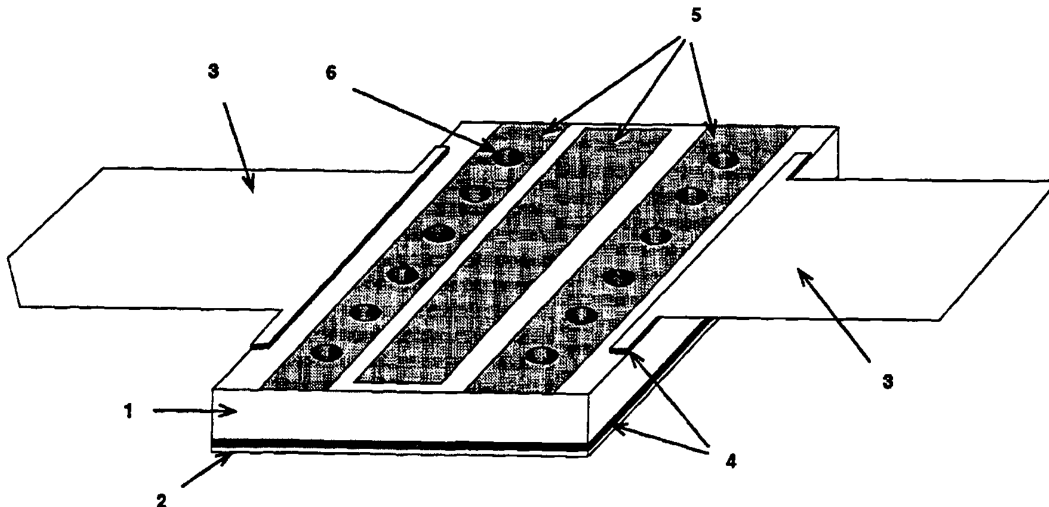

(57) Abstract

The present invention pertains to the packaging of electronic circuit. More particularly, the present invention pertains to methods for adherently bonding metals (4) to diamond (1) (i.e. the formation of a metal-diamond bonded structure) to yield metal-diamond substrates which are suitable for use in the fabrication of electronic packaging. These metal-diamond substrates exhibit both high thermal conductivity and dielectric isolation (where necessary), while being compatible with electronic package fabrication and the attachment of most semiconductor devices. The methods of the present invention include the formation of adherently bonded metal (5) by: the metallization of a bare diamond surface by the deposition of base coat or primer coat comprising certain carbide-forming metals such as molybdenum and tungsten; the metalization of a bare diamond surface using an active braze alloy; and by the growth of a diamond layer on a carbide-forming substrate by chemical vapor deposition (CVD).

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DIAMOND ELECTRONIC PACKAGES FEATURING BONDED METAL

TECHNICAL FIELD

The present invention pertains to the packaging of electronic circuits. More particularly, the present invention pertains to methods for adherently bonding metals to diamond (*i.e.*, the formation of a metal-diamond bonded structure) to yield metal-diamond substrates which are suitable for use in the fabrication of electronic packaging. These metal-diamond substrates exhibit both high thermal conductivity and dielectric isolation (where necessary), while being compatible with electronic package fabrication and the attachment of most semiconductor devices. The methods of the present invention include the formation of adherently bonded metal by: the metallization of a bare diamond surface by the deposition of base coat or primer coat comprising certain carbide-forming metals such as molybdenum and tungsten; the metallization of a bare diamond surface using an active braze alloy; and by the growth of a diamond layer on a carbide-forming substrate by chemical vapor deposition (CVD).

BACKGROUND

Throughout this application, various publications, patents, and published patent applications are referred to by an identifying citation. Corresponding complete citations are provided below under the heading "References." The disclosures of the publications, patents, and published patent specifications referenced in this application are hereby incorporated by reference into the present disclosure to more fully describe the state of the art to which this invention pertains.

Diamond has long been used as a heat spreader because of its superlative thermal conductivity, high electrical resistivity, low heat capacity and low dielectric constant. Historically, the high price of monocrystalline diamond has limited its exploitation in packaging to only a few applications, for example, in discrete laser diodes and microwave generating diodes (*e.g.*, IMPATT and Gunn diodes).

The use of monocrystalline diamond in electronic packaging has been reviewed (Seal, 1990) and the use of type IIa diamond monocrystals in electronic packages has been described (Seal, 1973). To be effective, the diamond must be larger in area than the heat generating area on the semiconductor die. For a given amount of heat dissipated from the
5 semiconductor, diamond is able to reduce the die temperature, thereby increasing the lifetime and performance of the device.

In general, for applications involving metal, the area of the diamond is much smaller than the area of the metal (usually copper) upon which it rests. The diamond is either bonded atop the copper (as a mesa), or embedded into a recess in the copper (as an
10 inlay). Inlay of diamond into the copper can be performed by an interference fit or by brazing. For example, Y.L. Potagenko *et al.*, describe a method of brazing metallized monocrystalline diamond into a recess in a copper holder using silver braze (Potagenko *et al.*, 1981). The size and strength of the copper enable it to be bonded or screwed onto a heat sink.

15 Similar methods of fabricating diamond heat spreaders embedded in metal have been described (Papanicolaou, 1984; Davies *et al.*, 1986). According to these methods, diamond substrates are first coated on all sides with a thin film metallization, typically titanium + platinum + gold *(i.e.,* Ti + Pt + Au) deposited by sputtering. The diamonds are then spaced evenly apart and bonded to an electrically conductive substrate. Steps are
20 taken so that all of the diamonds are electrically shorted together. The diamond array on its substrate is then immersed in a plating bath and electroplated with metal. The metal coats the diamond on all surfaces except the surface bonded to the substrate. Typically, the initial plating is 0.25 mm of copper, which may then be following by thin platings of nickel and gold. The diamonds are then de-bonded from the substrate, resulting in
25 diamonds embedded in copper to create a substrate ready to be mounted onto a heat sink.

The above-described technique is best suited to the processing of small pieces of diamond, typically monocrystalline diamond. The size and geometry of the copper surrounding the diamond is limited by the use of electroplating to deposit the copper.

Furthermore, this technique cannot be used to bond thick layers of metal to diamond, as is permitted by the methods of the present invention.

The introduction of freestanding chemically vapor deposited *(i.e.,* CVD) diamond has expanded the use of diamond in electronic packaging. The physical properties of CVD diamond now rival those of natural and synthetic diamond monocrystals. Freestanding CVD diamond is routinely synthesized with a thermal conductivity between 1000 and 1600 W/m°C and an electrical resistivity of 10^{15} Ω-cm. However, unlike monocrystalline diamond, CVD diamond can be grown and polished to areas up to about 120 mm diameter and thicknesses up to about 1.2 mm. The greater size of CVD diamonds has permitted an expansion of the electronic packages which incorporate them.

The use of freestanding CVD diamond substrates for the packaging of laser diodes and diode arrays has been described (Pickrell *et al.*, 1991; Bernstein, 1991). In these applications, the diamond is first metallized, typically by sputtering successive layers of titanium/platinum/gold *(i.e.,* Ti/Pt/Au), and the metallized diamond is then soldered or brazed to a copper heat sink. The III-V semiconductor laser is then soldered to the metallized diamond, typically using gold-tin *(i.e.,* Au-Sn) eutectic or indium *(i.e.,* In) solder. The low thermal expansion of diamond does not adversely affect the semiconductor die so long as the die area is less than about 4 mm^2. The metal sputtered onto the diamond is sufficiently thick to carry the electrical currents required for laser diode operation. In these applications, the utilization of CVD diamond is not much different than that of monocrystalline diamond; the major advantage of using CVD diamond in this case is lower cost.

The metallization of diamond has played a key role in the development of diamond as an electronic packaging material. Efforts to achieve successful diamond metallization have focused on various goals, such as: (1) the formation of ohmic contacts to semiconducting diamond; (2) die attach to gallium arsenide (*i.e.,* GaAs); (3) maximizing the adhesion of thin films on diamond as measured by pull strength testing; and (4) filling of vias in diamond.

The formation of reliable thin film ohmic contacts on semiconducting diamond has been described (Moazed *et al.*, 1990, 1991). Molybdenum *(i.e.,* Mo) and gold *(i.e.,* Au) were evaporated onto diamond monocrystals in high vacuum; the Mo films were 10-15 nm thick and the gold films were 150-500 nm thick. The films were then transferred to a
5 furnace, and then annealed (to bind the Mo + Au onto the diamond substrate) under 1 atm of purified hydrogen (*i.e.,* H_2) in a quartz tube furnace. The annealing time at 950°C was varied to study the effect on contact electrical resistance. Contact resistance was minimized after an 8 minute anneal. After annealing, the formation of a dimolybdenum carbide *(i.e.,* Mo_2C) phase at the Mo/diamond interface was confirmed by X-ray
10 diffraction. Moazed *et al.* included a micrograph of a gold wire ultrasonically bonded to the optimized Mo/Au thin film on the diamond (Moazed *et al.*, 1990). Another metal system was prepared which interposed 15-50 μm of nickel *(i.e.,* Ni) between the aforementioned Mo and Au. The addition of the Ni layer did not provide any measured performance benefits.

15 Various thin film metallization systems on diamond have been described (Burgess *et al.,*, 1994; Iacovangelo *et al,* 1994a). In these works, three different metallizations deposited by magnetron sputtering are compared: 100 nm titanium *(i.e.,* Ti) + 200 nm platinum *(i.e.,* Pt) + 500 nm gold *(i.e.,* Au); 100 nm titanium:tungsten *(i.e.,* Ti:W) + 500 nm gold (*i.e.,* Au); and 100 niobium (*i.e.,* Nb) + 500 nm gold (*i.e.,* Au). The authors
20 noted that platinum is a difficult metal to etch, but that niobium and niobium carbide (*i.e.,* NbC) are easier to etch. Samples of each metallization were exposed to air for 4 hours at 300, 400, 500, and 600°C. Based on X-ray photoelectron spectroscopy (XPS) depth profiles, the Ti:W/Au system was the most stable in terms of resisting the in-diffusion of oxygen and the out-diffusion of titanium. Again, the Ti:W system performed
25 well in wire bond and pull testing.

Iacovangelo *et al.* also describe a method for achieving die attachment between diamond and a larger gallium arsenide *(i.e.,* GaAs) die without the large coefficient of thermal expansion (CTE) mismatch damaging the GaAs die (Iacovangelo *et al.*, 1994b).

The diamond was laser sawn with grooves and the grooves were backfilled with a ductile metal which has a better CTE match to GaAs. Thus, there is no direct, rigid bond between the diamond and the large GaAs die and heat is transferred from the ductile interface to the large surface area of grooved diamond.

5 Naseen *et al.* compared three different thin film metallizations on diamond. The metallizations were titanium:tungsten (*i.e.*, Ti:W) + gold (*i.e.* , Au); chromium (*i.e.*, Cr) + gold (*i.e.* , Au); and titanium (*i.e.*, Ti) + gold (*i.e.*, Au); and were formed by sputtering and evaporation (Naseen *et al.*, 1993). The authors measured the adhesion of the films as a function several parameters, including (1) annealing the metallizations in 1 atm dry

10 nitrogen (*i.e.*, N_2) for 30 minutes at temperatures up to 450°C and (2) *in-situ* sputter etching of the diamond immediately prior to sputter deposition of the base metallization. The authors concluded that the most adherent and refractory metallization was the Cr + Au film as evaporated on diamond and annealed at 450°C. The other metallizations suffered from extensive intermixing of the gold with the underlying metals.

15 Bachili *et al.* described the interaction between 135 nm thick sputter-deposited tungsten films and a CVD diamond substrate (Bachili *et al.*, 1994a). The films were annealed in vacuum between 700 and 1100°C for 1 hour. The composition of the film after annealing was measured by several methods. It was determined that as the temperature increases, ditungsten carbide (*i.e.*, W_2C) forms first, followed by

20 monotungsten carbide (*i.e.*, WC). Ditungsten carbide formed first at the open metal surface and not at the metal-diamond interface.

Bachili *et al.* also described the interaction between 130 nm thick sputter-deposited molybdenum (*i.e.*, Mo) films and a CVD diamond substrate (Bachili *et al.*, 1994b). The films were annealed in vacuum between 600 and 1100°C for 1 hour. The composition of

25 the film after annealing was measured. Over the temperature range of 700 to 1100°C, the only carbide phase observed was dimolybdenum carbide (*i.e.*, Mo_2C); monomolybdenum carbide (*i.e.*, MoC) was not observed. Above 1000°C, carbon (*i.e.*, C) diffused from the diamond through the Mo_2C layer and formed a graphite film at the open surface. The

authors also compared the interaction between Mo/diamond with previous results published on the interaction between tungsten/diamond, tantalum/diamond, and niobium/diamond. Mo_2C is formed after a 1 hour anneal at 700°C whereas Ta_2C and W_2C do not form until after a 1 hour anneal at 900°C.

5 Zarnoch *et al.* discuss the metallization of diamond by CVD tungsten (Zarnoch *et al.*, 1994). The optimal procedure for achieving adhesion between tungsten *(i.e.,* W) and diamond had the following three steps: (1) depositing a 200 nm tungsten layer at 450°C; (2) heating the thin tungsten layer to 960-990°C in hydrogen *(i.e.,* H_2) for 30 minutes; and (3) cooling to 650°C and depositing an additional 10-50 μm of tungsten.
10 The adhesion strength of the optimized tungsten films exceeded 10 kpsi (680 atm, 69 MPa).

Several methods for the formation and filling of metal vias in freestanding diamond substrates have been described. Iacovangelo *et al.* describe the filling of vias in diamond *(e.g.,* 50 μm diameter vias in 200 μm thick diamond substrates) with CVD tungsten
15 (Iacovangelo, *et al.*, 1995). Sputtering or evaporation were considered unsuitable for via filling because of their slow deposition rates, and their inability to fill vias with high aspect ratios. Low pressure chemical vapor deposition (LPCVD) of tungsten (from mixtures of tungsten hexafluoride, WF_6, and hydrogen, H_2) was selected because of the typical tungsten deposition rate of about 14 μm/hour, and its excellent "throwing power."
20 Diamond substrate temperatures during LPCVD of tungsten ranged from 450 to 650°C. Goldman describes via holes in diamond filled with metal using active brazing pastes or powder (Goldman, 1994). These active brazing formulations are heated in an inert atmosphere to form an electrically conductive path adherent to the diamond.

As shown by Table 1 below, which lists a number of physical properties of
25 materials used in electronic packages, diamond suffers from one physical property which makes its utilization in electronic packages difficult, namely, an unusually low coefficient of thermal expansion (CTE). This low CTE causes mismatch problems in three general areas: die attach, copper metallization, and hermetic package compatibility.

Table 1
Properties of various electronic packaging materials at room temperature

Material	85W/15Cu	Cu	Mo	Al_2O_3	AlN	BeO	GaAs	Si	CVD Diamond
Density (g/cm^3)	16.4	8.93	10.2 2	3.60	3.4	2.90	5.32	2.33	**3.51**
Specific Heat (J/kg°C)	170	380	250	840	750	960	320	702	**472**
Thermal Conductivity (W/cm°C)	1.90	3.98	1.38	0.17	1.7	2.5	0.44	1.51	**12**
Coefficient of Thermal Expansion (20-400°C, ppm/°C)	7.2	17.8	5.5	7.0	4.6	7.6	6.5	3.4	**1.2**
Dielectric Constant @ 1 MHz	n/a	n/a	n/a	9.8	8.5	6.6	13.2	11.8	**5.7**
Electrical Resistivity (Ω-cm)	5×10^{-6}	1.6×10^{-6}	5×10^{-6}	10^{13}	10^{14}	10^{15}	varies	varies	**10^{15}**

It is desirable to intimately bond gallium arsenide *(i.e.,* GaAs) and other III-V semiconductors to diamond or to thin metal layers bonded to diamond. However, since the CTE of GaAs (6.5 ppm/°C) is higher than the CTE of diamond (1.2 ppm/°C), the die will be placed in tension upon cool down from die attach soldering step, as well as during thermal cycling. This tensile stress can fracture the GaAs die. In the case of III-V semiconductors, various electrical properties (such as the bandgap) also change significantly as a function of stress. Diamond- or silver-filled epoxies are compliant enough to serve as a die attach medium between diamond and semiconductors, but these epoxies suffer from low thermal conductivity (*e.g.*, less than 12 W/m°C) and must be at least 3 mils (75 μm) thick.

Power hybrid circuits require thick (greater than 8 mils, 200 μm copper metallization lines on dielectric substrates in order to carry high currents. A noncompliant bond between thick copper and diamond may lead to cracking of the copper and/or diamond due to the high CTE of Cu (16.9 ppm/°C).

The substrate upon which the die is placed should have a similar CTE as the other structures, especially in hermetic packages. Hermetic packages must be able to withstand

a large number of thermal cycles without the failure of any component in the package, such as in MILSPEC thermal cycling stress tests. For example, an excessively low CTE substrate can promote the rupture of wire leads which bridge the die to the feed-throughs on the side of the package. A low CTE substrate can also promote the loss of hermeticity
5 at the joint between the package lid and its sides.

Another issue in the metallization of diamond is in the fabrication of brazed packages intended for high power, high frequency silicon devices. The thermal resistance of high frequency transistors cannot be reduced by increasing die area, since this will reduce the frequency response of the transistor. A diamond heatspreader beneath the
10 transistor enables greater heat dissipation, greater efficiency, and greater power-to-load without a reduction in the upper frequency limit of the device. Presently, a wide variety of high power silicon devices, especially radio frequency (RF) & microwave bipolar transistors and vertical-DMOS transistors, are mounted in brazed ceramic + metal packages. These particular devices must be die attached to an electrically isolated gold pad
15 on the ceramic. The most common package is comprised of pattern-metallized beryllium oxide *(i.e.,* beryllia, BeO) brazed to metal leads and a metal flange. Such brazed packages usually exhibit hermeticity and imperviousness to harsh environmental conditions such as repeated temperature cycling and mechanical shock.

High frequency, high power silicon transistors would benefit from the substitution
20 of diamond for BeO because of diamond's superlative thermal conductivity and lower dielectric constant, as shown in Table 1. To address this very important application of diamond, the metallization of diamond should permit a direct substitution of diamond for BeO to create similar brazed packages. Therefore, the metallization of the diamond should withstand the same unit operations used to fabricate BeO + metal packages, namely:
25 (1) pattern metallization; (2) brazing the diamond to metal leads and a metal flange using a high temperature braze such as copper-silver (*i.e.,* Cu-Ag) eutectic; and (3) electroplating gold onto the metal pads on the diamond.

After experiencing package fabrication, the metallization on the diamond should then support the attachment of the silicon die using gold/silicon *(i.e.,* Au/Si) eutectic at the braze joint. This die attach is performed by heating the package to 420°C in air and then scrubbing a gold metallized silicon die onto the gold pad atop the diamond. The quality of
5 the braze joint between the silicon and the diamond is very important since this interface must conduct all of the heat away from the die. A diamond heatspreader beneath a silicon die will not be able to reduce the die temperature unless the die attach joint is substantially free of voids. Therefore, providing a metallization on diamond which enables an essentially void-free Au/Si die attach is of particular importance in demonstrating the
10 utility of diamond packages for RF & microwave silicon devices.

There are non-destructive and destructive methods of determining the amount of voids in a Au/Si die attach joint. The most common non-destructive techniques are X-ray radiography and C-mode scanning acoustic microscopy (C-SAM). The most common destructive technique is die attach and die shear. If the silicon die is expendable, the die
15 can be mechanically sheared off the diamond with a chisel. If the die attach joint is good, then the silicon die will cleave above the joint over the entire die area. Regardless of the method used for evaluation, the void area in the die attach region is preferably less than 10%.

The three most common ceramics used as dielectric substrates are alumina
20 *(i.e.,* Al_2O_3), beryllium oxide (*i.e.,* beryllia, BeO) and aluminum nitride (*i.e.,* AlN). These particular dielectrics are widely used by the electronics industry because of their high thermal conductivities (which are higher than those of other dielectrics except diamond). Methods used to bond thick metal to these ceramics in electronic packaging have been reviewed (Intrater, 1989). With alumina and beryllia, three methods are commonly
25 employed: the molybdenum/manganese *(i.e.,* Mo/Mn) method, direct bond copper, and active brazing. These techniques are briefly summarized here.

In the Mo/Mn process, a paste containing the refractory metal powders molybdenum *(i.e.,* Mo) and manganese *(i.e.,* Mn) is screened onto the ceramic, the ceramic

is fired in a wet hydrogen *(i.e.,* H_2) atmosphere at 1400°C, and the resulting metallized surface is soldered or brazed to a metal in a hydrogen or nitrogen atmosphere. The Mo/Mn process is very effective for metallizing oxide ceramics such as alumina and beryllia, but it is unsuitable for metallizing diamond.

5 In the direct-bond copper (DBC) process, copper can be directly bonded to oxide ceramics such as alumina and beryllia by forming an oxide phase at the copper-ceramic interface. Proper heat treatment in an oxygen-bearing ambient will form a copper oxide *(i.e.,* CuO_x) phase at the interface which is highly adherent to both the copper and the ceramic. Typically, copper sheet between 8 and 25 mils thick is directly bonded to

10 ceramic plates whose thickness is about twice that of the copper. However, since carbon oxides are gaseous and since carbon is not soluble in copper, a similar direct bonding process between copper and diamond is not possible.

In active brazing, a special braze alloy, typically containing a few percent of titanium *(i.e.,* Ti) is placed between the ceramic and the metal. The braze is melted in a

15 vacuum furnace to prevent contamination of the titanium with oxygen, water vapor or nitrogen. Because aluminum nitride (*i.e.,* AlN) is not an oxide and does not include a silicate glass phase, the most common method of bonding thick metal to AlN is active brazing.

All three of these bonding methods are used to create electronic structures and

20 packages, such as dual in-line packages, flanged packages, surface mount packages, and various packages intended for high power semiconductor devices, especially high frequency devices.

Despite the extensive studies, including those briefly discussed above, the inventors are not aware of any prior publication which disclose a metallization on diamond

25 compatible with the following sequence of unit operations: (1) conventional methods of package braze assembly (*e.g.,* using Cu-Ag eutectic brazing); (2) electroplating with gold *(i.e.,* Au); and (3) gold/silicon (*i.e.,* Au/Si) die attachment in air which produces a joint with less than 10% void area. In contrast to the prior approaches, the methods of the

present invention permit the fabrication of diamond metallizations which are so compatible. The metal-diamond substrates prepared using the methods of the present invention offer high temperature stability (they tolerate thermal cyclic and brazing without metal detachment) and compatibility with gold electroplating.

5 None of the studies discussed above adequately address the issues addressed by the present invention, namely, (1) the bonding of metal to diamond to enable high current carrying capability of patterned metal conductors bonded to a diamond substrate, (2) the fabrication of packages containing a plurality of leads emanating from the sides of the diamond substrate, such as dual in-line packages, flanged packages and various surface 10 mount ("pill" style) packages, (3) a metallization on diamond which is compatible with package assembly using copper-silver *(i.e.,* Cu-Ag) eutectic brazing, and (4) metallization on diamond which is compatible with electroplating of gold, followed by gold/silicon *(i.e.,* Au/Si) eutectic die attachment in air.

In accordance with the present invention, the above-described electronic structures 15 and packages can be replicated using diamond instead of other ceramic materials. As discussed above, since diamond is not an oxide and does not include a silicate phase, it is incompatible with conventional Mo/Mn and direct bond copper procedures. Therefore, most procedures used to fabricate conventional, oxide ceramic packages are inapplicable to diamond. The present invention provides other methods for bonding metal to diamond to 20 produce metal-diamond substrates *(i.e.,* electronic packages) which are similar in design and function to conventional ceramic packages.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of a diamond surface-mount package intended 25 for high power, high frequency silicon bipolar transistors.

Figure 2 is a schematic illustration of an exploded view of the diamond package shown in Figure 1.

Figure 3 is a schematic illustration of a flange package with a diamond inlay.

SUMMARY OF THE INVENTION

One aspect of the present invention pertains to methods for fabricating metal-diamond substrates utilizable in an electronic package structure, said methods comprising the steps of: providing a sheet of freestanding CVD diamond having at least one bare diamond surface; depositing a first carbide-forming metal material comprising one or both of Mo and W on said at least one bare diamond surface; depositing a second metal material comprising one or more of Au, Ni, Pt, or Ag on said first material; and annealing the resulting structure to promote adhesion between said carbide-forming metal material and said CVD diamond, thereby forming a metal-diamond bonded structure. In some preferred embodiments, said first carbide-forming metal material comprises Mo, W, or both. In some preferred embodiments, said first carbide-forming metal material is Mo + W or Mo + Ti:W. In some preferred embodiments, said second metal material comprises Au or Pt or both. In some preferred embodiments, said first carbide-forming metal material is Mo and said second metal material comprises Au. In some preferred embodiments, said first carbide-forming metal material is Mo + Ti:W and said second metal material comprises Au. In some preferred embodiments, said first carbide-forming metal material and said second metal material are deposited on portions of said freestanding CVD diamond sheet with the aid of a masking device. In some preferred embodiments, said sheet of freestanding CVD diamond has a thickness 250-1500 μm; said first carbide-forming metal material comprising Mo has a thickness 10-1000 nm; and/or said second metal material has a thickness of 10-1000 nm. In some preferred embodiments, said annealing is performed at a temperature of 500-1050°C for 0.1-180 minutes. In some preferred embodiments, said annealing is performed at a temperature of 750-850°C for 1-30 minutes. In some preferred embodiments, said annealing is performed in a vacuum or in an atmosphere of a noble gas.

Another aspect of the present invention pertains to methods for fabricating metal-diamond substrates utilizable in an electronic package structure, said methods comprising the steps of: providing a sheet of freestanding CVD diamond having at least

one bare diamond surface; contacting said at least one bare diamond surface with an active braze alloy; and melting said active braze alloy, thereby forming a metal-diamond bonded structure. A related aspect of the present invention pertains to methods for fabricating metal-diamond substrates utilizable in an electronic package structure, said methods
5 comprising the steps of: providing a sheet of freestanding CVD diamond having at least one bare diamond surface; contacting said at least one bare diamond surface with an active braze alloy; contacting said active braze alloy with a metal; and melting said active braze alloy, thereby forming a metal-diamond bonded structure. In some preferred embodiments, said active braze alloy has the following properties: a lower melting point
10 than that of said metal (if present); the ability to wet and bond to both said CVD diamond and said metal; a yield strength of less than 400 MPa; and a thermal conductivity greater than 10 W/m°C. In some preferred embodiments, said active braze alloy is selected from the group of active braze alloys which comprise Au, Ni, and V; Ag, Cu, and Ti; and Ag, Cu, Sn, and Ti. In some preferred embodiments, said active braze alloy has an
15 approximate composition of 97.5% by weight Au, 0.75% by weight Ni, and 1.75% by weight V. In some preferred embodiments, said active braze alloy has an approximate composition of 63.0% by weight Ag, 35.25% by weight Cu, and 1.75% by weight Ti. In some preferred embodiments, said active braze alloy has an approximate composition of 34.25% by weight Cu, 63% by weight Ag, 1% by weight Sn, and 1.75% Ti. In some
20 preferred embodiments, said melting is performed in a vacuum or in an atmosphere of a noble gas. In some preferred embodiments, said melting is performed at a temperature 5-30°C above the liquidus temperature of the said active braze alloy for a time of 0.1-180 minutes.

Yet another aspect of the present invention pertains to methods for fabricating
25 metal-diamond substrates utilizable in an electronic package structure, said methods comprising the steps of: providing a carbide-forming substrate; and growing a diamond layer on said substrate utilizing chemical vapor deposition to form a metal-diamond bonded structure. In some preferred embodiments, said carbide-forming substrate has a

thickness less than 1.5 mm and said diamond layer has a thickness of 10-1200 μm. In some preferred embodiments wherein said carbide-forming substrate has a thickness greater than 1.5 mm, said method further comprises the step of: reducing the thickness of said carbide-forming substrate to less than 1.5 mm. In some preferred embodiments, said carbide-forming substrate is selected from the group consisting of Mo, Nb, V, Ti, Ta, W, Zr, Hf, Cr, and Si, more preferably Mo.

Related aspects of the present invention pertain to methods, as described above, further comprising the step of: depositing an additional layer of metal on said metal-diamond bonded structure. In some preferred embodiments, said additional layer of metal comprises Au, Ag, Cu, Ni, or Pt. In some preferred embodiments, said additional layer of metal has a thickness of 1-10 μm. In some preferred embodiments, said additional layer of metal is deposited by electroplating.

Other related aspects of the present invention pertain to methods, as described above, further comprising the step of: selectively removing a portion of the metal of said metal-diamond bonded structure to yield a patterned metal-diamond bonded structure. In some preferred embodiments, said patterned metal-diamond bonded structure forms electrically isolated conductor lines, leads, metal pads, or combinations thereof. In some preferred embodiments, said removal a portion of the metal of said metal-diamond bonded structure is achieved by ion-beam milling.

Still other related aspects of the present invention pertain to methods, as described above, further comprising the step of: contacting said, metal-diamond bonded substrate with a braze alloy; contacting said braze alloy with a metal; and melting said braze alloy, thereby brazing said metal to said metal-diamond bonded substrate. In some preferred embodiments, said braze alloy comprises Cu and Ag. In some preferred embodiments, said braze alloy is a Cu-Ag eutectic braze alloy. In some preferred embodiments, said metal is a metal foil, a metal sheet, a heat sink, or a metal flange. In some preferred embodiments, said metal is a Cu, a Cu alloy, or a Cu-containing composite. In some preferred embodiments, said metal is a Ag, a Ag alloy, or a Ag-containing composite.

Yet other related aspects of the present invention pertain to methods, as described above, further comprising the step of: attaching a semiconductor die to said metal-diamond bonded substrate.

Still other related aspects of the present invention pertain to methods, as described above, further comprising the steps of: depositing an additional layer of Au on said metal-diamond bonded structure; placing a silicon semiconductor die in contact with said additional layer of Au; and, heating the resulting structure to form a Au-Si eutectic at the Au-Si interface. In some preferred embodiments, said additional layer of Au is annealed prior to placing said silicon semiconductor die. In some preferred embodiments, said heating is performed at a temperature of 360-440°C.

Still another aspect of the present invention pertains to the assemblies obtained using the methods of the present invention.

As will become apparent, many preferred features and characteristics of one aspect of the invention are applicable to other aspects of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides methods for adherently bonding metal to diamond (*i.e.,* the formation of a metal-diamond bonded structure) so as to deliver the benefits of diamond, namely high thermal conductivity and dielectric isolation, while enabling the diamond to be compatible with package fabrication procedures (including, for example, brazing and electroplating) followed by die attachment.

The methods of the present invention are particularly useful in the preparation of metal-diamond substrates comprising a diamond-metal bonded structure wherein metal (*e.g.,* in the form of a foil, sheet, or plate typically with a thickness of 0.05-80 mils, 1-2000 μm) is adherently bonded to a diamond substrate (*e.g.,* in the form of a sheet typically with a thickness of 0.4-60 mils, 10-1500 μm more preferably 10-40 mils, 250-1000 μm). On a typical diamond-metal bonded structure, the metal bonded to the diamond can be of variable thickness; that is, it may be thin in some areas and thick in other areas of the same diamond. The diamond/metal system maintains a very strong bond

and a very low thermal resistance, Θ, despite thermal cycling (*e.g.*, from -40 to 150°C; thermal cycling does not cause fracture, cracking, peeling or spalling of the metal, the diamond or the bond joint).

Metal adherently bonded to diamond is useful in a variety of applications, particularly in the fabrication of electronic packages. More specifically, the metal-diamond bonded structures obtained using the methods for adherently bonding metal to diamond of the present invention permit one or more of the following applications: (1) brazing of metallized diamond to metal parts (*e.g.*, metal sheets/plates) using non-active, high temperature braze alloys such as copper-silver (*i.e.*, Cu-Ag) eutectic; (2) electroplating metallized diamond, for example, with gold (*i.e.*, Au); (3) direct attachment of silicon (*e.g.*, a silicon die) to metallized diamond using gold/silicon (*i.e.*, Au/Si) eutectic with a low amount of voids (*i.e.*, low void area) at the joint; (4) formation of thick metal leads or metal pads bonded to diamond; (5) metal filling of vias in diamond in a manner compatible with high temperature processing; (6) bonding of diamond to CTE mismatched dice such as gallium arsenide (*i.e.*, GaAs).

A. Methods for Adherently Bonding Metal to Diamond

The present invention pertains to methods for adherently bonding metal to diamond. Three general methods for adherently bonding metal to diamond are described in detail below. These methods may be employed alone or in combination in the fabrication of useful metal-diamond substrates, electronic packages, and electronic devices, which feature diamond.

A.1. Direct Chemical Vapor Deposition (CVD) of Diamond onto Metal.

The first general method of the present invention permits the deposition of highly adherent diamond films and particles onto carbide-forming metal substrates. By controlling the substrate temperature and process gas chemistry, diamond particles and films can be chemically bonded to carbide-forming metal surfaces which have been

previously polished to a mirror finish. In the case of molybdenum (see Example 1, below), the inventors theorize that the excellent smoothness of the molybdenum substrate eliminated mechanical anchoring as an adhesion mechanism between the diamond and the substrate, and that molybdenum carbide (*i.e.*, MoC_x) phases formed at the
5 diamond/molybdenum interface were responsible for the excellent adhesion.

According to the methods of the present invention, CVD diamond layers, for example, of thickness 0.4-47 mils (10-1200 μm), more preferably 0.4-40 mils (10-1000 μm) can be directly grown onto suitable carbide-forming metal substrates, such as molybdenum, to create a bonded structure. Suitable carbide-forming metal substrates
10 include molybdenum (*i.e.*, Mo), niobium (*i.e.*, Nb), vanadium (*i.e.*, V), titanium (*i.e.*, Ti), tantalum (*i.e.*, Ta), tungsten (*i.e.*, W), zirconium (*i.e.*, Zr), hafnium (*i.e.*, Hf), chromium (*i.e.*, Cr), and silicon (*i.e.*, Si). A preferred carbide-forming metal substrate is molybdenum (*i.e.*, Mo).

A metal substrate, for example, with a thickness of less than 60 mils (1.5 mm), can
15 be used directly as a substrate for the CVD of diamond. Alternatively, diamond can be grown on a metal substrate, for example, with a thickness of greater than 60 mils (1.5 mm), and the metal subsequently reduced to the required thickness (*e.g.*, less than 60 mils, 1.5 mm) by sawing, grinding and/or lapping. The latter process is demonstrated below in Example 1.

20 The metal layer adherently bonded to the diamond can be patterned and etched using standard methods to yield useful structures, or it may be used as a precoat or primer layer -which is in turn brazed or soldered to other materials such as a copper heatsink or a semiconductor die, as described herein.

25 A.2. Adherently Bonding Metal to Diamond Using Active Braze Alloys

Brazing is a method of bonding together materials by use of a liquid phase. Typically, a braze alloy is introduced and melted between two surfaces. To form a strong joint, the braze alloy must wet and bond to both materials. The flowing, liquid state of the

braze alloy promotes the elimination of voids and accelerates the inter-diffusion of the elements responsible for bonding. The optimal braze alloy for bonding diamond to metal (*e.g.*, a metal sheet) has the following properties: (1) the ability to wet both the (bare or metallized) diamond and the metal sheet; (2) a brazing temperature below the melting point of the metal sheet; (3) a low solubility in the metal sheet when liquid; (4) a low yield strength; and (5) a high thermal conductivity.

Several braze alloys, denoted herein as active braze alloys, permit the direct attachment of metals to bare diamond; that is, without the need of a base coat or primer coat (although one may be present). The term "active braze alloy" is used herein to refer to braze alloys which contain from about 0.5 to about 4 percent by weight active metals, such as titanium (*i.e.*, Ti), molybdenum (*i.e.*, Mo), and/or vanadium (*i.e.*, V). A wide variety of active metal braze alloys are available from commercial suppliers and are typically available as a foil, typically 2-6 mils (50-150 μm) thick, wire, powder or paste.

Active braze alloys are preferably melted (*e.g.*, in a brazing step) in a vacuum (*e.g.*, a high vacuum furnace with a low leak-up rate) or in an atmosphere of a noble gas to prevent oxidation of the active metal. The terms "vacuum" and "high vacuum" are used herein to refer to pressure of less than about 1×10^{-4} mm Hg (0.013 Pa), more preferably less than about 1×10^{-5} mm Hg (0.0013 Pa), still more preferably less than about 1×10^{-6} mm Hg (0.00013 Pa). Typically, melting is performed at a temperature 5-30°C above the liquidus temperature of the braze alloy for a time of 0.1-180 minutes, more typically 1-30 minutes.

Preferred active brazes have the following properties: (1) a lower melting point than that of the metal being bonded (if present); (2) the ability to wet and bond to both said CVD diamond and the metal being bonded (if present); (3) a yield strength of less than 400 MPa; and (4) a thermal conductivity greater than 10 W/m°C. Suitable active braze alloys include those which comprise gold (*i.e.*, Au), vanadium (*i.e.*, V), and nickel (*i.e.*, Ni), such as those which have the approximate composition of 96.4% by weight Au, 1.75% by weight V, and 0.25% by weight Ni. See Example 5 below. Other suitable active

braze alloys include those which comprise silver (*i.e.*, Ag), copper (*i.e.*, Cu), and titanium (*i.e.*, Ti), such as those which have the approximate composition of 63.0% by weight Ag, 35.25% by weight Cu, and 1.75% by weight Ti. See Example 2 below. Still other suitable active braze alloys include those which comprise copper (*i.e.*, Cu), silver (*i.e.*, Ag), tin (*i.e.*, Sn) and titanium (*i.e.*, Ti), such as those which have the approximate composition of 34.25% by weight Cu, 63% by weight Ag, 1% by weight Sn, and 1.75% Ti. See Examples 3, 4, and 6 below.

Active braze alloys may be used in at least two ways to achieve diamond metallization (*i.e.,* the formation of a metal-diamond bonded structure). A first method comprises the steps of: (1) providing a sheet of freestanding CVD diamond with at least one bare diamond surface; (2) contacting that bare diamond surface with an active braze alloy; (3) contacting the active braze alloy with a metal; and (4) melting the active braze alloy, thereby forming a metal-diamond bonded structure. For example, the active braze alloy may be interposed between the bare diamond and a metal to be bonded to the diamond (*e.g.,* in the form of a metal sheet), and the active braze alloy melted. Examples of such processes are described below in Examples 2, 3, and 4.

In another method, in which the active braze alloy itself forms the metallization on the diamond, the active braze alloy is placed in contact with the bare diamond and melted. Thus, a second method comprises the steps of: (1) providing a sheet of freestanding CVD diamond having at least one bare diamond surface; (2) contacting the bare diamond surface with an active braze alloy; and (3) melting the active braze alloy, thereby forming a metal-diamond bonded structure. An advantage of this method is evident when it is noted that it is faster to melt 2 mils (50 μm) of active braze onto a diamond than it is to deposit the same thickness by evaporation or sputtering. Examples of such processes are described below in Examples 5 and 6.

A.3. Adherently Bonding Metal to Diamond by Solid State Diffusion and Reaction Bonding (Followed by Brazing)

Many braze alloys, denoted herein as non-active braze alloys permit the attachment of metals to diamond, but only if the diamond is pre-coated with a base coat or primer coat. 5 The term "non-active braze alloy" is used herein to refer to braze alloys which are essentially free of titanium (*i.e.*, Ti), molybdenum (*i.e.*, Mo), and/or vanadium (*i.e.*, V). Like active braze alloys, a wide variety of non-active metal braze alloys are available from commercial suppliers and are typically available as a foil, typically 2-6 mils (50-150 μm) thick, wire, powder or paste.

10 A variety of materials will diffuse and bond to diamond in a solid state reaction, thereby forming a base coat or primer coat suitable for subsequent non-active brazing. A common example (which has been used in the past) is a thin film of sputtered or evaporated titanium (*i.e.*, Ti), which bonds to diamond and forms the adhesion layer for conventional titanium/platinum/gold (*i.e.*, Ti/Pt/Au) metallization of diamond. Titanium 15 bonds to diamond at low temperatures (*e.g.*, between 20 and 200°C) because of the high diffusivity of titanium and the strong tendency of titanium to form titanium carbide (*i.e.*, TiC_x).

The use of titanium as the adhesion layer is suitable when the diamond does not need to be exposed to high temperatures after metallization. For example, the conventional 20 titanium/platinum/gold (*i.e.*, Ti/Pt/Au) metallization is adequate when the warmest temperature experienced by the metallized diamond is a 300°C gold/tin (*i.e.*, Au/Sn) eutectic die attach.

However, a titanium base coat is incompatible with copper-silver (*i.e.*, Cu-Ag) brazing or gold/silicon (*i.e.*, Au/Si) die attach performed in air. When heated, titanium is 25 capable of reacting with most gases and vapors except the noble gases. For example, hot titanium will react with nitrogen (*i.e.*, N_2) to form titanium nitride (*i.e.*, TiN) and with hydrogen (*i.e.*, H_2) to form titanium hydride (*i.e.*, TiH_2). If a titanium thin film on

diamond is heated above 400°C in vacuum, titanium rapidly diffuses away from the diamond/titanium interface and adhesion is lost between the metal and the diamond.

The inadequacy of these base coats in such applications is demonstrated by the following comparative examples. Polished diamond substrates were sputter coated with 100 nm titanium (*i.e.*, Ti) + 200 nm platinum (*i.e.*, Pt) + 3000 nm gold (*i.e.*, Au). The samples were not annealed after coating. Metallized silicon (*i.e.*, Si) dice were attached to the metallized diamond using gold/silicon (*i.e.*, Au/Si) eutectic, and the die attach joints were then imaged by X-ray radiography. The images revealed over 50% void areas between the diamond and the silicon. Similar Ti/Pt/Au samples were annealed at 800°C for 5 minutes in dry hydrogen (*i.e.*, H_2). Silicon die attach and die shear experiments resulted in complete removal of the silicon and the metallization from the diamond.

In another comparative example, two polished diamonds were coated with 82 nm titanium:tungsten (*i.e.*, Ti:W) + 1520 nm gold (*i.e.*, Au) and two more were coated with 81 nm titanium:tungsten (*i.e.*, Ti:W) + 400 nm nickel (*i.e.*, Ni) + 1500 nm gold (*i.e.*, Au). One diamond with each metallization was directly attached to silicon via *in-situ* formation of gold/silicon (*i.e.*, Au/Si) eutectic, and the other diamond was die attached to silicon using gold/silicon (*i.e.*, Au/Si) preforms. No post-metallization anneal was performed on any of these samples. Shearing of all silicon dice on all four samples resulted in removal of the metallization from the polished diamond. In all four cases, there was insufficient adhesion between the Ti:W layer and the diamond to withstand the rigor of die attach.

The methods of the present invention overcome the above inadequacies of conventional Ti/Pt/Au and Ti:W/Au metallizations. The solid state diffusion and reaction bonding methods of the present invention, which employ a base coat or primer coat comprising certain carbide forming metals (*i.e.*, molybdenum, Mo and tungsten, W), more preferably molybdenum (*i.e.*, Mo), as a metallization, offer better high temperature compatibility. Examples of molybdenum-containing base coats suitable for use in the methods of the present invention include Mo/M, Mo/W/M, and Mo/Ti:W/M, where M denotes a metal such as Au, Ni, Pt, or Ag. Examples of tungsten-containing base coats

suitable for use in the methods of the present invention include W/M and W/Ti:W/M, where M denotes a metal such as Au, Ni, Pt, or Ag. Typically, the base coat layer and the layer of metal M have thicknesses of 10-1000 nm. The methods for depositing the base coats are typically sputtering or evaporation, and the resulting metallization may require annealing (*e.g.*, prior to brazing, often preferably in a vacuum or in an atmosphere of a noble gas) to enhance adhesion to the diamond. Base coats may be deposited on portions of said freestanding CVD diamond sheet with the aid of a masking device (*e.g.*, a contact shadow mask).

Such thin films (*i.e.*, a primer coat or base coat) (1) promote a void-free die attach between diamond and material (*e.g.*, semiconductor die); (2) form a strong bond with (*e.g.*, non-active) braze alloys used to bond thick metals or ceramics onto the diamond; (3) coat the inside surfaces of via holes (*i.e.*, vias) in diamond to render them electrically conductive; and (4) provide a surface which can support the electroplating of highly adherent metals such as gold or nickel + gold.

The diamond metallizations obtained using the methods of the present invention (which employ a base coat comprising certain carbide forming metals) facilitate the attachment of other materials, as described herein. These metallizations are compatible with copper-silver (*i.e.*, Cu-Ag) eutectic brazing, gold (*i.e.*, Au) electroplating, and subsequent gold/silicon (*i.e.*, Au/Si) die attach in air, as described below in the Examples 7, 8, 9, 10, and 11.

B. Fabrication of Electronic Packages Using the Methods of the Present Invention

The metal-diamond substrates prepared using the methods of the present invention can be processed in a variety of ways to fabricate other useful metal-diamond substrates and/or devices incorporating metal-diamond substrates.

B.1 Deposition of Additional Metal Layers

The metal component of a metal-diamond bonded structure may be thickened by the deposition of one or more additional layers of metal, for example, gold (*i.e.*, Au), silver (*i.e.*, Ag), copper (*i.e.*, Cu), nickel (*i.e.*, Ni), or platinum (*i.e.*, Pt). Such additional layers of metal may be deposited, for example, by evaporation, sputtering, or electroplating. Typical thicknesses of such layers are about 1-10 μm.

B.2. Attachment of Other Materials

Adherently bonded metal may used to facilitate the attachment (*e.g.*, by brazing and/or the formation of an interfacial eutectic) of other materials, such as metal sheets/foils, heat sinks, flanges, ceramics, and semiconductor dice (*e.g.*, silicon, gallium arsenide). For example, the metal component of a metal-diamond bonded structure may be thickened by the additional bonding (*e.g.*, by brazing) of a metal sheet/foil.

For example, the surface of a diamond substrate can be covered with an adherent metal layer or sheet. A metal (*e.g.*, in the form of a sheet or foil) may be brazed to the metal-diamond bonded substrate to form a thicker adherently bonded metal layer. Such brazing is typically performed by (1) contacting the metal-diamond bonded substrate with a braze alloy; (2) contacting the braze alloy with a metal; and (3) melting the braze alloy, thereby brazing the metal to the metal-diamond bonded substrate. Examples of one group of suitable braze alloys are those which comprise copper (*i.e.*, Cu) and silver (*i.e.*, Ag), such as Cu-Ag braze alloys. Among other uses, this facilitates the attachment of the diamond to other materials, such as flanges or heat sinks, which are typically made of copper (*i.e.*, Cu) or aluminum (*i.e.*, Al) and often nickel (*i.e.*, Ni) plated.

Metals may be brazed to the metal-diamond bonded substrate by active brazing or non-active brazing. The term "active brazing" is used herein to refer to brazing employing an active braze alloy, as described above. In contrast, the term "non-active brazing" is used herein to refer to brazing employing a non-active braze alloy. For example, a non-active braze alloy is placed between a metal foil/sheet and a metallized diamond substrate,

and the non-active braze alloy subsequently melted to bond the diamond to the metal foil/sheet. Active brazing and non-active brazing offer particular advantages in different applications.

For example, a non-active braze alloy, when liquid (*e.g.,* when melted), will only wet, flow over, and bond to a metal surface. It will not wet or "blush" over bare ceramic surfaces, diamond or graphite. If the non-active braze alloy is applied to an isolated metallized area on a diamond substrate, the braze will tend not to flow across the metal-free areas which surround the metal island. Prevention of blushing prevents the braze alloy from electrically shorting together otherwise isolated metal pads on the diamond substrate. In contrast, active braze alloys, when liquid (*e.g.,* when melted), tend to wet, flow over, and bond to practically all materials. Therefore, braze fixturing (*e.g.,* graphite blocks, disks, or endplates used for evenly applying pressure) must be carefully configured to prevent any contact between the active braze alloy and the fixturing. It is common for active braze alloys to blush uncontrollably and thus irrevocably bond the workpiece to the fixturing. In contrast, fixturing for non-active braze alloys can be made of graphite, ceramics or ceramic-coated metals. Inadvertent contact between a non-active braze alloy and a graphite fixture will not result in adhesion.

In the fabrication of certain electronic package designs, two or more braze steps must be performed in sequence. This process, known as "step brazing," uses braze alloys of successively lower braze temperatures. "Step brazing" is easily performed using the appropriate set of non-active braze alloys. However, a joint created by active brazing cannot withstand subsequent high temperature treatments. The joint created by an active braze alloy on diamond does not retain its strength if heated to within about 200°C of the original brazing temperature. This is because the TiC_x phase formed on the diamond during the active braze step will tend to decompose due to out-diffusion of the titanium during the subsequent heating. The metal will detach from the diamond after the titanium has diffused away from the metal-diamond joint.

As discussed above, a number of braze alloys are available in an active and non-active formulation, for example, a non-active copper-silver (*i.e.*, Cu-Ag) eutectic braze and an active Cu-Ag braze. The addition of elements like titanium (*i.e.*, Ti) to render an alloy "active" reduces the thermal conductivity of the alloy. Thus, if the braze joint sits along
5 the path of heat flow away from the semiconductor device, then a non-active braze alloy is often preferred.

Non-active braze alloys can be used to increase the electrical conductivity of vias. Complete metal filling of vias in diamond entails the risk of cracking of the diamond after thermal cycling to temperatures of greater than or equal to 800°C due to the coefficient of
10 thermal expansion (CTE) mismatch between diamond and the metal (see, for example, Iacovangelo *et al.*, 1995; Goldman, 1994). A better approach is to only partially fill the diameter of the via with a metal wire during brazing. The wire creates a narrow gap between the wire and the metallized sidewalls of the via. This gap will typically be sufficiently narrow to lead to bridging of gold between the wire and sidewalls during
15 electroplating. Since the wire does not fill the via, it will not apply a significant stress to the diamond sidewalls during thermal cycling.

Adherently bonded metal may also be used to facilitate the attachment (*e.g.*, by brazing and/or the formation of an interfacial eutectic) of materials such as ceramics (*e.g.*, alumina, Al_2O_3) and semiconductor dice (*e.g.*, silicon, gallium arsenide). For
20 example, adherently bonded thin metal films (*e.g.*, base coats or primer coats) can promote die attach, for example, silicon and gallium arsenide die attach. A silicon semiconductor die can readily be attached to an adherently bonded gold-containing metal layer by the formation of an interfacial gold-silicon (*i.e.*, Au-Si) by (1) optionally depositing an additional layer of Au on said metal-diamond bonded structure; (2) annealing said
25 additional layer of Au; (3) placing a silicon semiconductor die in contact with said additional layer of Au; and (4) heating the resulting structure (*e.g.*, temperature of 360-440°C) to form a Au-Si eutectic at the Au-Si interface. Similarly, an alumina

(*i.e.*, Al_2O_3) frame can be bonded to a metal-diamond substrate; metal leads may be bonded to the alumina frame before or after the frame is bonded to the diamond.

Metal sheets/foils can be bonded to diamond to facilitate the attachment of a material (*e.g.*, metal sheets/foils, heat sinks, flanges, ceramics, and semiconductor dice) with a higher coefficient of thermal expansion (CTE) than diamond. One or more layers (or shims) of metal and/or braze alloy may be used to create a gradient in the CTE between the diamond and the material.

A list of materials (*e.g.*, metals), usually in the form of sheets/foils, which are useful to be bonded to diamond (*e.g.*, by brazing and/or the formation of an interfacial eutectic) for electronic packaging includes, but is not limited to: Invar®, Kovar®, and other nickel (*i.e.*, Ni) alloys; monocrystalline, polycrystalline and amorphous silicon (*i.e.*, Si); molybdenum (*i.e.*, Mo) and molybdenum alloys; Alloy 42; Alloy 46; clad bi-layer and tri-layer sheets, including, for example, copper/molybdenum (*i.e.*, Cu/Mo) and copper/Invar® (*i.e.*, Cu/Invar®); copper + tungsten (*i.e.*, Cu + W) composites (*e.g.*, a foam of tungsten infiltrated with copper); copper + molybdenum (*i.e.*, Cu + Mo) composites; aluminum matrix composites, including, for example, silicon/aluminum (*i.e.*, Si/Al), graphite/aluminum (*i.e.*, C/Al), alumina/aluminum (*i.e.*, Al_2O_3/Al), and silicon carbide/aluminum (*i.e.*, SiC/Al); copper (*i.e.*, Cu) and copper alloys; silver (*i.e.*, Ag), silver alloys, and silver-containing composites (such as Silvar®, a foam of nickel-iron alloy infiltrated with silver); gold (*i.e.*, Au) and gold alloys; aluminum (*i.e.*, Al) and aluminum alloys (such as Al 6061).

B.3. Cutting/Patterning of Adherently Bonded Metal

Adherently bonded metal (*e.g.*, the optionally thickened metal component of a metal-diamond bonded structure) can be cut into leads which are bonded to the diamond and which extend beyond the boundaries of the diamond. These leads, which facilitate the conduction of electrical current at a high electrical conductance, may be useful in the

fabrication of an electronic device, for example, they can be shorted together or electrically isolated from each other.

Adherently bonded metal may also be selectively removed to yield a patterned metal-diamond bonded structure. For example, adherently bonded metal may be patterned and etched to generate electrically isolated conductor lines and pads (such as electrically isolated conductor lines, leads, metal pads, or combinations thereof) which facilitate the conduction of electrical current at a high electrical conductance on the surface of the diamond. Patterning of the adherently bonded metal can be accomplished using standard ion-beam milling techniques (*e.g.*, using a Kaufmann gun). Patterning may also be accomplished by known wet acid/photoresist methods.

The methods of bonding metal to diamond as taught in the present invention can be used to fabricate a wide range of electronic packages. Using the methods of the present invention, packages can be fabricated where diamond is substituted for ceramics such as beryllium oxide (*i.e.*, beryllia, BeO), aluminum nitride (*i.e.*, AlN) or alumina (*i.e.*, Al_2O_3). This substitution can be achieved without sacrificing important features of the package such as brazed construction, patterned gold metallization, metal-filled vias, hermeticity, and compatibility with gold/silicon (*i.e.*, Au/Si) die attach in air. The fabrication of such packages are described below in Examples 12, 13, 14, 15, and 16.

C. Examples

Several of the methods of the present invention are described in the following examples, which are offered by way of illustration and not by way of limitation.

Example 1

Direct Chemical Vapor Deposition of Diamond onto Molybdenum

This example demonstrates a method of the present invention which permits the fabrication of a molybdenum surface adherently bonded to the diamond, which can subsequently be processed into an electronic package.

A water-cooled, polished molybdenum (*i.e.,* Mo) substrate was placed beneath a DC (*i.e.,* direct current) arcjet plume used for diamond deposition. The heated gas mixture incident on the Mo provided heating of the Mo substrate. Typically, the chamber pressure and torch power were fixed. Substrate temperature was varied during the run by changing
5 the distance between the substrate and the aperture of the arcjet.

The plasma jet was fed a mixture of 210 standard liters per minute (*i.e.,* slpm) argon (*i.e.,* Ar) + 130 slpm hydrogen (*i.e.,* H_2) + 10 slpm methane (*i.e.,* CH_4). This gas mixture was heated by a DC arc power of 100 kW. A diamond film was nucleated at 800-900°C for 5 minutes at a chamber pressure fixed at 75 mm Hg (*i.e.,* 10 kPa). The
10 substrate temperature was then increased to 1000-1100°C and the methane flow reduced to 5 slpm to grow the diamond film. The temperature increase was achieved by decreasing the distance between the substrate and the torch. When the diamond film was grown to a thickness of approximately 1-5 μm, the methane flow was temporarily turned off. The substrate temperature was increased to 1200-1400°C for approximately 2 minutes by
15 moving the substrate toward the arcjet. (This *in-situ* heat treatment is believed to form a molybdenum carbide, MoC_x, phase which strongly adheres the diamond film to the molybdenum substrate.) The temperature was quickly restored to 1000°C by moving the substrate away from the arcjet, and the methane flow was restored to 5 slpm. Diamond growth resumed at 1000-1100°C until the final, desired thickness was achieved
20 (*e.g.,* 500 μm).

Upon cooling to room temperature, the diamond film was highly adherent to the molybdenum substrate. The molybdenum was sawn off at about 100 mils (2.5 mm) beneath the diamond film, and the remaining molybdenum was then ground and lapped to a final thickness of 20 mils (0.5 mm).

25

Example 2

Active Brazing: Thin Copper to Diamond Using Ag-Cu-Ti Active Braze

This example demonstrates the successful use of active metal brazing to bond copper (with a thermal expansion coefficient of 16.9 ppm/°C) to diamond (thermal
5 expansion coefficient of 1.2 ppm/°C).

A sheet of CVD diamond was grown and polished on both faces to a final thickness of 24 mils (0.6 mm). The diamond sheet was laser cut into a rectangle of dimensions 250 mils by 380 mils (6.4 mm x 9.6 mm). A sheet of copper 10 mils (0.25 mm) thick was cut into two squares of dimensions approximately 300 mils by 300 mils (7.6 mm x
10 7.6 mm). The diamond was sandwiched between the two copper squares. Between each copper square and the diamond, a foil of braze alloy 2 mils (0.05 mm) thick having dimensions approximately 300 mils by 300 mils (7.6 mm x 7.6 mm) was positioned. The selected braze metal was a silver-copper-titanium active braze (WESGO® Cusil-ABA®) which is a single phase alloy of 63% by weight silver (*i.e.*, Ag) + 35.25% by weight copper
15 (*i.e.*, Cu) + 1.75 % by weight titanium (*i.e.*, Ti). The sandwich was placed in a fixture to prevent sideways motion of the materials and a weight was applied on the top copper square. The sandwich was placed in a vacuum furnace which was pumped down to a vacuum of less than 10^{-5} mm Hg (1.3 mPa) and had a leak rate of less than 5×10^{-3} mm Hg/hour (0.67 Pa/hour). The furnace was then heated to 830°C, which is
20 15°C hotter than the liquidus temperature of Cusil-ABA® and maintained for 10 minutes. The temperature was then steadily decreased at a rate of 10°C/minute. The resulting assembly was a strongly bonded Cu/diamond/Cu sandwich.

The shear strength of the sandwich was measured destructively. Opposite corners of the two copper squares were brazed to pulling chucks. The chucks pulled opposite
25 corners of the two copper squares as the displacement and load were measured and recorded. The sandwich failed at the braze joint at 22,000 psi (1500 atmospheres, 152 MPa). This result is similar to the pull strength reported for direct bond copper on

alumina substrates (Dickson *et al.*, 1982). The high strength of the braze joint is remarkable in light of the large thermal expansion mismatch between diamond and copper.

Example 3

5 Active Brazing: Thick Copper to Diamond Using Cu-Ag-Sn-Ti Active Braze

A copper-silver-tin-titanium active braze foil (WESGO® Cusin1-ABA®, 2 mils, 50 μm thick; approximate composition 34.25% by weight copper (*i.e.,* Cu) + 63% by weight silver (*i.e.,* Ag) + 1% by weight tin (*i.e.,* Sn) + 1.75% titanium (*i.e.*, Ti)) was interposed between a polished diamond of dimensions 7.5 mm x 3.0 mm x 0.54 mm and a
10 large face of a copper heat sink of dimensions 19 mm x 17 mm x 4.5 mm. The metal sheet and diamond were compressed together and the braze alloy was melted in vacuum at 830°C for a soak time of 5 minutes. The furnace was subsequently cooled at 3-5°C/minute. After the assemblies were removed from the furnace, the diamond and the braze joint were free of cracks, fissures or de-adhesion. The diamond and its attached heat
15 sink were then metallized with titanium/platinum/gold (*i.e.,* Ti/Pt/Au) by evaporation. A laser diode manufacturer was able to solder laser diodes to the metallized diamond. Pre-brazing diamond to its heat sink eliminated one joining operation which the laser manufacturer formerly had to perform in-house.

20 Example 4

Active Brazing: Silvar® to Diamond Using Cu-Ag-Sn-Ti Active Braze

A copper-silver-tin-titanium active braze foil (WESGO® Cusinl-ABA®, 2 mils, 50 μm thick; approximate composition 34.25% by weight copper (*i.e.,* Cu) + 63% by weight silver (*i.e.,* Ag) + 1% by weight tin (*i.e.,* Sn) + 1.75% titanium (*i.e.*, Ti)) was used
25 to braze one face of diamonds 25 mils (635 μm) thick to a sheet of Silvar® 5 mils (125 μm) thick. The metal sheet and diamond were compressed together and the active braze alloy was melted in vacuum at 830°C for a soak time of 5 minutes. After removal from the furnace, no cracking or peeling of the diamond or the metal was observed.

The Silvar® face of the Silvar®/diamond substrate was sputter coated with approximately 1 μm of gold (*i.e.*, Au). A gallium arsenide (*i.e.*, GaAs) die was soldered to the 5 mils thick Silvar® using gold/tin (*i.e.*, Au/Sn) solder. The 5 mils (125 μm) thick Silvar® layer reduced the CTE mismatch between diamond and the GaAs die.

5

Example 5

Active Braze (Au) Metallization of Diamond

A gold active braze foil (WESGO® Au-ABA-V®, 2 mils, 50 μm thick) was bonded to the diamond and used as the gold metallization. A diamond substrate of
10 dimensions 540 mils x 400 mils x 20 mils (14 mm x 10 mm x 0.5 mm) was sandwiched between two rectangles of industrial graphite gasket material (Graphoil) of similar dimensions. A rectangle of gold active braze foil of dimensions 540 mils by 400 mils (14 mm x 10 mm) was interposed at both diamond/graphite interfaces. The stack was aligned together with graphite disks and weight was applied to stack.

15 The stack was vacuum brazed at a peak temperature of 1100°C. The two graphite end plates were necessary to apply a uniform pressure to the gold braze foil during brazing. After brazing, both graphite plates were removed by grinding, leaving behind a diamond coated on both faces with 2 mils (50 μm) of an alloy having more than 97% gold. After grinding away the graphite, the metallized diamond was compatible with direct
20 gold/silicon (*i.e.*, Au/Si) die attach performed in air, with die shear revealing less than 5% void area. The blanket metallized diamond substrates were patterned using a diamond saw. The diamond saw was able to cut through the thin VC_x, phase at the gold/diamond interface, and define electrically isolated pads of gold.

25 Example 6

Active Braze (Cu-Ag-Sn-Ti) Metallization of Diamond Followed by Au Electroplating

Gold active braze foil (*e.g.*, WESGO® Au-ABA-V® is expensive and 50 μm of gold is twenty times the thickness which is sufficient to support good Au/Si die

attachment. Therefore, a lower cost active braze was used to metallize the diamond, followed by Au electroplating.

A diamond substrate of dimensions 540 mils x 400 mils x 20 mils (14 mm x 10 mm x 0.5 mm) was sandwiched between two rectangles of industrial graphite gasket
5 material (Graphoil) of similar dimensions. At both diamond/graphite interfaces, a copper-silver-tin-titanium (*i.e.*, Cu-Ag-Sn-Ti) active braze foil (WESGO® Cusin1-ABA® 2 mils, 50 μm thick; approximate composition 34.25% by weight copper (*i.e.*, Cu) + 63% by weight silver (*i.e.*, Ag) + 1% by weight tin (*i.e.*, Sn) + 1.75% titanium (*i.e.*, Ti)) of dimensions 540 mils by 400 mils (14 mm x 10 mm) was interposed. The stack was
10 aligned together with graphite disks and weight was applied to stack.

The stack was vacuum brazed at a peak temperature of 830°C. The two graphite end plates were necessary to apply a uniform pressure to the gold braze foil during brazing. After brazing, both graphite sheets were removed by grinding, leaving behind a diamond coated on both faces with 2 mils (50 μm) of an alloy which was substantially a copper-
15 silver (*i.e.*, Cu-Ag) eutectic. The exposed metallization was then electroplated with 2.5 μm of gold (*i.e.*, Au), followed by a 30 minute anneal at 375°C in dry hydrogen (*i.e.*, H_2). The Au-plated Cu-Ag was compatible with direct Au/Si die attach performed in air, with die shear revealing of less than 5% void area.

It is also preferable that the braze alloy have as low a yield strength as possible.
20 The best possible brazes accommodate CTE and modulus mismatch between the diamond and the metal sheet through plastic deformation without de-bonding. Therefore, WESGO®'s Silver ABA® (yield strength 136 MPa) and Cusil-ABA® (yield strength 271 MPa) are preferable to WESGO®'s Nioro ABA® (yield strength 483 MPa).

25 <u>Example 7</u>

<u>Solid State Diffusion and Reaction Bonding: Mo + W + Au.</u>

A diamond substrate was sputter coated with 25 nm molybdenum (*i.e.*, Mo) + 100 nm tungsten (*i.e.*, W) + 100-250 nm gold (*i.e.*, Au). The Mo base layer is thought to

provide adhesion to the diamond by forming a carbide, Mo_2C, after annealing. The W is adherent to the Mo/Mo_2C and reduces the out-diffusion of Mo and carbon to the gold. The gold outer layer provides an oxidation resistant protective encapsulant which enables the addition of more gold after the anneal. Since the total film thickness is less than about 500 nm, a contact shadow mask can be placed on the diamond to create a patterned metallization. (The thin metallization also is compatible with other patterning techniques such as ion beam milling or lift-off.) The metallization is preferably annealed in a vacuum or an atmosphere of noble gas in order to bond the molybdenum to the diamond and the other metals to each other. For reasons not yet understood, heating the metallization in an ambient containing hydrogen (*i.e.*, H_2) at 800°C or higher creates poor adhesion.

The thermal budget (time plus temperature) experienced by this metallization should be carefully controlled to produce optimal results. If the metallization will not experience subsequent heat treatments at temperatures greater than 400°C, then the preferred anneal is performed at 800°C for 15 minutes in a vacuum of less than 1×10^{-6} mm Hg (0.13 mPa). If the metallization will experience a Cu-Ag brazing step at 800-820°C, then the vacuum annealing step should be 800°C for 1-10 minutes. By keeping the overall metallization thickness below 500 nm, blistering or buckling of the metallization due to CTE mismatch with the diamond is minimized during the temperature cycles to about 800°C.

This metallization is compatible with copper-silver (*i.e.*, Cu-Ag) brazing performed in vacuum or noble gas (*e.g.*, high purity argon). The liquid braze wets and bonds well to this Mo/W/Au metallization.

After Cu-Ag brazing, 1-10 µm of additional gold (*i.e.*, Au) must be added to metallized areas on the diamond to support Au/Si die attachment. The most popular method of adding gold is by electroplating, for two good reasons: (1) it is the lowest cost method for depositing several microns of gold (*i.e.*, Au), and (2) it deposits gold only on premetallized surfaces. Therefore, if the diamond has been pattern metallized, gold is electroplated only on the pre-existing metal islands. (Although it is more costly, additional

gold may also be deposited by thin film methods such as sputtering or evaporation.) Because of the high CTE of gold (14.2 ppm/°C), layers of gold 1-10 μm thick on diamond cannot be cycled at temperatures above 500°C since blistering of buckling of the gold will occur. Electroplating is an efficient method of depositing thick gold onto a diamond after
5 all of the high temperature annealing and brazing steps have been performed.

The Mo/W/Au metallization is compatible with the electroplating of gold. The W layer is thought to reduce the outdifussion of Mo to the surface of the gold. (A small amount of Mo surface contamination will oxidize in the plating bath, and prevent the electroplating of adherent gold.) After additional gold is deposited, adhesion of this
10 electroplated gold to the underlying metal is enhanced by an anneal at 375°C for 30 minutes; this anneal can be performed in an inert or reducing ambient (*e.g.*, dry hydrogen or forming gas).

Example 8

15 Solid State Diffusion and Reaction Bonding: Mo + Ti:W + Au

A diamond substrate was sputter coated with 25 nm molybdenum (*i.e.*, Mo) + 100 nm Ti: W + 100-250 nm gold (*i.e.*, Au). "Ti:W" is abbreviation for a material with 10-15 atomic % titanium (*i.e.*, Ti) and the balance tungsten (*i.e.*, W), which is a two phase mixture of a few percent of elemental Ti + a W-rich Ti/W solid solution. In the 1960's it
20 was discovered that the addition of Ti to W improves the adhesion of the W to other metals such as gold. This improved adhesion was also observed by the inventors for metallization systems for diamond. The Mo base layer is thought to provide adhesion to the diamond by forming a carbide, Mo_2C, after annealing. The Ti:W is adherent to the Mo/Mo_2C and reduces the out-diffusion of Mo and carbon to the gold. The Ti:W is also well adherent to
25 gold. The gold outer layer provides an oxidation resistant protective encapsulant which enables the addition of more gold after the anneal. Since the total film thickness is less than 500 nm, a contact shadow mask can be placed on the diamond to create a patterned metallization. The metallization must be annealed in vacuum or in an atmosphere of noble

gas in order to bond the molybdenum to the diamond and the other metals to each other. For reasons not yet understood, heating the metallization in an ambient containing hydrogen (*i.e.*, H_2) at 800°C or higher creates poor adhesion.

The thermal budget (time plus temperature) experienced by this metallization must be carefully controlled to produce the optimal results. If the metallization will not experience subsequent heat treatments at temperatures greater than 450°C, then the preferred anneal is performed at 800°C for 15 minutes in a vacuum of less than 1×10^{-6} mm Hg (0.13 mPa). If the metallization will experience a Cu-Ag brazing step at 800-820°C, then the vacuum annealing step should be 800°C for 1-10 minutes. By keeping the overall metallization thickness below 500 nm, blistering or buckling of the metallization due to CTE mismatch with the diamond is minimized while the diamond is cycled in temperature to about 800°C.

This Mo/Ti:W/Au metallization is compatible with Cu-Ag brazing performed in vacuum or noble gas. The liquid braze wets and bonds well to this metallization.

After Cu-Ag brazing, the metallization is compatible with the electroplating of gold. Typically, 2-8 μm of additional gold (*i.e.*, Au) must be added to provide sufficient thickness to support Au/Si die attachment. Gold may also be applied by thin film methods such as sputtering or evaporation. After additional gold is deposited, adhesion of this thick gold to the underlying metal is enhanced by an anneal at 375°C for 30 minutes; this anneal can be performed in an inert or reducing ambient (*e.g.*,, dry hydrogen, H_2, or forming gas).

Example 9

Non-active Brazing: Mo + Ti:W + Au and Cu-Ag Eutectic

25 nm molybdenum (*i.e.*, Mo) + 100 nm Ti:W + 250 nm gold (*i.e.*, Au) were deposited onto a diamond substrate by sputtering or evaporation, followed by an anneal in vacuum at 800°C for 5 minutes. A foil or paste of copper-silver (*i.e.*, Cu-Ag) eutectic braze alloy was interposed between the coating and a metal sheet or flange (*e.g.*, Kovar®, Alloy 42, Invar®, Silvar®, Al/SiC or Cu-W). (Optionally, these metals may be nickel

plated prior to brazing). Pressure was applied, and the sandwich was heated in vacuum at 810°C to melt the Cu-Ag. While molten, it is believed that all of the gold atop the diamond dissolves into the Cu-Ag. Dissolution stops at the Ti:W layer, which has a low solubility in Cu-Ag yet still wets the braze.

5 Instead of Cu-Ag eutectic braze alloy, similar success in brazing has been observed by substituting Cu-Ag alloyed with up to 15% indium (*e.g.*, WESGO®'s Incusil-15®)

Example 10

Non-active Brazing: Mo + Au and Cu-Ag Eutectic

10 35 nm molybdenum (*i.e.*, Mo) + 250 µm gold (*i.e.*, Au) were deposited onto a diamond substrate by sputtering or evaporation. The metallization was annealed at 800°C for 1-5 minutes in vacuum. A foil or paste of copper-silver (*i.e.*, Cu-Ag) eutectic was interposed between the coating and a metal sheet or flange (*e.g.*, Kovar®, Alloy 42, Invar®, Silvar®, Al/SiC or Cu-W). (Optionally, these metals may be nickel plated prior to

15 brazing). Pressure was applied, and the sandwich was heated in vacuum at 810°C to melt the Cu-Ag. While molten, it is believed that all of the gold atop the diamond dissolves into the Cu-Ag. Dissolution stops at the Mo/Mo_2C layer, which has a low solubility in Cu-Ag yet still wets the braze.

20 Example 11

Non-active Brazing: Via Filling: Mo + Ti:W + Au and Cu-Ag Eutectic

A diamond substrate 24 mils (610 µm) thick was laser cut with a plurality of via holes. These via holes were conical; their diameter was 20 mils (510 µm) at the top face and 12-15 mils (305-380 µm) diameter at the backside. 25 nm molybdenum (*i.e.*, Mo) +

25 100 nm Ti:W + 250 nm gold (*i.e.*, Au) was deposited onto both faces of the diamond by sputtering through contact shadow masks, followed by an anneal in vacuum at 800°C for 5 minutes. In preparation for brazing, the entire backside of the diamond was placed upon a copper-silver (*i.e.*, Cu-Ag) foil atop a sheet of 5 mils (130 µm) thick Silvar®. Pure

copper wire or Cu-Ag-Pd wire (WESGO® Palcusil-5®), 7-15 mils (180-380 μm) in diameter by 23 mils (580 μm) in length was placed into via holes from the top. The Cu-Ag-Pd wire had a solidus temperature (794°C) and liquidus temperature (814°C) which straddled the braze temperature of 810°C. This led to only partial melting of the wire during brazing, so that these wires bonded to the cusil layer at the bottom of each via, or to the Mo/Ti:W/Au metal along the sidewalls of each via.

After brazing, the diamond was electroplated with 2-3 μm of gold and then annealed at 375°C. Every via containing a wire showed bridging of gold between the wire and the sidewalls of the via. The electrical resistance between the topside via pads and the backside was acceptable (*i.e.,* less than 0.01 Ω).

Example 12

Surface Mount Package Assembled Using Active Brazing

In Figure 1 is illustrated a schematic of a diamond surface mount package intended for high power, high frequency Si bipolar transistors. An "exploded" view of this package is illustrated in Figure 2. This "flangeless" package is intended to be surface mounted onto a heat sink, yielding what is often referred to as a "pill" style package. Typical dimensions of the diamond substrate (**1**) are 360 mils x 230 mils x 24 mils (9.1 mm x 5.8 mm x 0.6 mm), which is large enough to provide excellent heat spreading for the silicon dice, which are typically soldered onto a metal pad of dimensions 50 mils x 300 mils (1.3 mm x 7.6 mm). This package was fabricated using a procedure in which active brazing was employed.

A diamond coupon was grown and polished on both faces to the desired thickness (24 mil, 0.6 mm). The top face of the diamond was polished to a mirror finish, R_a = 5 nm. The final diamond substrate (**1**) was laser cut from the diamond coupon to a size 360 mils x 230 mils (9.1 mm x 5.8 mm). Both of the 360 mils x 24 mils (9.1 mm x 0.6 mm) sidewalls of the diamond were polished to a mirror finish. Two rows of via holes (**6**) were trepanned into the diamond with the laser. The laser beam was adjusted so that the

thru-holes were conical, with the hole diameter at the top face equal to 20 mils (0.5 mm) and the diameter at the backside equal to 10-15 mils (0.25-0.38 mm).

The 5 mils (125 μm) thick Kovar® leads (3) and the 4 mils (100 μm) thick copper base (2) were simultaneously brazed to the diamond in a vacuum brazing run. The braze
5 alloy was Cusin1-ABA in the form of preforms. The braze alloy (4) was 2 mils (50 μm) thick between the diamond substrate (1) and the Kovar® leads (3), and 4 mils (100 μm) thick between the diamond substrate (1) and the copper base (2). The inventors have discovered that unwanted blushing of the active braze alloy can be minimized by polishing the diamond to a mirror finish. On the top face, little or no blushing of braze was observed
10 away from the Kovar® leads (3). Polishing of the two sidewalls of the diamond minimizes the blushing of braze along the sidewalls, which is necessary to prevent electrical shorting of the Kovar® leads (3) to the copper base (2).

The pill package was then pattern metallized on the top face through a shadow mask. A specially made shadow mask was fabricated which snugly fit between the
15 Kovar® leads (3) and lay flush against the surface of the diamond substrate (1). A 50 nm molybdenum (*i.e.*, Mo) + 200 nm gold (*i.e.*, Au) metallization (5) was applied to the diamond by two cathodic ion sources. The Mo was applied by partially implanting Mo ions into the diamond to achieve adhesion, followed by deposition of the gold. This cathodic implantation/deposition of Mo + Au onto the diamond substrate was found to
20 produce a metallization compatible with gold/silicon (*i.e.*, Au/Si) die attachment without the need for high temperature (*e.g.*, 800°C) annealing. The metallized regions (5) include three parallel pads which ran the length of the diamond. The central pad was intended for die attach. The two via pads, which are electrically shorted to the backside copper base (2), were used for the attachment of two rows of Si capacitors which flank the transistors.
25 The pattern metallized pads (5) as well as the Kovar® leads (3) and copper base (2) were electroplated with 2.5 μm of gold (*i.e.*, Au), followed by a 30 minute anneal in dry hydrogen (*i.e.*, H_2) at 375°C.

The diamond package was compared directly with a 40 mils (1 mm) thick beryllium oxide (*i.e.*, BeO) equivalent package. The BeO package was manufactured by Kyocera America®. Four identical 16 Watt, 900 MHz silicon (*i.e.*, Si) bipolar transistor die were attached to the central pad with gold/silicon (*i.e.*, Au/Si) eutectic at 420°C. X-ray
5 radiography confirmed good die attach. The package was clamped onto a heat sink maintained at 100°C. To measure the thermal resistance (Θ) of the package, the silicon dice were heated with DC current while the surface temperature (*i.e.*, junction temperature, T_j) of the Si was measured by a microfocus pyrometer. The data are summarized in Table 2.
10

Table 2
Comparison of a diamond package to a BeO package

	BeO	Diamond
Junction Temperature (T_J) (°C)	183	150
Heat Sink Temperature (T_{HS}) (°C)	100	100
mean ΔT (junction-heat sink) (°C)	83	50
Power dissipated (P) (W)	65	65
$\Theta_{J-HS} = \Delta T/P$ (°C/W)	1.28	0.77
$\Theta_{J-C} = \Theta_{J-HS} - 0.3$ (°C/W)	0.98†	0.47†

†Assuming the thermal impedance of the package-heat sink interface is 0.3°C/W

The diamond package yielded a 40% reduction in the junction-to-heat sink
15 temperature (*i.e.*, from 83°C to 50°C). Accounting for the package-to-heat sink interface, the junction-to-case thermal impedance (Θ_{J-C}) drops over 50% (*i.e.*, from 0.98 to 0.47°C/W) using a diamond package.

The diamond substrate simultaneously lowered the mean temperature of the Si die by 33°C (*i.e.*, from 183°C to 150°C) and reduced the temperature variation over the silicon
20 surface. The temperature range over the surface of the die atop the BeO package was 46°C compared to only 20°C on the diamond package.

A 50% reduction in overall thermal impedance (Θ_{J-C}) can be expected with minor modifications to the package and heatsink. The greatly reduced thermal impedance will allow up to twice the power dissipation at acceptable junction temperature, or improved reliability at present operating levels. The reduced temperature variation across the die on
5 diamond provides redesign opportunities for more efficient and more powerful devices.

Example 13

Surface Mount Package Assembled Using Non-active Brazing

This example demonstrates the fabrication of the surface mount diamond package
10 illustrated in Figures 1 and 2 by another method which features non-active metallization.

A diamond coupon was grown, polished, laser cut, and trepanned to yield a diamond substrate (**1**) as described above in Example 12.

The diamond substrate (**1**) was then sputter metallized on both faces with Mo + Ti:W + Au as described in Example 8. A contact shadow mask was placed flush against
15 each face of the diamond during sputtering. The shadow mask on the backside prevented metal coating of the sidewalls of the diamond. The top face shadow mask created five isolated metal pads (**5**): two pads for the leads, two via pads (for the two rows of capacitors) and the central pad (for the transistors). The metallization was annealed at 800°C for 5 minutes in high vacuum at a pressure of less than 1 x 10^{-6} mm Hg (0.13 mPa).
20 The 5 mils (125 μm) thick Kovar® leads (**3**) and a 5 mils (125 μm) thick Silvar® base (**2**) were simultaneously brazed to the diamond substrate (**1**) in a vacuum brazing run. The braze alloy (**4**) was a Cu-Ag eutectic in the form of preforms. The preform thickness was 2 mils (50 μm) between the Kovar® leads (**3**) and the diamond substrate (**1**) and 4 mils (100 μm) between the Silvar® base (**2**) and the diamond substrate (**1**). The inventors have
25 discovered that unwanted blushing of the braze alloy can be minimized by polishing the diamond to a mirror finish. On the top face, little or no blushing of braze was observed away from the Kovar® leads (**3**). Polishing of the two sidewalls of the diamond substrate

(1) minimizes the blushing of braze along the sidewalls, which is necessary to prevent electrical shorting of the Kovar® leads (3) to the Silvar® base (2).

The pattern metallized pads (5) as well as the Kovar® leads (3) and Silvar® base (2) were electroplated with 2.5 nm of gold (*i.e.*, Au), followed by a 30 minute anneal in dry
5 hydrogen (*i.e.*, H_2) at 375°C.

The surface mount package illustrated in Figures 1 and 2 can be modified for various reasons. For example, a ceramic "picture frame" can be brazed atop the diamond. Metal leads would be brazed to the ceramic frame instead of directly to the diamond. The ceramic may feature a multi-layer metallized design for highly hermetic packages. The
10 ceramic frame may be brazed to the diamond using a non-active braze alloy (*e.g.*, Cu-Ag eutectic) or an active braze alloy (*e.g.*, Cusin1-ABA®). Also, the thin base metal (2) on the backside of the diamond can be replaced by a full sized flange. For the diamond size described below in Examples 14 & 15, the diamond pill could be brazed atop a 10-90 copper-tungsten (*i.e.*, Cu-W) flange of dimensions 800 mils x 230 mils x 60 mils (20 mm x
15 5.8 mm x 1.5 mm). The flange should be nickel (*i.e.*, Ni) plated prior to brazing. The diamond pill can be brazed to the diamond using a non-active braze alloy (*e.g.*, Cu-Ag eutectic) or an active braze alloy (*e.g.*, Cusin1-ABA®).

Example 14

20 Flange Package with Diamond Inlay

The diamond surface mount package illustrated in Figures 1 and 2 minimizes the thermal resistance of the package by maximizing the amount of diamond along the heat path beneath the semiconductor devices. As shown in Example 13, the heat path beneath the semiconductor is comprised of the gold/silicon (*i.e.*, Au/Si) die attach joint, the thin
25 film metallization on the diamond, 24 mils (600 μm) of diamond, 4 mils (100 μm) of copper-silver (*i.e.*, Cu-Ag) braze joint and 5 mils (125 μm) of base material (Silvar®).

However, many consumers of packaged silicon die are not equipped to utilize surface mount components. Instead, they prefer a package whose base is a metal flange. The flange includes one or two holes which enable it to be bolted onto a heat sink.

The inventors have fabricated packages featuring a diamond inlaid into a metal
5 flange, as illustrated in Figure 3. The flange (**7**) contains two through holes (**8**) to enable bolt-down to a heat sink. The conventional flange material is Cu-W because of its combination of high thermal conductivity and moderate thermal expansion (Table 1). However, a diamond inlay (**12**) substitutes diamond for flange material along the thermal path beneath the semiconductor. Therefore, it is possible to substitute less expensive
10 materials such as molybdenum for the flange in a diamond inlay package. Another benefit of the diamond inlay package is the ability to mount matching capacitors directly onto the flange instead of onto metallized via pads atop the dielectric. Since the flange is usually grounded, the electrical quality of the ground is always superior on the flange than on a via pad.

15 At least two different methods have been successfully used to fabricate flanged packages with a diamond inlay.

A diamond coupon was grown and polished on both faces to the desired thickness (37 mil, 0.94 mm). The top face of the diamond was polished to a mirror finish, R_a = 5 nm. The final diamond insert (**12**) was laser cut from the coupon to a size 395 mils x
20 70 mils x 37 mils (10 mm x 1.8 mm x 9.4 mm).

The diamond insert (**12**) was then sputter coated with Mo + Ti:W + Au as described above in Example 8. A contact shadow mask was placed flush against the top face of the diamond during sputtering to create an electrically isolated metal pad (**11**) with an 8 mils (200 μm) wide metal-free "pullback." The backside and four sidewalls of each diamond
25 were also metallized, taking care not to electrically short the isolated gold pad on the top face. The metallization was annealed at 800°C for 5 minutes in high vacuum at a pressure of less than 1 x 10^{-6} mm Hg (0.13 mPa).

A metal flange (7) (*e.g.*, copper tungsten, Cu-W or molybdenum, Mo) 40 mils (1 mm) thick was machined to have a through-slot to accept the diamond insert (**12**) and mounting holes (8). The flange was then electroplated with 2.5 μm of nickel (*i.e.*, Ni) and then sintered at 800°C in dry hydrogen (*i.e.*, H_2). The diamond was vacuum brazed into the slot using copper-silver (*i.e.*, Cu-Ag) eutectic. The 8 mils (200 μm) wide metal-free pullback surrounding the gold pad (**11**) on the diamond prevented the braze alloy from electrically shorting this gold pad. Excess braze on the backside of the flange was lapped away so that the backside of the flange was flat and homogeneous. The need for lapping the backside of the flange is eliminated if a blind slot is machined into the flange instead of a through-slot.

In a separate operation, Kovar® leads (**10**) were pre-brazed to a pattern metallized alumina picture frame (9) using copper-silver (*i.e.*, Cu-Ag) eutectic. These lead-frame assemblies were then vacuum brazed to the flange (7) (which had previously been inlaid with a diamond insert (**12**)), using an indium-copper-silver (*i.e.*, In-Cu-Ag) braze (Incusil-15®, which brazes at 720°C).

The entire package, including the isolated metal pad atop the diamond, was electroplated with 3 μm of gold (*i.e.*, Au), followed by an anneal at 375°C for 30 minutes in dry hydrogen (*i.e.*, H_2).

Example 15

Flange Package Retrofitted with Diamond Inlay

Flanged packages similar to that illustrated in Figure 3, but lacking a diamond inlay, are commercially available from various manufacturers. These packages are usually comprised of a copper-tungsten (*i.e.*, Cu-W) flange (7), an alumina picture frame (9) and Kovar® leads (**10**) which have been brazed together using copper-silver (*i.e.*, Cu-Ag) eutectic. These packages are intended for semiconductor devices that are to be die attached directly to a grounded flange. (Examples of devices which require die attach to a grounded flange include lateral-DMOS silicon transistors and many III-V devices.) The addition of a

diamond inlay to such a package enables a greater variety of devices to be accommodated. If the diamond is blanket metallized on all surfaces, then devices requiring grounded die attach can still be accommodated. If the diamond has an electrically isolated metal pad on its top surface, then the package is suitable for devices such as Si bipolar transistors and 5 vertical DMOS transistors.

The inventors have retrofitted such packages with a diamond inlay. The diamond was brazed into a slot machined into the flange. The inlay braze used alloys whose braze temperatures was below the melting point of Cu-Ag eutectic (780°C) and well above die attach temperature (420°C).

10 A diamond coupon was grown and polished on both faces to the desired thickness (24 mil, 0.6 mm). The top face of the diamond was polished to a mirror finish, $R_a = 5$ nm. The final diamond insert (**12**) was laser cut from the coupon to a size of 350 mils x 100 mils x 24 mils (8.9 mm x 2.5 mm x 0.6 mm).

The diamond insert (**12**) was then sputter coated with Mo + Ti:W + Au as described 15 above in Example 8. A contact shadow mask was placed flush against the top face of the diamond insert during sputtering to create an electrically isolated metal pad (**11**) with an 8 mils (200 µm) wide metal-free "pullback." The backside and four sidewalls of each diamond were also metallized, taking care not to electrically short the isolated gold pad on the top face. The metallization was annealed at 800°C for 5 minutes in high vacuum at a 20 pressure of less than 1 x 10^{-6} mm Hg (0.13 mPa).

A package manufactured by Kyocera America® was selected for retrofit. A blind slot 26 mils (0.66 mm) deep was machined into the 60 mils (1.5 mm) thick copper-tungsten (*i.e.*, Cu-W) flange (within the interior of the alumina picture frame (**9**)) to accept the diamond insert (**12**). Since bare Cu-W does not wet most non-active braze alloys, the 25 metallized diamond insert was brazed into the flange using an indium-copper-silver (*i.e.*, In-Cu-Ag) active braze (Incusil-ABA®) at a braze temperature of 725°C in vacuum.

If the surfaces of the blind slot in the flange can be metallized with nickel, then the pre-metallized diamond insert can be brazed into the flange using a non-active braze such as copper-silver-indium (*i.e.*, Cu-Ag-In) braze (*e.g.*, Incusil-10®).

The entire package, including the isolated metal pad atop the diamond, was
5 electroplated with 3 μm of gold (*i.e.*, Au), followed by an anneal at 375°C for 30 minutes in dry hydrogen (*i.e.*, H_2).

Example 16

Direct-Bond Copper Package with Diamond Inlay

10 Surface mount packages can be manufactured by a direct bond copper process. Some of these packages are intended for semiconductor devices which must be die attached to metal. For example, Brush Wellman® manufactures CuPack® surface mount packages RFO-24® and HP-3®. These packages feature an alumina picture frame. The base of the frame is bonded to a copper sheet or copper-molybdenum-copper laminate,
15 typically 8-24 mils (200-600 μm) thick, which spans the interior of the alumina. Semiconductor dice are attached directly to the base metal. Atop the alumina frame, electrically isolated copper leads are bonded to the alumina. The direct bond copper process for fabricating these packages makes them low in cost.

Brazing a pattern metallized diamond atop the metal base of these packages enables
20 them to be used with dice which must be attached to an electrically isolated metal pad.

A diamond coupon 10 mils (255 μm) thick was grown and polished on both faces. Both faces of the diamond coupon were then sputter coated with Mo + Ti:W + Au as described above in Example 8. The metallization was annealed at 800°C for 5 minutes in high vacuum at a pressure of less than 1 x 10^{-6} mm Hg (0.13 mPa). The diamond coupon
25 was then laser diced into rectangular diamond inserts of dimensions 110 mils x 70 mils (2.8 mm x 1.8 mm). The diamond inserts were carefully cut and cleaned so that both metallized faces were electrically isolated to better than 2 MΩ.

A direct bond copper package (CuPack® RFO-24®) manufactured by Brush-Wellman® was selected for retrofit. These packages are available with a nickel (*i.e.*, Ni) + gold (*i.e.*, Au) plating or a nickel (*i.e.*, Ni) plating. The inserts are vacuum brazed onto the copper base of the package using copper-silver (*i.e.*, Cu-Ag) eutectic braze preforms 2 mils (50 μm) thick. (Since the direct bond copper process occurs at temperatures of less than 1000°C, high temperature brazes like Cu-Ag eutectic can be employed). Cu-Ag brazes alloyed with indium (*i.e.*, In) (*e.g.*, Incusil-10®) can also be used in order to reduce the brazing temperature.

After brazing, the copper leads, the copper base and the metal pad atop the diamond are electroplated with 2.5 μm of gold (*i.e.*, Au). The plated gold was then annealed at 375°C for 30 minutes in dry hydrogen (*i.e.*, H_2).

An alternative method of inlaying diamond into the CuPack® package employs a lower temperature braze. A diamond coupon 10 mils (255 μm) thick was grown and polished on both faces. Both faces of the diamond coupon were then sputter coated with Mo + Ti:W + Au as described above in Example 8. The metallization was annealed at 800°C for 5 minutes in high vacuum at a pressure of less than 1×10^{-6} mm Hg (0.13 mPa). After annealing, the top face of the diamond was coated with an additional 2.5 μm of gold (*i.e.*, Au). This additional gold was added by sputtering, but evaporation or electroplating could have been used as well. After the additional gold was added, it was annealed at 375°C for 30 minutes in vacuum or dry hydrogen (*i.e.*, H_2). The diamond coupon was then laser diced into rectangular diamond inserts of dimensions 110 mils x 70 mils (2.8 mm x 1.8 mm). The diamond inserts were carefully cut and cleaned so that both metallized faces were electrically isolated to better than 2 MΩ.

A direct bond copper package (CuPack® RFO-24®) manufactured by Brush-Wellman® was selected for retrofit. The inserts are vacuum brazed onto the copper base of the package using 2 mils (50 μm) thick preforms made of gold-silicon (*i.e.*, Au-Si) eutectic (96.85% Au + 3.15% Si). The braze preform is placed against the face of the diamond with the thin gold coating. The braze is performed in air at 420°C using a

standard Si die attach machine. After brazing the metallized diamond onto the copper base, the assembly is ready for use. Subsequent Au/Si die attach can be performed atop the diamond so long as the package is not heated in air above 370°C for more than about 3 minutes.

5

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CLAIMS

1. A method for fabricating a metal-diamond substrate utilizable in an electronic package structure, said method comprising the steps of:

providing a sheet of freestanding CVD diamond having at least one bare diamond surface;

depositing a first carbide-forming metal material comprising one or both of Mo and W on said at least one bare diamond surface;

depositing a second metal material comprising one or more of Au, Ni, Pt, or Ag on said first material; and

annealing the resulting structure to promote adhesion between said carbide-forming metal material and said CVD diamond, thereby forming a metal-diamond bonded structure.

2. The method according to claim 1, wherein said first carbide-forming metal material comprises Mo.

3. The method according to claim 1, wherein said first carbide-forming metal material comprises W.

4. The method according to claim 1, wherein said first carbide-forming metal material comprises Mo and W.

5. The method according to claim 1, wherein said first carbide-forming metal material is Mo + W.

6. The method according to claim 1, wherein said first carbide-forming metal material is Mo + Ti:W.

7. The method according to claim 1, wherein said second metal material comprises Au or Pt or both.

8. The method according to claim 1, wherein said first carbide-forming metal material is Mo and said second metal material comprises Au.

9. The method according to claim 1, wherein said first carbide-forming metal material is Mo + Ti:W and said second metal material comprises Au.

10. The method according to claim 1, wherein said first carbide-forming metal material and said second metal material are deposited on portions of said freestanding CVD diamond sheet with the aid of a masking device.

11. The method according to claim 1, wherein said sheet of freestanding CVD diamond has a thickness 250-1500 μm.

12. The method according to claim 1, wherein said first carbide-forming metal material comprising Mo has a thickness 10-1000 nm.

5 13. The method according to claim 1, wherein said second metal material has a thickness of 10-1000 nm.

14. The method according to claim 1, wherein said annealing is performed at a temperature of 500-1050°C for 0.1-180 minutes.

15. The method according to claim 1, wherein said annealing is performed at a
10 temperature of 750-850°C for 1-30 minutes.

16. The method according to claim 1, wherein said annealing is performed in a vacuum or in an atmosphere of a noble gas.

17. A method for fabricating a metal-diamond substrate utilizable in an electronic package structure, said method comprising the steps of:

15 providing a sheet of freestanding CVD diamond having at least one bare diamond surface;

contacting said at least one bare diamond surface with an active braze alloy; and

melting said active braze alloy, thereby forming a metal-diamond bonded
20 structure.

18. The method according to claim 17, wherein said active braze alloy has the following properties:

the ability to wet and bond to both said CVD diamond and said metal;

a yield strength of less than 400 MPa; and

25 a thermal conductivity greater than 10 W/m°C.

19. The method according to claim 17, wherein said active braze alloy is selected from the group of active braze alloys which comprise Au, Ni, and V; Ag, Cu, and Ti; and Ag, Cu, Sn, and Ti.

20. The method according to claim 17, wherein said active braze alloy comprises Au,
30 Ni, and V.

21. The method according to claim 17, wherein said active braze alloy has an approximate composition of 97.5% by weight Au, 0.75% by weight Ni, and 1.75% by weight V.

22. The method according to claim 17, wherein said active braze alloy comprises Ag, Cu, and Ti.

23. The method according to claim 17, wherein said active braze alloy has an approximate composition of 63.0% by weight Ag, 35.25% by weight Cu, and 1.75% by weight Ti.

24. The method according to claim 17, wherein said active braze alloy comprises Ag, Cu, Sn, and Ti.

25. The method according to claim 17, wherein said active braze alloy has an approximate composition of 34.25% by weight Cu, 63% by weight Ag, 1% by weight Sn, and 1.75% Ti.

26. The method according to claim 17, wherein said melting is performed in a vacuum or in an atmosphere of a noble gas.

27. The method according to claim 17, wherein said melting is performed at a temperature 5-30°C above the liquidus temperature of the said active braze alloy for a time of 0.1-180 minutes.

28. A method for fabricating a metal-diamond substrate utilizable in an electronic package structure, said method comprising the steps of:

providing a sheet of freestanding CVD diamond having at least one bare diamond surface;

contacting said at least one bare diamond surface with an active braze alloy;

contacting said active braze alloy with a metal; and

melting said active braze alloy, thereby forming a metal-diamond bonded structure.

29. The method according to claim 28, wherein said active braze alloy has the following properties:

a lower melting point than that of said metal;

the ability to wet and bond to both said CVD diamond and said metal;

a yield strength of less than 400 MPa;

and a thermal conductivity greater than 10 W/m°C.

30. The method according to claim 28, wherein said active braze alloy is selected from the group of active braze alloys which comprise Au, Ni, and V; Ag, Cu, and Ti; and Ag, Cu, Sn, and Ti.

31. The method according to claim 28, wherein said active braze alloy comprises Au,
5 Ni, and V.

32. The method according to claim 28, wherein said active braze alloy has an approximate composition of 97.5% by weight Au, 0.75% by weight Ni, and 1.75% by weight V.

33. The method according to claim 28, wherein said active braze alloy comprises Ag,
10 Cu, and Ti.

34. The method according to claim 28, wherein said active braze alloy has an approximate composition of 63.0% by weight Ag, 35.25% by weight Cu, and 1.75% by weight Ti.

35. The method according to claim 28, wherein said active braze alloy comprises Ag,
15 Cu, Sn, and Ti.

36. The method according to claim 28, wherein said active braze alloy has an approximate composition of 34.25% by weight Cu, 63% by weight Ag, 1% by weight Sn, and 1.75% Ti.

37. The method according to claim 28, wherein said melting is performed in a vacuum
20 or in an atmosphere of a noble gas.

38. The method according to claim 28, wherein said melting is performed at a temperature 5-30°C above the liquidus temperature of the said active braze alloy for a time of 0.1-180 minutes.

39. A method for fabricating a metal-diamond substrate utilizable in an electronic
25 package structure, said method comprising the steps of:

providing a carbide-forming substrate; and

growing a diamond layer on said substrate utilizing chemical vapor deposition to form a metal-diamond bonded structure.

40. The method according to claim 39, wherein said carbide-forming substrate has a
30 thickness less than 1.5 mm and said diamond layer has a thickness of 10-1200 μm.

41. The method according to claim 39, further comprising the step of:
reducing the thickness of said carbide-forming substrate to less than 1.5 mm.

42. The method according to claim 39, wherein said carbide-forming substrate is selected from the group consisting of Mo, Nb, V, Ti, Ta, W, Zr, Hf, Cr, and Si.

43. The method according to claim 39, wherein said carbide-forming substrate is Mo.

44. The method according to any one of claims 1 to 43, further comprising the step of:
depositing an additional layer of metal on said metal-diamond bonded structure.

45. The method according to claim 44, wherein said additional layer of metal comprises Au, Ag, Cu, Ni, or Pt.

46. The method according to claim 44, wherein said additional layer of metal has a thickness of 1-10 μm.

47. The method according to claim 44, wherein said additional layer of metal is deposited by electroplating.

48. The method according to any one of claims 1 to 43, further comprising the step of:
selectively removing a portion of the metal of said metal-diamond bonded structure to yield a patterned metal-diamond bonded structure.

49. The method according to claim 48, wherein said patterned metal-diamond bonded structure forms electrically isolated conductor lines, leads, metal pads, or combinations thereof.

50. The method according to claim 48, wherein said removal a portion of the metal of said metal-diamond bonded structure is achieved by ion-beam milling.

51. The method according to any one of claims 1 to 43, further comprising the steps of:
contacting said, metal-diamond bonded substrate with a braze alloy;
contacting said braze alloy with a metal; and
melting said braze alloy, thereby brazing said metal to said metal-diamond bonded substrate.

52. The method according to claim 51, wherein said braze alloy comprises Cu and Ag.

53. The method according to claim 51, wherein said braze alloy is a Cu-Ag eutectic braze alloy.

54. The method according to claim 51, wherein said metal is a metal foil, a metal sheet, a heat sink, or a metal flange.

55. The method according to claim 51, wherein said metal is a Cu, a Cu alloy, or a Cu-containing composite.

5 56. The method according to claim 51, wherein said metal is a Ag, a Ag alloy, or a Ag-containing composite.

57. The method according to any one of claims 1 to 43, further comprising the step of:

attaching a semiconductor die to said metal-diamond bonded substrate.

58. The method according to any one of claims 1 to 43, further comprising the step of.:

10 depositing an additional layer of Au on said metal-diamond bonded structure;

placing a silicon semiconductor die in contact with said additional layer of Au; and,

heating the resulting structure to form a Au-Si eutectic at the Au-Si

15 interface.

59. The method according to any one of claims 1 to 43, further comprising the step of:

depositing an additional layer of Au on said metal-diamond bonded structure;

annealing said additional layer of Au;

20 placing a silicon semiconductor die in contact with said additional layer of Au; and,

heating the resulting structure to form a Au-Si eutectic at the Au-Si interface.

60. The method according to claim 59, wherein said heating is performed at a

25 temperature of 360-440°C.

61. The assembly obtained using a method according to claim 44.

62. The assembly obtained using a method according to claim 48.

63. The assembly obtained using a method according to claim 57.

64. The assembly obtained using a method according to claim 58.

30 65. The assembly obtained using a method according to claim 59.

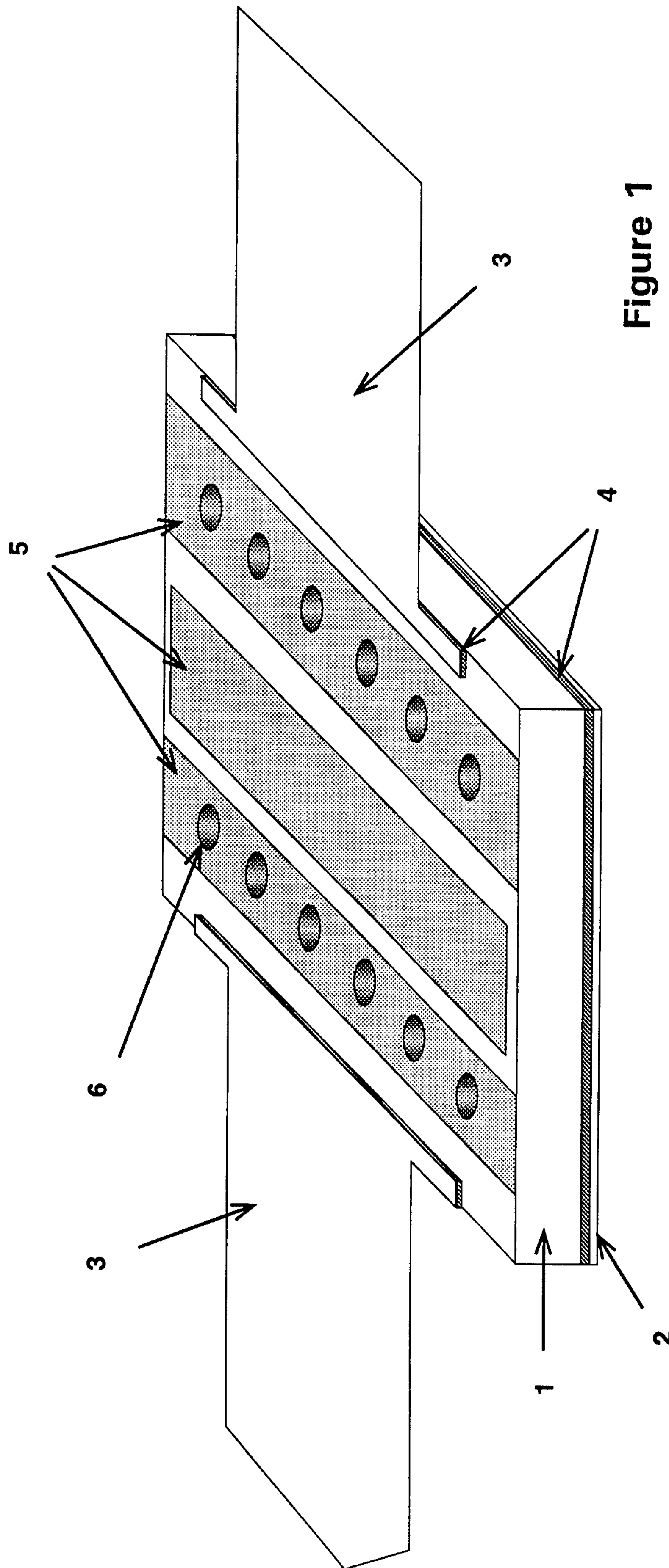

Figure 1

SUBSTITUTE SHEET (RULE 26)

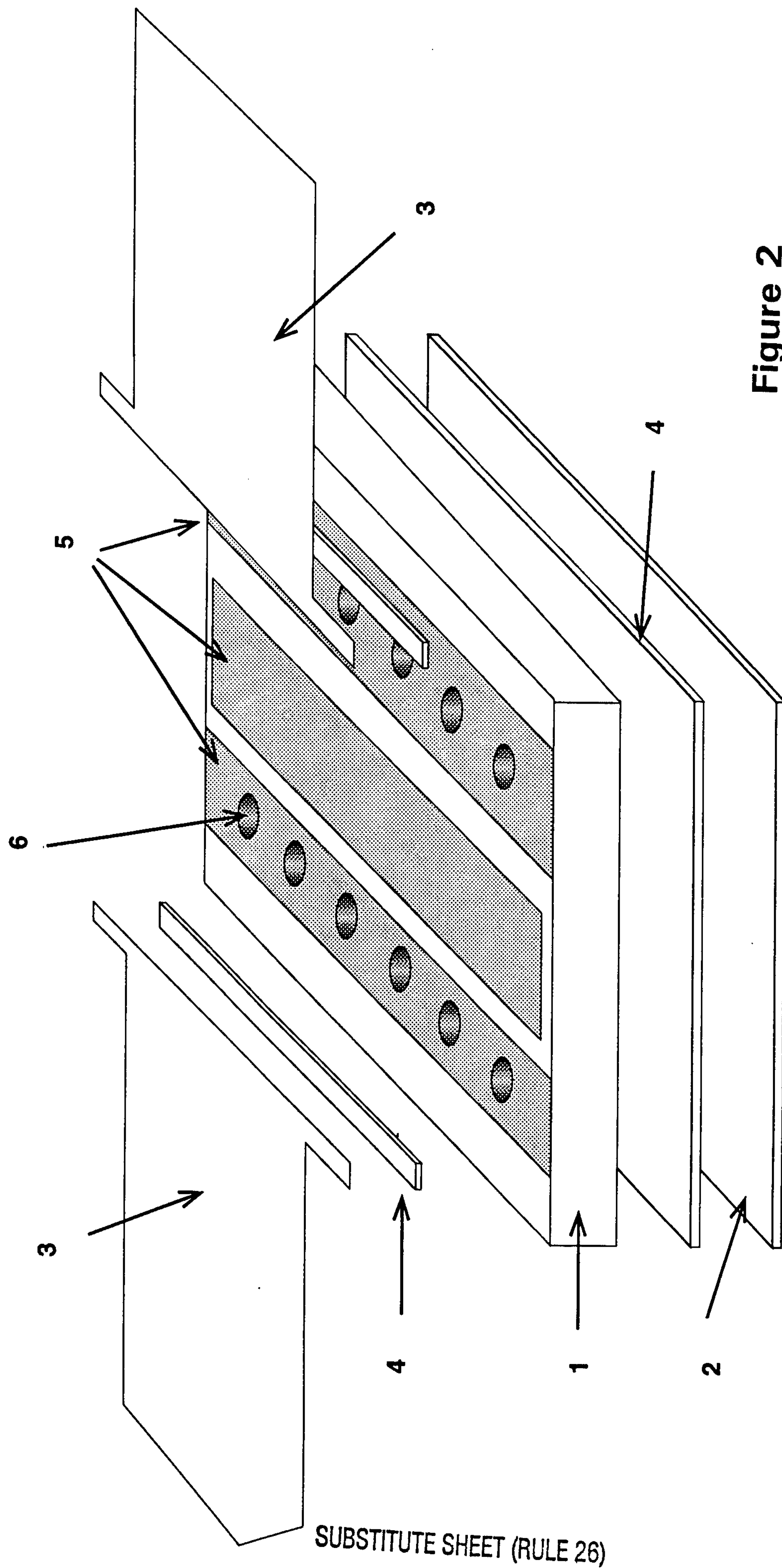

Figure 2

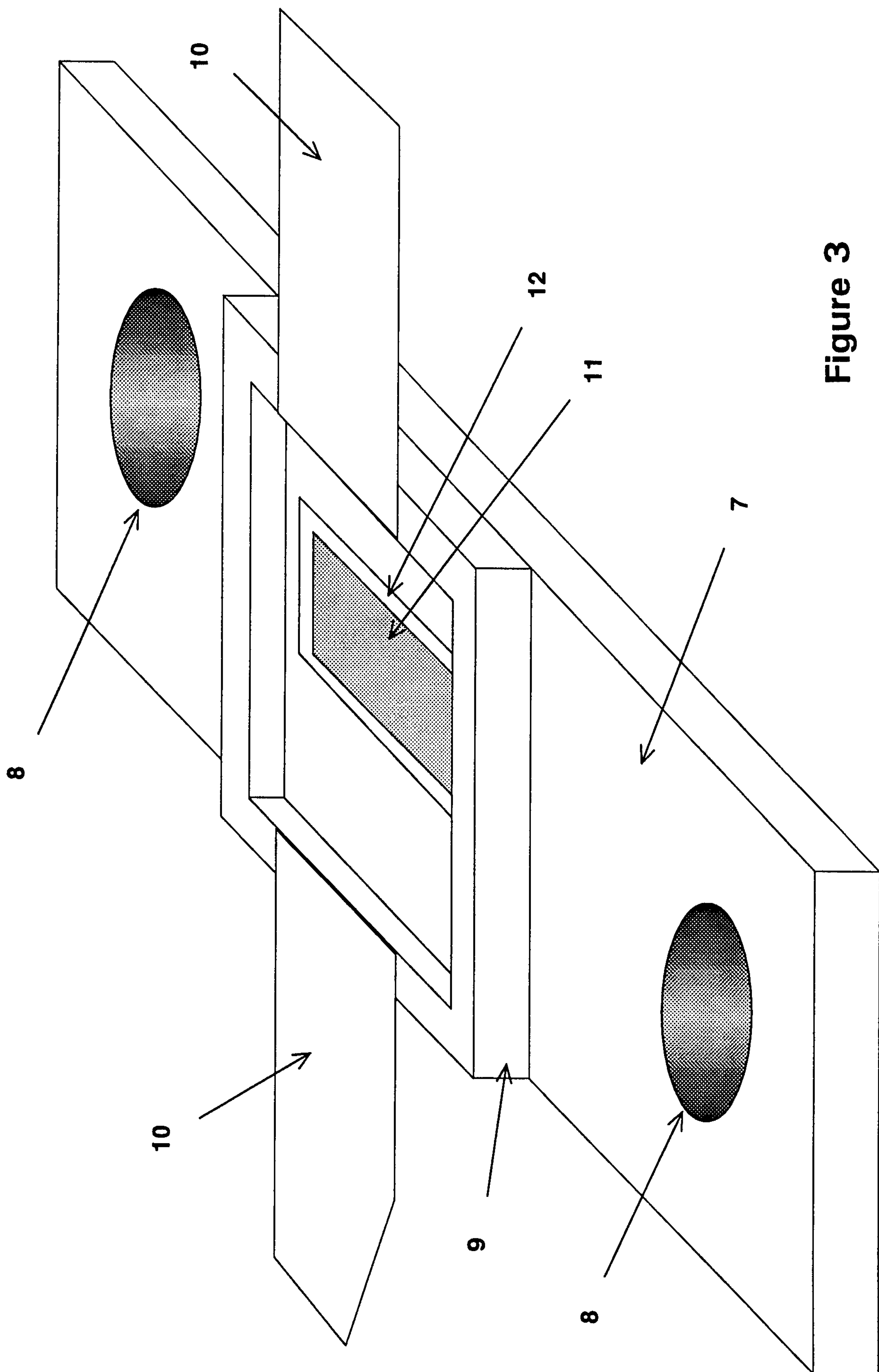

Figure 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12574

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 29/846, 851; 156/81, 272.2; 228/179.1, 194, 195; 423/446; 427/249, 250, 577; 428/552, 698

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 5,299,214 (Nakamura et al.) 29 March 1994, col. 5, lines 35-65; Example 3 on pages 6-10; claim 1. US 4,875,284 (Ogata et al.), 24 Otober 1989, see Figures 3-5, col. 6, lines 55-61, col. 9-10	17-20, 22, 24, 26-31, 33, 35, 37-43, 44-47, 57-61, 63-65 ------------ 1-16, 48-53, 62
X,P	US 5,492,770 (Kawarada et al.), 20 Feburary 1996, see Example 3, Figures 2A, 2B, col. 2, lines 31-53.	39-43
A	US 5,239,746 (Goldman), 31 August 1993, see Figure 1, the entire specification.	17-65
A	US 5,015,528 (Pinneo), 14 May 1991, see Examples 1 and 8	1-16, 39-43

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 OCTOBER 1996	02 DEC 1996

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12574

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12574

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

H05K 3/02; H01L 23/34; B23K 20/00, 31/02; B01J 3/06; C23C 16/00; B32B 9/00

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

29/846, 851; 257/712; 228/179.1, 194, 195; 423/446; 427/249, 250, 577; 428/552, 698

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

Group I, claims 1-16 and their multiple dependent claims 44-65, drawn to an annealing method to form a metal-diamond substrate and the product made.
Group II, claim(s)17-38 and their multiple dependent claims 44-65, drawn to a brazing method to form a metal-diamond substrate and the product made.
Group III, claim(s) 39-43 and their multiple dependent claims 44-65, drawn to a brazing method to form a metal-diamond substrate and the product made. In particular:

Group I has a special technical feature of annealing the metal material on a diamond surface of a sheet to form a bonded structure.

Group II has a special technical feature of melting the braze metal to form a bonded metal-diamond structure.

Group III has a special technical feature of utilizing the chemical vapor deposition to form a bonded metal-diamond structure.

The inventions listed as Groups I,II and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: Group I does not have the special features of Groups II and III; Group II does not have the special technical features of Groups I and III; and Group III does not have the special technical features of Groups I and II, as listed above.