understood that various features disclosed in this specification and in the drawings can be used in any and all combinations. By way of non-limiting example the various features may be combined with one another as set forth in the following aspects:

[0018] According to a first aspect, there is provided an article, comprising:

a carrier with a carrier bonding surface;

a sheet with at least one via therein, the sheet further comprising a sheet bonding surface;

a surface modification layer, wherein the surface modification layer comprises one of:

a) a plasma polymerized fluoropolymer and

b) aromatic silane;

the carrier bonding surface being bonded with the sheet bonding surface with the surface modification layer therebetween, wherein the surface modification layer is of such a character that at least one of:

(i) after subjecting the article to a temperature cycle by heating in an chamber cycled from room temperature to 500°C at a rate of 9.2 °C per minute, held at a temperature of 500°C for 10 minutes, and then cooled at furnace rate to 300 °C, and then removing the article from the chamber and allowing the article to cool to room temperature, the carrier and sheet do not separate from one another if one is held and the other subjected to the force of gravity, and the sheet may be separated from the carrier without breaking the thinner one of the carrier and the sheet into two or more pieces when separation is performed at room temperature; and

(ii) after subjecting the article to a temperature cycle by heating in an chamber cycled from room temperature to 400°C at a rate of 9.2 °C per minute, held at a temperature of 400°C for 10 minutes, and then cooled at furnace rate to 300 °C, and then removing the article from the chamber and allowing the article to cool to room temperature, the carrier and sheet do not separate from one another if one is held and the other subjected to the force of gravity, there is no outgassing from the surface modification layer according to test #2, and the sheet may be separated from the carrier without breaking the thinner one of the carrier and the sheet into two or more pieces when separation is performed at room temperature, wherein test #2 comprises bonding the sheet to the carrier via the surface modification layer, and using a change in percent bubble area during the heating steps to determine outgassing,

and using a change in percent bubble area during the heating steps to determine outgassing, wherein a change in % bubble area of ≥ 5% indicates outgassing.

[0019] According to a second aspect, there is provided a method of making an interposer, comprising:

obtaining a carrier with a carrier bonding surface;

obtaining a sheet with at least one via therein, the sheet further comprising a sheet bonding surface, wherein at least one of the carrier bonding surface and the sheet bonding surface comprises a surface modification layer thereon, wherein the surface modification layer comprises one of:

a) a plasma polymerized fluoropolymer and

b) aromatic silane;

bonding the carrier to the sheet with the bonding surfaces and the surface modification layer to form an article;

subjecting the article to front-end-of-line (FEOL) processing at a temperature of ≥ 500°C, wherein after FEOL processing the carrier and sheet do not separate from one another if one is held and the other subjected to the force of gravity;

removing the sheet from the carrier without breaking the thinner one of the carrier and the sheet into two or more pieces.

[0019a] Herein disclosed is an article, comprising:

a carrier with a carrier bonding surface;

a sheet with at least one via therein, the sheet further comprising a sheet bonding surface;

a surface modification layer;

the carrier bonding surface being bonded with the sheet bonding surface with the surface modification layer therebetween, wherein the surface modification layer is of such a character that after subjecting the article to a temperature cycle by heating in an chamber cycled from room temperature to 400°C at a rate of 9.2 °C per minute, held at a temperature of 400°C for 10 minutes, and then cooled at furnace rate to 300 °C, and then removing the article from the chamber and allowing the article to cool to room temperature, the carrier and sheet do not separate from one another if one is held and the other subjected to the force of gravity, there is no outgassing from the surface modification layer according to test #2, and

sheet do not separate from one another if one is held and the other subjected to the force of gravity, there is no outgassing from the surface modification layer according to test #2, and the sheet may be separated from the carrier without breaking the thinner one of the carrier and the sheet into two or more pieces when separation is performed at room temperature.

[0024] As mentioned in the above aspects, the sheet comprises at least one via therein.

[0025] The at least one via may have a diameter of $\leq$ 150 microns.

[0026] The at least one via may comprise electrically conductive material therein.

[0027] The sheet may comprise a device surface opposite the sheet bonding surface, the device surface comprising an array of devices selected from the group consisting of: integrated circuits; MEMS; CPU; microsensors; power semiconductors; light-emitting diodes; photonic circuits; interposers; embedded passive devices; and microdevices fabricated on or from silicon, silicon-germanium, gallium arsenide, and gallium nitride.

[0028] The sheet may comprise a device surface opposite the sheet bonding surface, the device surface comprising at least one structure selected from the group consisting of: solder bumps; metal posts; metal pillars; interconnection routings; interconnect lines; insulating oxide layers; and structures formed from a material selected from the group consisting of silicon, polysilicon, silicon dioxide, silicon (oxy)nitride, metal, low k dielectrics, polymer dielectrics, metal nitrides, and metal silicides.

[0029] The heating may be performed in Nitrogen.

[0030] There may be no outgassing from the surface modification layer during the heating, wherein outgassing from the surface modification layer is defined as at least one of:

(a) wherein the change in surface energy of a cover is $\geq$ 15 mJ/m^2 at a test-limit temperature of 600°C according to outgassing test #1; and

(b) wherein the change in % bubble area is ≥ 5 at a test limit temperature of 600°C according to outgassing test #2, wherein test #1 comprises providing the cover with a bare surface in close proximity to a surface of the carrier but not in contact, separated by spacers to hold the carrier and cover in a spaced relation from one another as a test article; measuring the surface energy of the bare surface of the cover and the surface of the carrier; heating the test article in a heating chamber at atmospheric pressure and under nitrogen gas; and measuring the change in the surface energy of the bare surface of the cover, and wherein test # 2 comprises bonding a thin sheet to a carrier via a surface modification layer, and using a change in percent bubble area to determine outgassing, wherein a change in % bubble area of ≥ 5% indicates outgassing.

[0045] The sheet may comprise a device surface opposite the sheet bonding surface, the device surface comprising at least one structure selected from the group consisting of: solder bumps; metal posts; metal pillars; interconnection routings; interconnect lines; insulating oxide layers; and structures formed from a material selected from the group consisting of silicon, polysilicon, silicon dioxide, silicon (oxy)nitride, metal, low k dielectrics, polymer dielectrics, metal nitrides, and metal silicides.

[0046] The heating may be performed in Nitrogen.

[0047] There may be no outgassing from the surface modification layer during the heating, wherein outgassing from the surface modification layer is defined as at least one of:

(a) wherein the change in surface energy of the cover is $\geq$ 15 mJ/m^2 at a test-limit temperature of 600°C according to outgassing test #1; and

(b) wherein the change in % bubble area is $\geq$ 5 at a test limit temperature of 600°C according to outgassing test #2, wherein test #1 comprises providing the cover with a bare surface in close proximity to a surface of the carrier but not in contact, separated by spacers to hold the carrier and cover in a spaced relation from one another as a test article; measuring the surface energy of the bare surface of the cover and the surface of the carrier; heating the test article in a heating chamber at atmospheric pressure and under nitrogen gas; and measuring the change in the surface energy of the bare surface of the cover; and wherein test # 2 comprises bonding a thin sheet to a carrier via a surface modification layer, and using a change in percent bubble area to determine outgassing, wherein a change in % bubble area of $\geq$ 5% indicates outgassing.

[0048] As mentioned in the above aspects, the surface modification layer comprises one of:

a) a plasma polymerized fluoropolymer; and

b) an aromatic silane.

[0049] The thickness of the surface modification layer may be from 0.1 to 100 nm.

[0050] The carrier may comprise glass.

[0051] The bonding surface of at least one of the carrier and the sheet may comprise an area of $\geq$ 100 square cm.

BRIEF DESCRIPTION OF THE DRAWINGS

outgassing, by mass-spectrometry. On the other hand, it is more challenging to measure the outgassing from thin surface treatments that are on the order of 10 nm thick or less, for example the plasma polymer or self-assembled monolayer surface modification layers described above, as well as for a thin layer of pyrolyzed silicone oil. For such materials, mass-spectrometry is not sensitive enough. There are a number of other ways to measure outgassing, however.

[00134] A first manner of measuring small amounts of outgassing (test #1) is based on surface energy measurements, and will be described with reference to FIG. 6. To carry out this test, a setup as shown in FIG. 6 may be used. A first substrate, or carrier, 900 having the to-be-tested surface modification layer thereon presents a surface 902, i.e., a surface modification layer corresponding in composition and thickness to the surface modification layer 30 to be tested. A second substrate, or cover, 910 is placed so that its surface 912 is in close proximity to the surface 902 of the carrier 900, but not in contact therewith. The surface 912 is an uncoated surface, i.e., a surface of bare material from which the cover is made. Spacers 920 are placed at various points between the carrier 900 and cover 910 to hold them in spaced relation from one another. The spacers 920 should be thick enough to separate the cover 910 from the carrier 900 to allow a movement of material from one to the other, but thin enough so that during testing the amount of contamination from the chamber atmosphere on the surfaces 902 and 912 is minimized. The carrier 900, spacers 920, and cover 910, together form a test article 901.

[00135] Prior to assembly of the test article 901, the surface energy of bare surface 912 is measured, as is the surface energy of the surface 902, i.e., the surface of carrier 900 having the surface modification layer provided thereon. The surface energies as shown in FIG. 7, both polar and dispersion components, were measured by fitting a theoretical model developed by S. Wu (1971) to three contact angles of three test liquids; water, diiodomethane and hexadecane. (Reference: S. Wu, J. Polym. Sci. C, 34, 19, 1971).

[00136] After assembly, the test article 901 is placed into a heating chamber 930, and is heated through a time-temperature cycle. The heating is performed at atmospheric pressure and under flowing N2 gas, i.e., flowing in the direction of arrows 940 at a rate of 2 standard liters per minute.

[00137] During the heating cycle, changes in the surface 902 (including changes to the surface modification layer due to evaporation, pyrolysis, decomposition, polymerization,

carrier and thin sheet surfaces are prepared makes a big difference in whether an article (thin sheet bonded together with a carrier via a surface modification layer) will survive FPD processing. Thus, although the example of Material #4 shown in FIG. 7 may not outgas, this material may or may not survive the 400°C or 600°C tests as noted in connection with the discussion of Table 2.

[00148] A second manner of measuring small amounts of outgassing (test #2) is based on an assembled article, i.e., one in which a thin sheet is bonded to a carrier via a surface modification layer, and uses a change in percent bubble area to determine outgassing. That is, during heating of the article, bubbles formed between the carrier and the thin sheet indicate outgassing of the surface modification layer. As noted above in connection with the first outgassing test, it is difficult to measure outgassing of very thin surface modification layers. In this second test, the outgassing under the thin sheet may be limited by strong adhesion between the thin sheet and carrier. Nonetheless, layers $\leq$ 10 nm thick (plasma polymerized materials, SAMs, and pyrolyzed silicone oil surface treatments, for example) may still create bubbles during thermal treatment, despite their smaller absolute mass loss. And the creation of bubbles between the thin sheet and carrier may cause problems with pattern generation, photolithography processing, and/or alignment during device processing onto the thin sheet. Additionally, bubbling at the boundary of the bonded area between the thin sheet and the carrier may cause problems with process fluids from one process contaminating a downstream process. A change in % bubble area of $\geq$ 5 is significant, indicative of outgassing, and is not desirable. On the other hand a change in % bubble area of $\leq$ 1 is insignificant and an indication that there has been no outgassing.

[00149] The average bubble area of bonded thin glass in a class 1000 clean room with manual bonding is 1%. The %bubbles in bonded carriers is a function of cleanliness of the carrier, thin sheet, and surface preparation. Because these initial defects act as nucleation sites for bubble growth after heat treatment, any change in bubble area upon heat treatment less than 1% is within the variability of sample preparation. To carry out this test, a commercially available desktop scanner with transparency unit (Epson Expression 10000XL Photo) was used to make a first scan image of the area bonding the thin sheet and carrier immediately after bonding. The parts were scanned using the standard Epson software using 508 dpi (50 micron/pixel) and 24 bit RGB. The image processing software first prepares an image by stitching, as necessary, images of different sections of a sample into a single image and

What is Claimed is:

1. An article, comprising:

a carrier with a carrier bonding surface;

a sheet with at least one via therein, the sheet further comprising a sheet bonding surface;

a surface modification layer, wherein the surface modification layer comprises one of:

a) a plasma polymerized fluoropolymer and

b) aromatic silane;;

the carrier bonding surface being bonded with the sheet bonding surface with the surface modification layer therebetween, wherein the surface modification layer is of such a character that at least one of:

(i) after subjecting the article to a temperature cycle by heating in an chamber cycled from room temperature to 500°C at a rate of 9.2 °C per minute, held at a temperature of 500°C for 10 minutes, and then cooled at furnace rate to 300 °C, and then removing the article from the chamber and allowing the article to cool to room temperature, the carrier and sheet do not separate from one another if one is held and the other subjected to the force of gravity, and the sheet may be separated from the carrier without breaking the thinner one of the carrier and the sheet into two or more pieces when separation is performed at room temperature; and

(ii) after subjecting the article to a temperature cycle by heating in an chamber cycled from room temperature to 400°C at a rate of 9.2 °C per minute, held at a temperature of 400°C for 10 minutes, and then cooled at furnace rate to 300 °C, and then removing the article from the chamber and allowing the article to cool to room temperature, the carrier and sheet do not separate from one another if one is held and the other subjected to the force of gravity, there is no outgassing from the surface modification layer according to test #2, and the sheet may be separated from the carrier without breaking the thinner one of the carrier and the sheet into two or more pieces when separation is performed at room temperature,

wherein test #2 comprises bonding the sheet to the carrier via the surface modification layer, and using a change in percent bubble area during the heating steps to determine outgassing, wherein a change in % bubble area of $\geq 5\%$ indicates outgassing.

2. The article of claim 1, wherein the sheet comprises silicon, quartz, sapphire, ceramic, or glass.

3. An article of claim 2, wherein the sheet is a wafer sheet comprising a thickness ≤ 200 microns.

4. The article of claim 1 or claim 2, the at least one via has a diameter of ≤ 150 microns and comprises electrically conductive material therein.

5. The article of any one of claims 1-4, the sheet comprising a device surface opposite the sheet bonding surface, the device surface comprising an array of devices selected from the group consisting of: integrated circuits; MEMS; CPU; microsensors; power semiconductors; light-emitting diodes; photonic circuits; interposers; embedded passive devices; and microdevices fabricated on or from silicon, silicon-germanium, gallium arsenide, and gallium nitride.

6. The article of any one of claims 1-5, wherein there is no outgassing from the surface modification layer during the heating, wherein outgassing from the surface modification layer is defined as at least one of:

(a) wherein the change in surface energy of a cover is ≥ 15 mJ/m^2 at a test-limit temperature of 600°C according to outgassing test #1; and

(b) wherein the change in % bubble area is ≥ 5 at a test limit temperature of 600°C according to outgassing test #2,

wherein test #1 comprises providing the cover with a bare surface in close proximity to a surface of the carrier but not in contact, separated by spacers to hold the carrier and cover in a spaced relation from one another as a test article;

measuring the surface energy of the bare surface of the cover and the surface of the carrier;

heating the test article in a heating chamber at atmospheric pressure and under nitrogen gas; and

measuring the change in the surface energy of the bare surface of the cover.

7. The article of any one of claims 1-6, the surface modification layer comprising a thickness ≤ 100 nm.

8. The article of any one of claims 1-7, the surface modification layer comprises a phenyl silane and is one of: phenyltriethoxysilane; diphenyldiethoxysilane; and 4-pentafluorophenyltriethoxysilane.

9. The article of any one of claims 1-7, the surface modification layer comprises a phenyl silane, and contains a chlorophenyl, fluorophenyl or silyl group.

10. The article of any one of claims 1-7, the surface modification layer comprises a plasma polymerized fluoropolymer and is one of: plasma polymerized polytetrafluroethylene; and a plasma polymerized fluoropolymer surface modification layer deposited from a CF_4-C_4F_8 mixture having ≤ 40% C_4F_8.

11. A method of making an interposer, comprising:

obtaining a carrier with a carrier bonding surface;

obtaining a sheet with at least one via therein, the sheet further comprising a sheet bonding surface, wherein at least one of the carrier bonding surface and the sheet bonding surface comprises a surface modification layer thereon, wherein the surface modification layer comprises one of:

a) a plasma polymerized fluoropolymer and

b) aromatic silane;

bonding the carrier to the sheet with the bonding surfaces and the surface modification layer to form an article;

subjecting the article to front-end-of-line (FEOL) processing at a temperature of ≥ 500°C, wherein after FEOL processing the carrier and sheet do not separate from one another if one is held and the other subjected to the force of gravity;

removing the sheet from the carrier without breaking the thinner one of the carrier and the sheet into two or more pieces.

12. The method of claim 11, the sheet comprises silicon, quartz, sapphire, ceramic, or glass.

13. A method of claim 12, wherein the sheet is a silicon wafer sheet comprising a thickness ≤ 200 microns.

14. The method of any one of claims 11-13, wherein the FEOL processing comprises at least one of:

(i) processing-chamber temperatures of from 500°C to 700°C; and

(ii) at least one of: DRIE (dry reactive ion etch); PVD; CVD TiN; PECVD SiO2; Electrolytic Cu Plating; Cu Annealing; Metrology; Cu CMP; Cu (H2O2 + H2SO4) + Ti (DHF) Wet Etch; Sputter Adhesion Layer; Sputter Seed Layer; Lithography (Photoresist, expose, strip, etch Cu).

15. The method of any one of claims 11, 12, or 14, the at least one via has a diameter of $\leq$ 150 microns and comprises electrically conductive material therein.

16. The method of any one of claims 11-15, the sheet comprising a device surface opposite the sheet bonding surface, the device surface comprising at least one of:

(i) an array of devices selected from the group consisting of: integrated circuits; MEMS; CPU; microsensors; power semiconductors; light-emitting diodes; photonic circuits; interposers; embedded passive devices; and microdevices fabricated on or from silicon, silicon-germanium, gallium arsenide, and gallium nitride; and

(ii) at least one structure selected from the group consisting of: solder bumps; metal posts; metal pillars; interconnection routings; interconnect lines; insulating oxide layers; and structures formed from a material selected from the group consisting of silicon, polysilicon, silicon dioxide, silicon (oxy)nitride, metal, low k dielectrics, polymer dielectrics, metal nitrides, and metal silicides.

17. The method of any one of claims 11-16, wherein there is no outgassing from the surface modification layer during the heating, wherein outgassing from the surface modification layer is defined as at least one of:

(a) wherein the change in surface energy of a cover is $\geq$ 15 mJ/m^2 at a test-limit temperature of 600°C according to outgassing test #1; and

(b) wherein the change in % bubble area is $\geq$ 5 at a test limit temperature of 600°C according to outgassing test #2, wherein test #1 comprises providing the cover with a bare surface in close proximity to a surface of the carrier but not in contact, separated by spacers to hold the carrier and cover in a spaced relation from one another as a test article;

measuring the surface energy of the bare surface of the cover and the surface of the carrier;

heating the test article in a heating chamber at atmospheric pressure and under nitrogen gas; and

measuring the change in the surface energy of the bare surface of the cover; and

wherein test # 2 comprises bonding a thin sheet to a carrier via a surface modification layer, and using a change in percent bubble area to determine outgassing, wherein a change in % bubble area of ≥ 5% indicates outgassing.

18. The method of any one of claims 11-16, wherein the surface modification layer comprises a thickness ≤ 100 nm.

19. The method of any one of claims 11-18, wherein the surface modification layer comprises a phenyl silane and is one of: phenyltriethoxysilane; diphenyldiethoxysilane; and 4-pentafluorophenyltriethoxysilane

20. The method of any one of claims 11-18, wherein the surface modification layer comprises a phenyl silane, and contains a chlorophenyl, fluorophenyl or silyl group.

21. The method of any one of claims 11-18, wherein the surface modification layer comprises a plasma polymerized fluoropolymer and is one of: plasma polymerized polytetrafluroethylene; and a plasma polymerized fluoropolymer surface modification layer deposited from a CF4-C4F8 mixture having ≤ 40% C4F8.