CARRIER-BONDING METHODS AND ARTICLES FOR SEMICONDUCTOR AND INTERPOSER PROCESSING

BACKGROUND

[0001] This application claims the benefit of priority of U.S. Provisional Application Serial No. 61/890524, filed on October 14, 2013, the content of which is relied upon and incorporated herein by reference in its entirety.

[0002] Field of the invention.

[0003] The present invention is generally directed to carriers bonded to and removed from thinner substrates to allow processing of the thinner substrates. More particularly, the present invention is directed to methods and apparatuses for bonding wafers to carriers for semiconductor and/or interposer processing, and then debonding the wafers from the carriers after such processing.

[0004] Technical Background.

[0005] Semiconductor devices are fabricated by forming active devices on or within a semiconductor wafer. The semiconductor wafer may comprise, for example, glass, silicon, polysilicon, single crystal silicon, silicon oxide, aluminum oxide, combinations of these, and/or the like. Hundreds or thousands of integrated circuits (ICs) or dies are typically manufactured on a single wafer. Typically, a plurality of insulating, conductive, and semiconductive material layers are sequentially deposited and patterned over the wafer to form the ICs. One of the uppermost-formed material layers typically comprises a layer for bond pads which make electrical connection to the underlying active areas and components within the wafer.

[0006] After the ICs are formed, the wafer may be subjected to backside processing. The backside processing may include thinning the wafer to prepare the wafer for packaging. For example, in some technologies, backside processing may include forming electrical connections to through-substrate vias formed through the wafer for providing backside contacts. In this example, the backside of the wafer is thinned through a process such as grinding in order to expose the conductive vias on the backside of the wafer. This process of thinning the wafer can damage the edges of the wafer and can make the wafer even more fragile and susceptible to damage during subsequent transportation and processing of the wafer.

[0007] To help alleviate these types of damage, a carrier is normally attached to the wafer. This carrier is attached using an adhesive, and is intended to allow handling of the wafer by handling the carrier. Additionally, the added strength of the carrier supports the wafer so that stresses caused by transportation and/or processing will not damage the wafer.

SUMMARY

[0008] A typical carrier may be a glass substrate attached to the wafer using an adhesive. It has been found, however, that the wafer may warp during processing and that the typical carrier does not provide sufficient support to prevent warping. As a result of the warpage of the wafer, processes may fail and/or cause alarm conditions. The first portion of the IC fabrication, where the active transistors, resistors and RC circuits, and local wiring to interconnect the transistors are patterned in the semiconductor, is called front-end-of-line (FEOL) processing. FEOL processing may also include: well formation; gate module formation; source and drain module formation; DRIE (dry reactive ion etch); PVD, Ti or Cu, or other; CVD TiN or other; PECVD SiO2, or other; Electrolytic Cu (or other) Plating; Cu (or other) annealing; Metrology (X-Ray or other); Cu (or other) CMP (Chemical Mechanical Polish); Cu (H_2O_2 + H_2SO_4) + Ti (DHF) Wet Etch; Sputter Adhesion Layer (Ti or other); Sputter Seed Layer (Cu or other); Lithography (Photoresist, expose, strip, etch Cu). Due to some of the high temperature (e.g., $\geq$ 500°C,in some instances, 500°C to 650°C, and in some cases up to 700°C) processes associated with FEOL processing, many adhesive based solutions cannot be used, as they may fail to hold the bond, they may outgas contaminants, or both. Many adhesives even outgas at much lower temperatures, e.g., around 300°C. The portion of IC fabrication line where the coarse wiring that connects longer distances across individual chip and goes to off chip locations are interconnected with wiring on the wafer is called back-end-of-line (BEOL) wiring. BEOL processing may also include one or more of formation of contacts, insulating layers, interconnect wiring, RF shielding, passivation, ESD protection, bonding pads and other bonding sites for chip-to-package solutions. Although BEOL processing temperatures are generally lower than FEOL processing temperatures, dielectric deposition typically occurs at 350-450°C and most adhesives outgas at these lower temperatures. Moreover, most temporary adhesives have high CTEs which are mismatched with the wafer and carrier materials, and are difficult to remove while leaving the delicate microstructures on the wafer intact. Additionally, the CTE mismatch between the adhesive and the wafer and/or carrier materials may cause undesirable warping of the wafer. Still

further, adhesive may find its way into the vias of an interposer when bonding to a carrier and undesirably prevent metallization of at least part of the via.

[0009] Thus, there is a need for an improved carrier-substrate solution that can withstand processing conditions, particularly the high temperature demands of FEOL processing. Additionally, a carrier-substrate solution that can withstand the rigors of FEOL, and yet provide for easy debonding thereafter, will allow a thinner initial substrate to be used from the get-go, thereby alleviating the need for back-end thinning. That is, typical existing semiconductor tools are designed to process wafers on the order of 500 microns and above. However, with a carrier supporting a wafer, the combined thickness need only be within the tools' processing thickness range. Thus, for example, a carrier having a thickness of 400 microns may be used to support a wafer of 100 microns, and the combination processed in the existing semiconductor tool. With the present solution, due to the controlled bonding that allows easy separation even after high temperature processing, 100 micron wafers may be used as substrates, thereby avoiding the waste and potential yield reductions of thinning after forming devices on the wafer. The ability to withstand FEOL processing will allow a carrier-substrate solution to start with a wafer having a thickness of $\leq$ 200 microns, for example, 200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, or 20 microns. The wafer of such a thickness ($\leq$ 200 microns for example) can be attached to a carrier, processed, and then removed from the carrier. This can be a major advantage when, for example, polysilicon or single crystal silicon wafers are used as the substrates because there can be avoided the removal and waste of a very expensive material; the material can simply be processed at its as-formed thickness.

[0010] Additionally, 3D IC technology has been widely accepted by the Semiconductor Industry as a major technology trend to improve performance of semiconductors without requiring ever more expensive advanced lithography solutions or requiring larger chip size to accommodate more circuitry. This technology for 3D ICs relies on thinned silicon ICs, and also on interposers to redistribute electrical signals between IC's directly on a single interposer in a planar configuration (2.5D IC) as well as to stack thinned IC's (3D IC).

[0011] These interposers, which can be made of polysilicon, single crystal silicon or glass, allow dramatic improvements in the speed of communications by reducing path lengths from millimeters to microns. The lead application for this new technology has been Field

Programmable Gate Arrays (FPGA), a high end specialized functionality manufactured by Xilinx (San Jose, CA, USA), for example.

[0012] Interposers are characteristically on the order of 50um to 100um thick, sized from 200mm OD to 300mm OD today, trending towards larger sized panels long term. The vias, through which electrical signals are processed following metallization, are from 5um OD to 150um OD with a density typically 1 to 20 vias per square millimeter, depending on design and application. Interposers are by definition thin, as thick interposers cause an unacceptable form factor (height) and performance (heat) obstacles. Thin is generally regarded as around 100 microns, but generally not to exceed 200 microns. On the other end, the International Technology Roadmap for Semiconductors (ITRS) allows for thicknesses down to 50um. Again, substrates of these thicknesses generally cannot be processed in existing tools. Thus, the present disclosure contemplates the advantageous use of a carrier, and one that may stay attached with the wafer even during high temperature processing, and yet still allow an easy release of the wafer after such processing.

[0013] Although the interposer technology is new, the dominant interposer substrate is single crystal silicon, with glass emerging as an alternative. The attractiveness of glass is performance and cost, but no solution has yet existed today to realize these advantages for glass. The concepts in the present disclosure will allow processing of a variety of thin substrates as wafers, including silicon and glass, as well as under a variety of conditions, including FEOL and BEOL, to provide a variety of devices including ICs, RC circuits, and interposers.

[0014] The bonding solutions of the present disclosure allow the processing of thin form at final thickness glass, as well as thinned Silicon, through all existing required process steps with high yield and with low processing time. After the thin wafer is processed through metallization, distribution layer placement, it can be debonded leaving the thinned and processed interposer, and/or IC, intact. Moreover, the use of carrier with an already-thinned (on the order of ≤ 200 microns) silicon wafer allows the wafer to be screened before any devices are processed thereon. Accordingly, costs can be reduced and/or yields improved.

[0015] In light of the above, there is a need for a thin sheet – carrier article that can withstand the rigors of the FEOL processing, including high temperature processing (without outgassing that would be incompatible with the semiconductor or display making processes in which it will be used), yet allow the entire area of the thin sheet to be removed (either all at

once, or in sections) from the carrier. The present specification describes ways to control the adhesion between the carrier and thin sheet to create a temporary bond sufficiently strong to survive FEOL processing (including high temperature processing) but weak enough to permit debonding of the sheet from the carrier, even after high-temperature processing. More specifically, the present disclosure provides surface modification layers (including various materials and associated surface heat treatments), that may be provided on the thin sheet, the carrier, or both, to control both room-temperature van der Waals, and/or hydrogen, bonding and high temperature covalent bonding between the thin sheet and carrier. Even more specifically, the room-temperature bonding may be controlled so as to be sufficient to hold the thin sheet and carrier together during vacuum processing, wet processing, and/or ultrasonic cleaning processing. And at the same time, the high temperature covalent bonding may be controlled so as to prevent a permanent bond between the thin sheet and carrier during high temperature processing, as well as maintain a sufficient bond to prevent delamination during high temperature processing. In alternative embodiments, the surface modification layers may be used to create various controlled bonding areas (wherein the carrier and sheet remain sufficiently bonded through various processes, including vacuum processing, wet processing, and/or ultrasonic cleaning processing). Still further, some surface modification layers provide control of the bonding between the carrier and sheet while, at the same time, reduce outgassing emissions during the harsh conditions in an FPD (for example LTPS) processing environment, including high temperature and/or vacuum processing, for example.

[0016] Additional features and advantages will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the various aspects as exemplified in the written description and the appended drawings. It is to be understood that both the foregoing general description and the following detailed description are merely exemplary of the various aspects, and are intended to provide an overview or framework to understanding the nature and character of the invention as it is claimed.

[0017] The accompanying drawings are included to provide a further understanding of principles of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s), and together with the description serve to explain, by way of example, principles and operation of the invention. It is to be

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

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.

[0020] The sheet may comprise silicon, quartz, sapphire, ceramic, or glass.

[0021] The sheet thickness may be ≤ 200 microns.

[0022] Herein disclosed is an article, comprising:

a carrier with a carrier bonding surface;

a wafer sheet comprising a thickness ≤ 200 microns, the sheet further comprising a sheet bonding surface, the sheet comprising silicon, quartz, or sapphire;

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 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.

[0023] Herein disclosed is an article, comprising:

a carrier with a carrier bonding surface;

a wafer sheet comprising a thickness ≤ 200 microns, the sheet further comprising a sheet bonding surface, the sheet comprising silicon, quartz, or sapphire;

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 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.

[0031] As mentioned in the above aspects, the surface modification layer comprises one of:

a) a plasma polymerized fluoropolymer; and

b) an aromatic silane.

[0032] Thickness of the surface modification layer may be from 0.1 to 100 nm.

[0033] The carrier may comprise glass.

[0034] The bonding surface of at least one of the carrier and the sheet may comprise an area of ≥ 100 square cm.

[0035] Herein disclosed is 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;

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, 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.

[0036] The sheet may comprise silicon, quartz, sapphire, ceramic, or glass.

[0037] The sheet thickness may be ≤ 200 microns.

[0038] Herein disclosed is a method of processing a silicon wafer sheet, comprising:

obtaining a carrier with a carrier bonding surface;

obtaining a wafer sheet with a thickness ≤ 200 microns, the sheet comprising silicon, quartz, or sapphire, 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;

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, 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.

[0039] As mentioned in the above aspects, the sheet comprises at least one via therein.

[0040] The FEOL processing may comprise 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).

[0041] The FEOL processing may comprise 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).

[0042] The at least one via may have a diameter of ≤ 150 microns.

[0043] The at least one via may comprise electrically conductive material therein.

[0044] The sheet may comprise 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.

[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

[0052] FIG. 1 is FIG. 1 is a schematic side view of an article having carrier bonded to a thin sheet with a surface modification layer therebetween.

[0053] FIG. 2 is an exploded and partially cut-away view of the article in FIG. 1.

[0054] FIG. 3 is a graph of surface hydroxyl concentration on silica as a function of temperature.

[0055] FIG. 4 is a graph of the surface energy of an SC1-cleaned sheet of glass as a function annealing temperature.

[0056] FIG. 5 is a graph of the surface energy of a thin fluoropolymer film deposited on a sheet of glass as a function of the percentage of one of the constituent materials from which the film was made.

[0057] FIG. 6 is a schematic view of a testing setup

[0058] FIG. 7 is a collection of graphs of surface energy (of different parts of the test setup of FIG. 6) versus time for a variety of materials under different conditions.

[0059] FIG. 8 is a graph of change in % bubble area versus temperature for a variety of materials.

[0060] FIG. 9 is another graph of change in % bubble area versus temperature for a variety of materials.

[0061] FIG. 10 is a top view of a thin sheet and carrier, having interposers.

[0062] FIG. 11 is a cross-sectional view of the thin sheet and carrier as taken along line 11-11 of FIG. 10.

[0063] FIG. 12 is a cross-sectional view, similar to that in FIG. 11, but having additional devices disposed on the thin sheet.

DETAILED DESCRIPTION

[0064] In the following detailed description, for purposes of explanation and not limitation, example embodiments disclosing specific details are set forth to provide a thorough understanding of various principles of the present invention. However, it will be apparent to one having ordinary skill in the art, having had the benefit of the present disclosure, that the present invention may be practiced in other embodiments that depart from the specific details disclosed herein. Moreover, descriptions of well-known devices, methods and materials may be omitted so as not to obscure the description of various principles of the present invention. Finally, wherever applicable, like reference numerals refer to like elements.

[0065] Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be

understood that the particular value forms another embodiment. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[0066] Directional terms as used herein—for example up, down, right, left, front, back, top, bottom—are made only with reference to the figures as drawn and are not intended to imply absolute orientation.

[0067] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including: matters of logic with respect to arrangement of steps or operational flow; plain meaning derived from grammatical organization or punctuation; the number or type of embodiments described in the specification.

[0068] As used herein, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a “component” includes aspects having two or more such components, unless the context clearly indicates otherwise.

[0069] It is desirable to be able to remove the thin sheet, or portions thereof, from the carrier to process more than one thin sheet substrate. The present disclosure sets forth articles and methods for enabling a thin sheet to be processed through high temperature processing—wherein high temperature processing is processing at a temperature $\geq 400^{\circ}C$, and may vary depending upon the type of device being made, for example, temperatures up to about $450^{\circ}C$ as in amorphous silicon or amorphous indium gallium zinc oxide (IGZO) backplane processing, up to about 500-550°C as in crystalline IGZO processing, or up to about 600-650°C as is typical in LTPS processes—and yet still allows the thin sheet to be easily removed from the carrier without damage (for example, wherein one of the carrier and the thin sheet breaks or cracks into two or more pieces) to the thin sheet or carrier. Although specific processes are mentioned, they are merely exemplary of processes having certain temperature requirements. Of course, if a thin sheet and carrier may be used in any one of the

above processes, it may be used in a different process having a similar temperature requirement.

[0070] As shown in FIGS. 1 and 2, an article 2 has a thickness 8, and includes a carrier 10 having a thickness 18, a thin sheet 20 (i.e., one having a thickness of ≤ 300 microns, including but not limited to thicknesses of, for example, 10-50 microns, 50-100 microns, 100-150 microns, 150-300 microns, 300, 250, 200 190, 180, 170, 160, 150 140, 130, 120 110 100, 90, 80, 70, 60, 50, 40 30, 20, or 10, microns) having a thickness 28, and a surface modification layer 30 having a thickness 38. The article 2 is designed to allow the processing of thin sheet 20 in equipment designed for thicker sheets (i.e., those on the order of ≥ .4mm, e.g., .4 mm, .5 mm, .6 mm, .7 mm, .8 mm, .9 mm, or 1.0 mm) although the thin sheet 20 itself is ≤ 300 microns. That is, the thickness 8, which is the sum of thicknesses 18, 28, and 38, is designed to be equivalent to that of the thicker sheet for which a piece of equipment—for example, equipment designed to dispose electronic device components onto substrate sheets—was designed to process. For example, if the processing equipment was designed for a 700 micron sheet, and the thin sheet had a thickness 28 of 300 microns, then thickness 18 would be selected as 400 microns, assuming that thickness 38 is negligible. That is, the surface modification layer 30 is not shown to scale; instead, it is greatly exaggerated for sake of illustration only. Additionally, the surface modification layer is shown in cut-away. In actuality, the surface modification layer would be disposed uniformly over the bonding surface 14. Typically, thickness 38 will be on the order of nanometers, for example 0.1 to 2.0, or up to 10 nm, and in some instances may be up to 100 nm. The thickness 38 may be measured by ellipsometer. Additionally, the presence of a surface modification layer may be detected by surface chemistry analysis, for example by ToF Sims mass spectrometry. Accordingly, the contribution of thickness 38 to the article thickness 8 is negligible and may be ignored in the calculation for determining a suitable thickness 18 of carrier 10 for processing a given thin sheet 20 having a thickness 28. However, to the extent that surface modification layer 30 has any significant thickness 38, such may be accounted for in determining the thickness 18 of a carrier 10 for a given thickness 28 of thin sheet 20, and a given thickness for which the processing equipment was designed.

[0071] Carrier 10 has a first surface 12, a bonding surface 14, a perimeter 16, and thickness 18. Further, the carrier 10 may be of any suitable material including glass, for example. The carrier need not be glass, but instead can be ceramic, glass-ceramic, or metal (as the

surface energy and/or bonding may be controlled in a manner similar to that described below in connection with a glass carrier). If made of glass, carrier 10 may be of any suitable composition including alumino-silicate, boro-silicate, alumino-boro-silicate, soda-lime-silicate, and may be either alkali containing or alkali-free depending upon its ultimate application. Thickness 18 may be from about 0.2 to 3 mm, or greater, for example 0.2, 0.3, 0.4, 0.5, 0.6, 0.65, 0.7, 1.0, 2.0, or 3 mm, or greater, and will depend upon the thickness 28, and thickness 38 when such is non-negligible, as noted above. Additionally, the carrier 10 may be made of one layer, as shown, or multiple layers (including multiple thin sheets) that are bonded together. Further, the carrier may be of a Gen 1 size or larger, for example, Gen 2, Gen 3, Gen 4, Gen 5, Gen 8 or larger (e.g., sheet sizes from 100 mm x 100 mm to 3 meters x 3 meters or greater).

[0072] The thin sheet 20 has a first surface 22, a bonding surface 24, a perimeter 26, and thickness 28. Perimeters 16 and 26 may be of any suitable shape, may be the same as one another, or may be different from one another. Further, the thin sheet 20 may be of any suitable material including silicon, polysilicon, single crystal silicon, sapphire, quartz, glass, ceramic, or glass-ceramic, for example. When made of glass, thin sheet 20 may be of any suitable composition, including alumino-silicate, boro-silicate, alumino-boro-silicate, soda-lime-silicate, and may be either alkali containing or alkali free depending upon its ultimate application. The coefficient of thermal expansion of the thin sheet could be matched relatively closely with that of the carrier to prevent warping of the article during processing at elevated temperatures. The thickness 28 of the thin sheet 20 is 300 microns or less, as noted above. Further, the thin sheet may be of a Gen 1 size or larger, for example, Gen 2, Gen 3, Gen 4, Gen 5, Gen 8 or larger (e.g., sheet sizes from 100 mm x 100 mm to 3 meters x 3 meters or greater).

[0073] Not only does the article 2 need to have the correct thickness to be processed in the existing equipment, it will also need to be able to survive the harsh environment in which the processing takes place. For example, processing may include wet ultrasonic, vacuum, and high temperature (e.g., $\geq 400°C$), processing. For some processes, as noted above, the temperature may be $\geq 500°C$, or $\geq 600°C$, and up to 650°C.

[0074] In order to survive the harsh environment in which article 2 will be processed, the bonding surface 14 should be bonded to bonding surface 24 with sufficient strength so that the thin sheet 20 does not separate from carrier 10. And this strength should be maintained

through the processing so that the thin sheet 20 does not separate from the carrier 10 during processing. Further, to allow the thin sheet 20 to be removed from carrier 10 (so that carrier 10 may be reused), the bonding surface 14 should not be bonded to bonding surface 24 too strongly either by the initially designed bonding force, and/or by a bonding force that results from a modification of the initially designed bonding force as may occur, for example, when the article undergoes processing at high temperatures, e.g., temperatures of ≥ 400°C. The surface modification layer 30 may be used to control the strength of bonding between bonding surface 14 and bonding surface 24 so as to achieve both of these objectives. The controlled bonding force is achieved by controlling the contributions of van der Waals (and/or hydrogen bonding) and covalent attractive energies to the total adhesion energy which is controlled by modulating the polar and non-polar surface energy components of the thin sheet 20 and the carrier 10. This controlled bonding is strong enough to survive processing (including wet, ultrasonic, vacuum, and thermal processes including temperatures ≥ 400°C, and in some instances, processing temperatures of ≥ 500°C, or ≥ 600°C, and up to 650°C.) and remain de-bondable by application of sufficient separation force and yet by a force that will not cause catastrophic damage to the thin sheet 20 and/or the carrier 10. Such de-bonding permits removal of thin sheet 20 and the devices fabricated thereon, and also allows for re-use of the carrier 10.

[0075] Although the surface modification layer 30 is shown as a solid layer between thin sheet 20 and carrier 10, such need not be the case. For example, the layer 30 may be on the order of 0.1 to 2 nm thick, and may not completely cover every bit of the bonding surface 14. For example, the coverage may be ≤ 100%, from 1% to 100%, from 10% to 100%, from 20% to 90%, or from 50% to 90%. In other embodiments, the layer 30 may be up to 10 nm thick, or in other embodiments even up to 100 nm thick. The surface modification layer 30 may be considered to be disposed between the carrier 10 and thin sheet 20 even though it may not contact one or the other of the carrier 10 and thin sheet 20. In any event, an important aspect of the surface modification layer 30 is that it modifies the ability of the bonding surface 14 to bond with bonding surface 24, thereby controlling the strength of the bond between the carrier 10 and the thin sheet 20. The material and thickness of the surface modification layer 30, as well as the treatment of the bonding surfaces 14, 24 prior to bonding, can be used to control the strength of the bond (energy of adhesion) between carrier 10 and thin sheet 20.

[0076] In general, the energy of adhesion between two surfaces is given by ("A theory for the estimation of surface and interfacial energies. I. derivation and application to interfacial tension", L. A. Girifalco and R. J. Good, J. Phys. Chem., V 61, p904):

$$W = \gamma_1 + \gamma_2 - \gamma_{12} \quad (1)$$

where , γ_1, γ_2 and γ_{12} are the surface energies of surface 1, surface 2 and the interfacial energy of surface 1 and 2 respectively. The individual surface energies are usually a combination of two terms; a dispersion component γ^d, and a polar component γ^p

$$\gamma = \gamma^d + \gamma^p \quad (2)$$

[0077] When the adhesion is mostly due to London dispersion forces (γ^d) and polar forces for example hydrogen bonding (γ^p), the interfacial energy could be given by(Girifalco and R. J. Good, as mentioned above):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p} \quad (3)$$

[0078] After substituting (3) in (1), the energy of adhesion could be approximately calculated as:

$$W \sim 2\left[\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p}\right] \quad (4)$$

[0079] In the above equation (4), only van der Waal (and/or hydrogen bonding) components of adhesion energies are considered. These include polar-polar interaction (Keesom), polar-non polar interaction (Debye) and nonpolar-nonpolar interaction (London). However, other attractive energies may also be present, for example covalent bonding and electrostatic bonding. So, in a more generalized form, the above equation is written as:

$$W \sim 2\left[\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p}\right] + w_c + w_e \quad (5)$$

where w_c and w_e are the covalent and electrostatic adhesion energies. The covalent adhesion energy is rather common, as in silicon wafer bonding where an initially hydrogen bonded pair of wafers are heated to a higher temperature to convert much or all the silanol-silanol hydrogen bonds to Si-O-Si covalent bonds. While the initial, room temperature, hydrogen bonding produces an adhesion energy of the order of ~100-200mJ/m^2 which allows separation of the bonded surfaces, a fully covalently bonded wafer pair as achieved during high temperature processing (on the order of 400 to 800 °C) has adhesion energy of ~ 1000-3000 mJ/m^2 which does not allow separation of the bonded surfaces; instead, the two wafers

act as a monolith. On the other hand, if both the surfaces are perfectly coated with a low surface energy material, for example a fluoropolymer, with thickness large enough to shield the effect of the underlying substrate, the adhesion energy would be that of the coating material, and would be very low leading to low or no adhesion between the bonding surfaces 14, 24, whereby the thin sheet 20 would not be able to be processed on carrier 10. Consider two extreme cases: (a) two standard clean 1 (SC1, as known in the art) cleaned glass surfaces saturated with silanol groups bonded together at room temperature via hydrogen bonding (whereby the adhesion energy is ~100-200 mJ/m^2) followed by heating to high temperature which converts the silanol groups to covalent Si-O-Si bonds (whereby the adhesion energy becomes1000-3000 mJ/m^2). This latter adhesion energy is too high for the pair of glass surfaces to be detachable; and (b) two glass surfaces perfectly coated with a fluoropolymer with low surface adhesion energy (~12 mJ/m^2 per surface) bonded at room temperature and heated to high temperature. In this latter case (b), not only do the surfaces not bond (because the total adhesion energy of ~ 24 mJ/m^2, when the surfaces are put together, is too low), they do not bond at high temperature either as there are no (or too few) polar reacting groups Between these two extremes, a range of adhesion energies exist, for example between 50-1000 mJ/m^2, which can produce the desired degree of controlled bonding. Accordingly, the inventors have found various manners of providing a surface modification layer 30 leading to an adhesion energy that is between these two extremes, and such that there can be produced a controlled bonding that is sufficient enough to maintain a pair of substrates (for example a carrier 10 and a thin sheet 20) bonded to one another through the rigors of FPD processing but also of a degree that (even after high temperature processing of, e.g. $\geq$ 400°C) allows the detachment of the thin sheet 20 from the carrier 10 after processing is complete. Moreover, the detachment of the thin sheet 20 from the carrier 10 can be performed by mechanical forces, and in such a manner that there is no catastrophic damage to at least the thin sheet 20, and preferably also so that there is no catastrophic damage to the carrier 10.

[0080] Equation (5) describes that the adhesion energy is a function of four surface energy parameters plus the covalent and electrostatic energy, if any.

[0081] An appropriate adhesion energy can be achieved by judicious choice of surface modifiers, i.e., of surface modification layer 30, and/or thermal treatment of the surfaces prior to bonding. The appropriate adhesion energy may be attained by the choice of chemical modifiers of either one or both of bonding surface 14 and bonding surface 24, which in turn

control both the van der Waal (and/or hydrogen bonding, as these terms are used interchangeably throughout the specification) adhesion energy as well as the likely covalent bonding adhesion energy resulting from high temperature processing (e.g., on the order of ≥ 400°C). For example, taking a bonding surface of SC1 cleaned glass (that is initially saturated with silanol groups with high polar component of surface energy), and coating it with a low energy fluoropolymer provides a control of the fractional coverage of the surface by polar and non-polar groups. This not only offers control of the initial van der Waals (and/or hydrogen) bonding at room temperature, but also provides control of the extent/degree of covalent bonding at higher temperature. Control of the initial van der Waals (and/or hydrogen) bonding at room temperature is performed so as to provide a bond of one surface to the other to allow vacuum and or spin-rinse-dry (SRD) type processing, and in some instances also an easily formed bond of one surface to the other—wherein the easily formed bond can be performed at room temperature without application of externally applied forces over the entire area of the thin sheet 20 as is done in pressing the thin sheet 20 to the carrier 10 with a squeegee, or with a reduced pressure environment. That is, the initial van der Waals bonding provides at least a minimum degree of bonding holding the thin sheet and carrier together so that they do not separate if one is held and the other is allowed to be subjected to the force of gravity. In most cases, the initial van der Walls (and/or hydrogen) bonding will be of such an extent that the article may also go through vacuum, SRD, and ultrasonic processing without the thin sheet delaminating from the carrier. This precise control of both van der Waal (and/or hydrogen bonding) and covalent interactions at appropriate levels via surface modification layer 30 (including the materials from which it is made and/or the surface treatment of the surface to which it is applied), and/or by heat treatment of the bonding surfaces prior to bonding them together, achieves the desired adhesion energy that allows thin sheet 20 to bond with carrier 10 throughout FPD style processing, while at the same time, allowing the thin sheet 20 to be separated (by an appropriate force avoiding damage to the thin sheet 20 and/or carrier) from the carrier 10 after FPD style processing. In addition, in appropriate circumstances, electrostatic charge could be applied to one or both glass surfaces to provide another level of control of the adhesion energy.

[0082] High temperature processing, FPD processing for example p-Si and oxide TFT fabrication, typically involve thermal processes at temperatures above 400˚C, above 500˚C,

and in some instances at or above 600°C, up to 650°C which would cause glass to glass bonding of a thin sheet 20 with a carrier 10 in the absence of surface modification layer 30. Therefore controlling the formation of Si-O-Si bonding leads to a reusable carrier. One method of controlling the formation of Si-O-Si bonding at elevated temperature is to reduce the concentration of surface hydroxyls on the surfaces to be bonded.

[0083] As shown in FIG. 3, which is Iler's plot (R. K. Iller: The Chemistry of Silica (Wiley-Interscience, New York, 1979) of surface hydroxyl concentration on silica as a function of temperature, the number of hydroxyls (OH groups) per square nm decreases as the temperature of the surface increases. Thus, heating a silica surface (and by analogy a glass surface, for example bonding surface 14 and/or bonding surface 24) reduces the concentration of surface hydroxyls, decreasing the probability that hydroxyls on two glass surfaces will interact. This reduction of surface hydroxyl concentration in turn reduces the Si-O-Si bonds formed per unit area, lowering the adhesive force. However, eliminating surface hydroxyls requires long annealing times at high temperatures (above 750°C to completely eliminate surface hydroxyls). Such long annealing times and high annealing temperatures result in an expensive process, and one which is not practical as it is likely to be above the strain point of typical display glass.

[0084] From the above analysis, the inventors have found that an article including a thin sheet and a carrier, suitable for high temperature, for example, FPD processing (including LTPS processing), can be made by balancing the following three concepts:

[0085] (1) Modification of the carrier and/or thin sheet bonding surface(s), by controlling initial room temperature bonding, which can be done by controlling van der Waals (and/or hydrogen) bonding, to create a moderate adhesion energy (for example, having a surface energy of >40 mJ/m^2 per surface prior to the surfaces being bonded) to facilitate initial room temperature bonding, and sufficient to survive non-high-temperature FPD processes, for example, vacuum processing, SRD processing, and/or ultrasonic processing;

[0086] (2) Surface modification of a carrier and/or a thin sheet in a manner that is thermally stable to survive high temperature processes without outgassing which can cause delamination and/or unacceptable contamination in the device fabrication, for example, contamination unacceptable to the semiconductor and/or display making processes in which the article may be used; and

[0087] (3) Controlling bonding at high temperatures, which can be done by controlling the carrier surface hydroxyl concentration, and concentration of other species capable of forming strong covalent bonds at elevated temperatures (e.g., temperature ≥ 400°C), whereby there can be controlled the bonding energy between the bonding surfaces of the carrier and the thin sheet such that even after high temperature processing (especially through thermal processes in the range of 500-650°C) the adhesive force between the carrier and thin sheet remains within a range that allows debonding of the thin sheet from the carrier with a separation force that does not damage at least the thin sheet (and preferably that does not damage either the thin sheet or the carrier), and yet sufficient enough to maintain the bond between the carrier and thin sheet so that they do not delaminate during processing.

[0088] Further, the inventors have found that the use of a surface modification layer 30, together with bonding surface preparation as appropriate, can balance the above concepts so as readily to achieve a controlled bonding area, that is, a bonding area that provides a sufficient room-temperature bond between the thin sheet 20 and carrier 10 to allow the article 2 to be processed in FPD type processes (including vacuum and wet processes), and yet one that controls covalent bonding between the thin sheet 20 and carrier 10 (even at elevated temperatures ≥ 400°C) so as to allow the thin sheet 20 to be removed from the carrier 10 (without damage to at least the thin sheet, and preferably without damage to the carrier also) after the article 2 has finished high temperature processing, for example, FPD type processing or LTPS processing. To evaluate potential bonding surface preparations, and surface modification layers, that would provide for full separation of the thin sheet from the carrier, suitable for high temperature processing, a series of tests were used to evaluate the suitability of each. Different FPD applications have different requirements, but LTPS and Oxide TFT processes appear to be the most stringent at this time and, thus, tests representative of steps in these processes were chosen, as these are desired applications for the article 2. Vacuum processes, wet cleaning (including SRD and ultrasonic type processes) and wet etching are common to many FPD applications. Typical aSi TFT fabrication requires processing up to 320°C. Annealing at 400°C is used in oxide TFT processes, whereas crystallization and dopant activation steps over 600°C are used in LTPS processing. Accordingly, the following five tests were used to evaluate the likelihood that a particular bonding surface preparation and surface modification layer 30 would allow a thin sheet 20 to remain bonded to a carrier 10 throughout FPD processing, while allowing the thin sheet 20 to be removed from the

carrier 10 (without damaging the thin sheet 20 and/or the carrier 10) after such processing (including processing at temperatures ≥ 400°C). The tests were performed in order, and a sample progressed from one test to the next unless there was failure of the type that would not permit the subsequent testing.

[0089] (1) Vacuum testing. Vacuum compatibility testing was performed in an STS Multiplex PECVD loadlock (available from SPTS, Newport, UK) –The loadlock was pumped by an Ebara A10S dry pump with a soft pump valve (available from Ebara Technologies Inc., Sacramento, CA. A sample was placed in the loadlock, and then the loadlock was pumped from atmospheric pressure down to 70 mTorr in 45sec. Failure, indicated by a notation of "F" in the "Vacuum" column of the tables below, was deemed to have occurred if there was: (a) a loss of adhesion between the carrier and the thin sheet (by visual inspection with the naked eye, wherein failure was deemed to have occurred if the thin sheet had fallen off of the carrier or was partially debonded therefrom); (b) bubbling between the carrier and the thin sheet (as determined by visual inspection with the naked eye – samples were photographed before and after the processing, and then compared, failure was determined to have occurred if defects increased in size by dimensions visible to the unaided eye); or (c) movement of the thin sheet relative to the carrier (as determined by visual observation with the naked eye – samples were photographed before and after testing, wherein failure was deemed to have occurred if there was a movement of bond defects, e.g., bubbles, or if edges debonded, or if there was a movement of the thin sheet on the carrier). In the tables below, a notation of "P" in the "Vacuum" column indicates that the sample did not fail as per the foregoing criteria.

[0090] (2) Wet process testing. Wet processes compatibility testing was performed using a Semitool model SRD-470S (available from Applied Materials, Santa Clara, CA). The testing consisted of 60seconds 500 rpm rinse, Q-rinse to 15 MOhm–cm at 500 rpm, 10seconds purge at 500rpm, 90seconds dry at 1800 rpm, and 180seconds dry at 2400 rpm under warm flowing nitrogen. Failure, as indicated by a notation of "F" in the "SRD" column of the tables below, was deemed to have occurred if there was: (a) a loss of adhesion between the carrier and the thin sheet (by visual inspection with the naked eye, wherein failure was deemed to have occurred if the thin sheet had fallen off of the carrier or was partially debonded therefrom); (b) bubbling between the carrier and the thin sheet (as determined by visual inspection with the naked eye – samples were photographed before and after the processing, and then

compared, failure was determined to have occurred if defects increased in size by dimensions visible to the unaided eye); or (c) movement of the thin sheet relative to the carrier (as determined by visual observation with the naked eye – samples were photographed before and after testing, wherein failure was deemed to have occurred if there was a movement of bond defects, e.g., bubbles, or if edges debonded, or if there was a movement of the thin sheet on the carrier); or (d) penetration of water under the thin sheet (as determined by visual inspection with an optical microscope at 50x, wherein failure was determined to have occurred if liquid or residue was observable). In the tables below, a notation of "P" in the "SRD" column indicates that the sample did not fail as per the foregoing criteria.

[0091] (3) Temperature to 400°C testing. 400°C process compatibility testing was performed using an Alwin21 Accuthermo610 RTP (available from Alwin21, Santa Clara CA. A carrier with a thin sheet bonded thereto was heated in a chamber cycled from room temperature to 400°C at 6.2°C/min, held at 400°C for 600seconds, and cooled at 1°C/min to 300°C. The carrier and thin sheet were then allowed to cool to room temperature. Failure, as indicated by a notation of "F" in the "400°C" column of the tables below, was deemed to have occurred if there was: (a) a loss of adhesion between the carrier and the thin sheet (by visual inspection with the naked eye, wherein failure was deemed to have occurred if the thin sheet had fallen off of the carrier or was partially debonded therefrom); (b) bubbling between the carrier and the thin sheet (as determined by visual inspection with the naked eye – samples were photographed before and after the processing, and then compared, failure was determined to have occurred if defects increased in size by dimensions visible to the unaided eye); or (c) increased adhesion between the carrier and the thin sheet whereby such increased adhesion prevents debonding (by insertion of a razor blade between the thin sheet and carrier, and/or by sticking a piece of Kapton™ tape, 1" wide x 6" long with 2-3" attached to 100mm square thin glass (K102 series from Saint Gobain Performance Plastic, Hoosik NY) to the thin sheet and pulling on the tape) of the thin sheet from the carrier without damaging the thin sheet or the carrier, wherein a failure was deemed to have occurred if there was damage to the thin sheet or carrier upon attempting to separate them, or if the thin sheet and carrier could not be debonded by performance of either of the debonding methods. Additionally, after the thin sheet was bonded with the carrier, and prior to the thermal cycling, debonding tests were performed on representative samples to determine that a particular material, including any associated surface treatment, did allow for debonding of the thin sheet from the carrier prior

to the temperature cycling. In the tables below, a notation of "P" in the "400°C" column indicates that the sample did not fail as per the foregoing criteria.

[0092] (4) Temperature to 600°C testing. 600°C process compatibility testing was performed using an Alwin21 Accuthermo610 RTP. A carrier with a thin sheet was heated in a chamber cycled from room temperature to 600°C at 9.5°C/min, held at 600°C for 600seconds, and then cooled at 1°C/min to 300°C. The carrier and thin sheet were then allowed to cool to room temperature. Failure, as indicated by a notation of "F" in the "600°C" column of the tables below, was deemed to have occurred if there was: (a) a loss of adhesion between the carrier and the thin sheet (by visual inspection with the naked eye, wherein failure was deemed to have occurred if the thin sheet had fallen off of the carrier or was partially debonded therefrom); (b) bubbling between the carrier and the thin sheet (as determined by visual inspection with the naked eye – samples were photographed before and after the processing, and then compared, failure was determined to have occurred if defects increased in size by dimensions visible to the unaided eye); or (c) increased adhesion between the carrier and the thin sheet whereby such increased adhesion prevents debonding (by insertion of a razor blade between the thin sheet and carrier, and/or by sticking a piece of Kapton™ tape as described above to the thin sheet and pulling on the tape) of the thin sheet from the carrier without damaging the thin sheet or the carrier, wherein a failure was deemed to have occurred if there was damage to the thin sheet or carrier upon attempting to separate them, or if the thin sheet and carrier could not be debonded by performance of either of the debonding methods. Additionally, after the thin sheet was bonded with the carrier, and prior to the thermal cycling, debonding tests were performed on representative samples to determine that a particular material, and any associated surface treatment, did allow for debonding of the thin sheet from the carrier prior to the temperature cycling. In the tables below, a notation of "P" in the "600°C" column indicates that the sample did not fail as per the foregoing criteria.

[0093] (5) Ultrasonic testing. Ultrasonic compatibility testing was performed by cleaning the article in a four tank line, wherein the article was processed in each of the tanks sequentially from tank #1 to tank #4. Tank dimensions, for each of the four tanks, were 18.4"L x 10"W x 15"D. Two cleaning tanks (#1 and #2) contained 1%Semiclean KG available from Yokohama Oils and Fats Industry Co Ltd., Yokohama Japan in DI water at 50°C. The cleaning tank #1 was agitated with a NEY prosonik 2 104 kHz ultrasonic generator (available from Blackstone-NEY Ultrasonics, Jamestown, NY), and the cleaning tank #2 was agitated

with a NEY prosonik 2 104 kHz ultrasonic generator. Two rinse tanks (tank #3 and tank #4) contained DI water at 50°C. The rinse tank #3 was agitated by NEY sweepsonik 2D 72 kHz ultrasonic generator and the rinse tank #4 was agitated by a NEY sweepsonik 2D 104 kHz ultrasonic generator. The processes were carried out for 10 min in each of the tanks #1-4, followed by spin rinse drying (SRD) after the sample was removed from tank #4. Failure, as indicated by a notation of "F" in the ""Ultrasonic" column of the tables below, was deemed to have occurred if there was: (a) a loss of adhesion between the carrier and the thin sheet (by visual inspection with the naked eye, wherein failure was deemed to have occurred if the thin sheet had fallen off of the carrier or was partially debonded therefrom); (b) bubbling between the carrier and the thin sheet (as determined by visual inspection with the naked eye – samples were photographed before and after the processing, and then compared, failure was determined to have occurred if defects increased in size by dimensions visible to the unaided eye); or (c) formation of other gross defects (as determined by visual inspection with optical microscope at 50x, wherein failure was deemed to have occurred if there were particles trapped between the thin sheet and carrier that were not observed before; or (d) penetration of water under the thin sheet (as determined by visual inspection with an optical microscope at 50x, wherein failure was determined to have occurred if liquid or residue was observable. In the tables below, a notation of "P" in the "Ultrasonic" column indicates that the sample did not fail as per the foregoing criteria. Additionally, in the tables below, a blank in the "Ultrasonic" column indicates that the sample was not tested in this manner.

[0094] Preparation of Bonding Surfaces via Hydroxyl Reduction by Heating

[0095] The benefit of modifying one or more of the bonding surfaces 14, 24 with a surface modification layer 30 so the article 2 is capable of successfully undergoing FPD processing (i.e., where the thin sheet 20 remains bonded to the carrier 10 during processing, and yet may be separated from the carrier 10 after processing, including high temperature processing) was demonstrated by processing articles 2 having carriers 10 and thin sheets 20 without a surface modification layer 30 therebetween. Specifically, first there was tried preparation of the bonding surfaces 14, 24 by heating to reduce hydroxyl groups, but without a surface modification layer 30. The carriers 10 and thin sheets 20 were cleaned, the bonding surfaces 14 and 24 were bonded to one another, and then the articles 2 were tested. A typical cleaning process for preparing glass for bonding is the SC1 cleaning process where the glass is cleaned in a dilute hydrogen peroxide and base (commonly ammonium hydroxide, but

tetramethylammonium hydroxide solutions for example JT Baker JTB-100 or JTB-111 may also be used). Cleaning removes particles from the bonding surfaces, and makes the surface energy known, i.e., it provides a base-line of surface energy. The manner of cleaning need not be SC1, other types of cleaning may be used, as the type of cleaning is likely to have only a very minor effect on the silanol groups on the surface. The results for various tests are set forth below in Table 1.

[0096] A strong but separable initial, room temperature or van der Waal and/or Hydrogen-bond was created by simply cleaning a thin glass sheet of 100mm square x 100 micron thick, and a glass carrier 150mm diameter single mean flat (SMF) wafer 0.50 or 0.63 mm thick, each comprising Eagle XG® display glass (an alkali-free, alumino-boro-silicate glass, having an average surface roughness Ra on the order of 0.2 nm, available from Corning Incorporated, Corning, NY). In this example, glass was cleaned 10 min in a 65°C bath of 40:1:2 DI water: JTB-111:Hydrogen peroxide. The thin glass or glass carrier may or may not have been annealed in nitrogen for 10min at 400°C to remove residual water – the notation "400°C" in the "Carrier" column or the "Thin Glass" column in Table 1 below indicates that the sample was annealed in nitrogen for 10 minutes at 400 °C. FPD process compatibility testing demonstrates this SC1-SC1 initial, room temperature, bond is mechanically strong enough to pass vacuum, SRD and ultrasonic testing. However, heating at 400°C and above created a permanent bond between the thin glass and carrier, i.e., the thin glass sheet could not be removed from the carrier without damaging either one or both of the thin glass sheet and carrier. And this was the case even for Example 1c, wherein each of the carrier and the thin glass had an annealing step to reduce the concentration of surface hydroxyls. Accordingly, the above-described preparation of the bonding surfaces 14, 24 via heating alone and then bonding of the carrier 10 and the thin sheet 12, without a surface modification layer 30, is not a suitable controlled bond for processes wherein the temperature will be ≥ 400°C.

[0097] Table 1 - process compatibility testing of SC1-treated glass bonding surfaces

Example	Carrier	Thin Glass	Vacuum	SRD	400C	600C	Ultrasonic
1a	SC1	SC1	P	P	F	F	P
1b	SC1, 400C	SC1	P	P	F	F	P
1c	SC1, 400C	SC1, 400C	P	P	F	F	P

[0098] Preparation of Bonding Surfaces by Hydroxyl Reduction and Surface Modification Layer

[0099] Hydroxyl reduction, as by heat treatment for example, and a surface modification layer 30 may be used together to control the interaction of bonding surfaces 14, 24. For example, the bonding energy (both van der Waals and/or Hydrogen-bonding at room temperature due to the polar/dispersion energy components, and covalent bonding at high temperature due to the covalent energy component) of the bonding surfaces 14, 24 can be controlled so as to provide varying bond strength from that wherein room-temperature bonding is difficult, to that allowing easy room-temperature bonding and separation of the bonding surfaces after high temperature processing, to that which—after high temperature processing—prevents the surfaces from separating without damage. In some applications, it may be desirable to have no, or very weak bonding. In other applications, for example providing a carrier for high temperature processes (wherein process temperatures $\geq 500°C$, or $\geq 600°C$, and up to 650°C, may be achieved), it is desirable to have sufficient van der Waals and/or Hydrogen-bonding, at room temperature to initially put the thin sheet and carrier together, and yet prevent or limit high temperature covalent bonding. For still other applications, it may be desirable to have sufficient room temperature bonding to initially put the thin sheet and carrier together, and also to develop strong covalent bonding at high temperature. Although not wishing to be bound by theory, in some instances the surface modification layer may be used to control room temperature bonding by which the thin sheet and carrier are initially put together, whereas the reduction of hydroxyl groups on the surface (as by heating the surface, or by reaction of the hydroxyl groups with the surface modification layer, for example) may be used to control the covalent bonding, particularly that at high temperatures.

[00100] A material for the surface modification layer 30 may provide a bonding surface 14, 24 with an energy (for example, and energy < 40 mJ/m^2, as measured for one surface, and including polar and dispersion components) whereby the surface produces only weak bonding. In one example, hexamethyldisilazane (HMDS) may be used to create this low energy surface by reacting with the surface hydroxyls to leave a trimethylsilyl (TMS) terminated surface. HMDS as a surface modification layer may be used together with surface heating to reduce the hydroxyl concentration to control both room temperature and high temperature bonding. By choosing a suitable bonding surface preparation for each bonding surface 14, 24, there can be achieved articles having a range of capabilities. More specifically, of interest to high temperature processing, there can be achieved a suitable bond

between a thin sheet 20 and a carrier 10 so as to survive (or pass) each of the vacuum SRD, 400°C (parts a and c), and 600°C (parts a and c), processing tests.

[00101] In one example, following SC1 cleaning by HMDS treatment of both thin glass and carrier creates a weakly bonded surface which is challenging to bond at room temperature with van der Waals (and/or hydrogen bonding) forces. Mechanical force is applied to bond the thin glass to the carrier. As shown in example 2a of Table 2, this bonding is sufficiently weak that deflection of the carrier is observed in vacuum testing and SRD processing, bubbling (likely due to outgassing) was observed in 400°C and 600°C thermal processes, and particulate defects were observed after ultrasonic processing.

[00102] In another example, HMDS treatment of just one surface (carrier in the example cited) creates stronger room temperature adhesion which survives vacuum and SRD processing. However, thermal processes at 400°C and above permanently bonded the thin glass to the carrier. This is not unexpected as the maximum surface coverage of the trimethylsilyl groups on silica has been calculated by Sindorf and Maciel in J. Phys. Chem. 1982, 86, 5208-5219 to be 2.8/nm^2 and measured by Suratwala et. al. in Journal of Non-Crystalline Solids 316 (2003) 349–363 as 2.7/nm^2, vs. a hydroxyl concentration of 4.6-4.9/nm^2 for fully hydroxylated silica. That is, although the trimethylsilyl groups do bond with some surface hydroxyls, there will remain some un-bonded hydroxyls. Thus one would expect condensation of surface silanol groups to permanently bond the thin glass and carrier given sufficient time and temperature.

[00103] A varied surface energy can be created by heating the glass surface to reduce the surface hydroxyl concentration prior to HMDS exposure, leading to an increased polar component of the surface energy. This both decreases the driving force for formation of covalent Si-O-Si bonds at high temperature and leads to stronger room-temperature bonding, for example, van der Waal (and/or hydrogen) bonding. FIG. 4 shows the surface energy of an Eagle XG® display glass carrier after annealing, and after HMDS treatment. Increased annealing temperature prior to HMDS exposure increases the total (polar and dispersion) surface energy (line 402) after HMDS exposure by increasing the polar contribution (line 404). It is also seen that the dispersion contribution (line 406) to the total surface energy remains largely unchanged by the heat treatment. Although not wishing to be bound by theory, increasing the polar component of, and thereby the total, energy in the surface after

HMDS treatment appears to be due to there being some exposed glass surface areas even after HMDS treatment because of sub-monolayer TMS coverage by the HMDS.

[00104] In example 2b, the thin glass sheet was heated at a temperature of 150°C in a vacuum for one hour prior to bonding with the non-heat-treated carrier having a coating of HMDS. This heat treatment of the thin glass sheet was not sufficient to prevent permanent bonding of the thin glass sheet to the carrier at temperatures ≥ 400°C.

[00105] As shown in examples 2c-2e of Table 2, varying the annealing temperature of the glass surface prior to HMDS exposure can vary the bonding energy of the glass surface so as to control bonding between the glass carrier and the thin glass sheet.

[00106] In example 2c, the carrier was annealed at a temperature of 190°C in vacuum for 1 hour, followed by HMDS exposure to provide surface modification layer 30. Additionally, the thin glass sheet was annealed at 450°C in a vacuum for 1 hour before bonding with the carrier. The resulting article survived the vacuum, SRD, and 400°C tests (parts a and c, but did not pass part b as there was increased bubbling), but failed the 600°C test. Accordingly, although there was increased resistance to high temperature bonding as compared with example 2b, this was not sufficient to produce an article for processing at temperatures ≥ 600°C wherein all of the thin sheet may be removed from the carrier.

[00107] In example 2d, the carrier was annealed at a temperature of 340°C in a vacuum for 1 hour, followed by HMDS exposure to provide surface modification layer 30. Again, the thin glass sheet was annealed at 450°C for 1 hour in a vacuum before bonding with the carrier. The results were similar to those for example 2c, wherein the article survived the vacuum, SRD, and 400°C tests (parts a and c, but did not pass part b as there was increased bubbling), but failed the 600°C test.

[00108] As shown in example 2e, annealing both thin glass and carrier at 450°C in vacuum for 1 hour, followed by HMDS exposure of the carrier, and then bonding of the carrier and thin glass sheet, improves the temperature resistance to permanent bonding. An anneal of both surfaces to 450°C prevents permanent bonding after RTP annealing at 600°C for 10 min, that is, this sample passed the 600°C processing test (parts a and c, but did not pass part b as there was increased bubbling; a similar result was found for the 400°C test).

[00109] Table 2 - process compatibility testing of HMDS surface modification layers

Example	Carrier	Thin Glass	Vacuum	SRD	400C	600C	Ultrasonic
2a	SC1, HMDS	SC1, HMDS	F	F	P	P	F
2b	SC1, HMDS	SC1 , 150C	P	P	F	F	
2c	SC1, 190C, HMDS	SC1 , 450C	P	P	P	F	
2d	SC1, 340C, HMDS	SC1 , 450C	P	P	P	F	
2e	SC1, 450C, HMDS	SC1 , 450C	P	P	P	P	

[00110] In Examples 2a to 2e above, each of the carrier and the thin sheet were Eagle XG® glass, wherein the carrier was a 150 mm diameter SMF wafer 630 microns thick and the thin sheet was 100 mm square 100 microns thick. The HMDS was applied by pulse vapor deposition in a YES-5 HMDS oven (available from Yield Engineering Systems, San Jose CA) and was one atomic layer thick (i.e., about 0.2 to 1 nm), although the surface coverage may be less than one monolayer, i.e., some of the surface hydroxyls are not covered by the HMDS as noted by Maciel and discussed above. Because of the small thickness in the surface modification layer, there is little risk of outgassing which can cause contamination in the device fabrication. Also, as indicated in Table 2 by the "SC1" notation, each of the carriers and thin sheets were cleaned using an SC1 process prior to heat treating or any subsequent HMDS treatment.

[00111] A comparison of example 2a with example 2b shows that the bonding energy between the thin sheet and the carrier can be controlled by varying the number of surfaces which include a surface modification layer. And controlling the bonding energy can be used to control the bonding force between two bonding surfaces. Also, a comparison of examples 2b-2e, shows that the bonding energy of a surface can be controlled by varying the parameters of a heat treatment to which the bonding surface is subjected before application of a surface modification material. Again, the heat treatment can be used to reduce the number of surface hydroxyls and, thus, control the degree of covalent bonding, especially that at high temperatures.

[00112] Other materials, that may act in a different manner to control the surface energy on a bonding surface, may be used for the surface modification layer 30 so as to control the room temperature and high temperature bonding forces between two surfaces. For example, a thin sheet that may be completely removed from a carrier can also be created if one or both bonding surfaces are modified to create a moderate bonding force with a surface modification layer that either covers, or sterically hinders species for example hydroxyls to prevent the formation at elevated temperature of strong permanent covalent bonds between carrier and thin sheet. One way to create a tunable surface energy, and cover surface hydroxyls to

prevent formation of covalent bonds, is deposition of plasma polymer films, for example fluoropolymer films. Plasma polymerization deposits a thin polymer film under atmospheric or reduced pressure and plasma excitation (DC or RF parallel plate, Inductively Coupled Plasma (ICP) Electron Cyclotron Resonance (ECR) downstream microwave or RF plasma) from source gases for example fluorocarbon sources (including CF4, CHF3, C2F6, C3F6, C2F2, CH3F, C4F8, chlorofluoro carbons, or hydrochlorofluoro carbons), hydrocarbons for example alkanes (including methane, ethane, propane, butane), alkenes (including ethylene, propylene), alkynes (including acetylene), and aromatics (including benzene, toluene), hydrogen, and other gas sources for example SF6. Plasma polymerization creates a layer of highly cross-linked material. Control of reaction conditions and source gases can be used to control the film thickness, density, and chemistry to tailor the functional groups to the desired application.

[00113] FIG. 5 shows the total (line 502) surface energy (including polar (line 504) and dispersion (line 506) components) of plasma polymerized fluoropolymer (PPFP) films deposited from CF4-C4F8 mixtures with an Oxford ICP380 etch tool (available from Oxford Instruments, Oxfordshire UK). The films were deposited onto a sheet of Eagle XG ® glass, and spectroscopic ellipsometry showed the films to be 1-10 nm thick. As seen from FIG. 5, glass carriers treated with plasma polymerized fluoropolymer films containing less than 40% C4F8 exhibit a surface energy >40 mJ/m^2 and produce controlled bonding between the thin glass and carrier at room temperature by van der Waal or hydrogen bonding. Facilitated bonding is observed when initially bonding the carrier and thin glass at room temperature. That is, when placing the thin sheet onto the carrier, and pressing them together at a point, a wave front travels across the carrier, but at a lower speed than is observed for SC1 treated surfaces having no surface modification layer thereon. The controlled bonding is sufficient to withstand all standard FPD processes including vacuum, wet, ultrasonic, and thermal processes up to 600°C, that is this controlled bonding passed the 600°C processing test without movement or delamination of the thin glass from the carrier. De-bonding was accomplished by peeling with a razor blade and/or Kapton™ tape as described above. The process compatibility of two different PPFP films (deposited as described above) is shown in Table 3. PPFP 1 of example 3a was formed with C4F8/(C4F8+CF4)=0, that is, formed with CF4/H2 and not C4F8, and PPFP 2 of example 3b was deposited with C4F8/(C4F8+CF4)=0.38. Both types of PPFP films survived the vacuum, SRD, 400°C and

600°C processing tests. However, delamination is observed after 20 min of ultrasonic cleaning of PPFP 2 indicating insufficient adhesive force to withstand such processing. Nonetheless, the surface modification layer of PPFP2 may be useful for some applications, as where ultrasonic processing is not necessary.

[00114] Table 3 - process compatibility testing of PPFP surface modification layers

Example	Carrier	Thin Glass	Vacuum	SRD	400C	600C	Ultrasonic
3a	PPFP 1	SC1 , 150C	P	P	P	P	P
3b	PPFP2	SC1 , 150C	P	P	P	P	F

[00115] In Examples 3a and 3b above, each of the carrier and the thin sheet were Eagle XG® glass, wherein the carrier was a 150 mm diameter SMF wafer 630 microns thick and the thin sheet was 100 mm square 100 microns thick. Because of the small thickness in the surface modification layer, there is little risk of outgassing which can cause contamination in the device fabrication. Further, because the surface modification layer did not appear to degrade, again, there is even less risk of outgassing. Also, as indicated in Table 3, each of the thin sheets was cleaned using an SC1 process prior to heat treating at 150°C for one hour in a vacuum.

[00116] Still other materials, that may function in a different manner to control surface energy, may be used as the surface modification layer to control the room temperature and high temperature bonding forces between the thin sheet and the carrier. For example, a bonding surface that can produce controlled bonding can be created by silane treating a carrier and/or glass thin sheet. Silanes are chosen so as to produce a suitable surface energy, and so as to have sufficient thermal stability for the application. The carrier or thin sheet to be treated may be cleaned by a process for example O2 plasma or UV-ozone, and SC1 or standard clean two (SC2, as is known in the art) cleaning to remove organics and other impurities (metals, for example) that would interfere with the silane reacting with the surface silanol groups. Washes based on other chemistries may also be used, for example, HF, or H2SO4 wash chemistries. The carrier or thin sheet may be heated to control the surface hydroxyl concentration prior to silane application (as discussed above in connection with the surface modification layer of HMDS), and/or may be heated after silane application to complete silane condensation with the surface hydroxyls. The concentration of unreacted hydroxyl groups after silanization may be made low enough prior to bonding as to prevent permanent bonding between the thin sheet and carrier at temperatures $\geq 400°C$, that is, to form a controlled bond. This approach is described below.

[00117] Example 4a

[00118] A glass carrier with its bonding surface O2 plasma and SC1 treated was then treated with 1% dodecyltriethoxysilane (DDTS) in toluene, and annealed at 150°C in vacuum for 1 hour to complete condensation. DDTS treated surfaces exhibit a surface energy of 45 mJ/m^2. As shown in Table 4, a glass thin sheet (having been SC1 cleaned and heated at 400°C in a vacuum for one hour) was bonded to the carrier bonding surface having the DDTS surface modification layer thereon. This article survived wet and vacuum process tests but did not survive thermal processes over 400°C without bubbles forming under the carrier due to thermal decomposition of the silane. This thermal decomposition is expected for all linear alkoxy and chloro alkylsilanes $R1_xSi(OR2)_y(Cl)_z$ where x=1 to 3, and y+z = 4-x except for methyl, dimethyl, and trimethyl silane (x=1 to 3, $R1=CH_3$) which produce coatings of good thermal stability.

[00119] Example 4b

[00120] A glass carrier with its bonding surface O2 plasma and SC1 treated was then treated with 1% 3,3,3, trifluoropropyltritheoxysilane (TFTS) in toluene, and annealed at 150°C in vacuum for 1 hour to complete condensation. TFTS treated surfaces exhibit a surface energy of 47 mJ/m^2. As shown in Table 4, a glass thin sheet (having been SC1 cleaned and then heated at 400°C in a vacuum for one hour) was bonded to the carrier bonding surface having the TFTS surface modification layer thereon. This article survived the vacuum, SRD, and 400°C process tests without permanent bonding of the glass thin sheet to the glass carrier. However, the 600°C test produced bubbles forming under the carrier due to thermal decomposition of the silane. This was not unexpected because of the limited thermal stability of the propyl group. Although this sample failed the 600°C test due to the bubbling, the material and heat treatment of this example may be used for some applications wherein bubbles and the adverse effects thereof, for example reduction in surface flatness, or increased waviness, can be tolerated.

[00121] Example 4c

[00122] A glass carrier with its bonding surface O2 plasma and SC1 treated was then treated with 1% phenyltriethoxysilane (PTS) in toluene, and annealed at 200°C in vacuum for 1 hour to complete condensation. PTS treated surfaces exhibit a surface energy of 54 mJ/m^2. As shown in Table 4, a glass thin sheet (having been SC1 cleaned and then heated at 400°C in a vacuum for one hour) was bonded to the carrier bonding surface having the PTS surface

modification layer. This article survived the vacuum, SRD, and thermal processes up to 600°C without permanent bonding of the glass thin sheet with the glass carrier.

[00123] Example 4d

[00124] A glass carrier with its bonding surface O2 plasma and SC1 treated was then treated with 1% diphenyldiethoxysilane (DPDS) in toluene, and annealed at 200°C in vacuum for 1 hour to complete condensation. DPDS treated surfaces exhibit a surface energy of 47 mJ/m^2. As shown in Table 4, a glass thin sheet (having been SC1 cleaned and then heated at 400°C in a vacuum for one hour) was bonded to the carrier bonding surface having the DPDS surface modification layer. This article survived the vacuum and SRD tests, as well as thermal processes up to 600°C without permanent bonding of the glass thin sheet with the glass carrier.

[00125] Example 4e.

[00126] A glass carrier having its bonding surface O2 plasma and SC1 treated was then treated with 1% 4-pentafluorophenyltriethoxysilane (PFPTS) in toluene, and annealed at 200°C in vacuum for 1 hour to complete condensation. PFPTS treated surfaces exhibit a surface energy of 57 mJ/m^2. As shown in Table 4, a glass thin sheet (having been SC1 cleaned and then heated at 400°C in a vacuum for one hour) was bonded to the carrier bonding surface having the PFPTS surface modification layer. This article survived the vacuum and SRD tests, as well as thermal processes up to 600°C without permanent bonding of the glass thin sheet with the glass carrier.

[00127] Table 4 - process compatibility testing of silane surface modification layers

Example	Carrier	Thin Glass	Vacuum	SRD	400C	600C
4a	SC1, DDTS	SC1, 400C	P	P	F	F
4b	SC1, TFTS	SC1, 400C	P	P	P	F
4c	SC1, PTS	SC1, 400C	P	P	P	P
4d	SC1, DPDS	SC1, 400C	P	P	P	P
4e	SC1, PFPTS	SC1, 400C	P	P	P	P

[00128] In Examples 4a to 4e above, each of the carrier and the thin sheet were Eagle XG® glass, wherein the carrier was a 150 mm diameter SMF wafer 630 microns thick and the thin sheet was 100 mm square 100 microns thick. The silane layers were self-assembled monolayers (SAM), and thus were on the order of less than about 2 nm thick. In the above examples, the SAM was created using an organosilane with an aryl or alkyl non-polar tail and a mono, di, or tri-alkoxide head group. These react with the silanol surface on the glass to directly attach the organic functionality. Weaker interactions between the non-polar head

groups organize the organic layer. Because of the small thickness in the surface modification layer, there is little risk of outgassing which can cause contamination in the device fabrication. Further, because the surface modification layer did not appear to degrade in examples 4c, 4d, and 4e, again, there is even less risk of outgassing. Also, as indicated in Table 4, each of the glass thin sheets was cleaned using an SC1 process prior to heat treating at 400°C for one hour in a vacuum.

[00129] As can be seen from a comparison of examples 4a-4e, controlling surface energy of the bonding surfaces to be above 40 mJ/m^2 so as to facilitate the initial room temperature bonding is not the only consideration to creating a controlled bond that will withstand FPD processing and still allow the thin sheet to be removed from the carrier without damage. Specifically, as seen from examples 4a-4e, each carrier had a surface energy above 40 mJ/m^2, which facilitated initial room temperature bonding so that the article survived vacuum and SRD processing. However, examples 4a and 4b did not pass 600°C processing test. As noted above, for certain applications, it is also important for the bond to survive processing up to high temperatures (for example, ≥ 400°C, ≥ 500°C, or ≥600°C, up to 650°C, as appropriate to the processes in which the article is designed to be used) without degradation of the bond to the point where it is insufficient to hold the thin sheet and carrier together, and also to control the covalent bonding that occurs at such high temperatures so that there is no permanent bonding between the thin sheet and the carrier. As shown by the examples in Table 4, aromatic silanes, in particular phenyl silanes, are useful for providing a controlled bond that will facilitate initial room temperature bonding, and that will withstand high temperature processing and still allow the thin sheet to be removed from the carrier without damage.

[00130] The above-described separation in examples 4, 3, and 2, is performed at room temperature without the addition of any further thermal or chemical energy to modify the bonding interface between the thin sheet and carrier. The only energy input is mechanical pulling and/or peeling force.

[00131] The materials described above in examples 3 and 4 can be applied to the carrier, to the thin sheet, or to both the carrier and thin sheet surfaces that will be bonded together.

[00132] Outgassing

[00133] Polymer adhesives used in typical wafer bonding applications are generally 10-100 microns thick and lose about 5% of their mass at or near their temperature limit. For such materials, evolved from thick polymer films, it is easy to quantify the amount of mass loss, or

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,

reaction with the carrier, and de-wetting, for example) are evidenced by a change in the surface energy of surface 902. A change in the surface energy of surface 902 by itself does not necessarily mean that the surface modification layer has outgassed, but does indicate a general instability of the material at that temperature as its character is changing due to the mechanisms noted above, for example. Thus, the less the change in surface energy of surface 902, the more stable the surface modification layer. On the other hand, because of the close proximity of the surface 912 to the surface 902, any material outgassed from surface 902 will be collected on surface 912 and will change the surface energy of surface 912. Accordingly, the change in surface energy of surface 912 is a proxy for outgassing of the surface modification layer present on surface 902.

[00138] Thus, one test for outgassing uses the change in surface energy of the cover surface 912. Specifically, if there is a change in surface energy—of surface 912—of $\geq$ 10 mJ/m2, then there is outgassing. Changes in surface energy of this magnitude are consistent with contamination which can lead to loss of film adhesion or degradation in material properties and device performance. A change in surface energy of $\leq$ 5 mJ/m2 is close to the repeatability of surface energy measurements and inhomogeneity of the surface energy. This small change is consistent with minimal outgassing.

[00139] During testing that produced the results in FIG. 7, the carrier 900, the cover 910, and the spacers 920, were made of Eagle XG glass, an alkali-free alumino-boro-silicate display-grade glass available from Corning Incorporated, Corning, NY, although such need not be the case. The carrier 900 and cover 910 were 150mm diameter 0.63mm thick. Generally, the carrier 910 and cover 920 will be made of the same material as carrier 10 and thin sheet 20, respectively, for which an outgassing test is desired. During this testing, silicon spacers 0.63 mm thick, 2mm wide, and 8cm long, thereby forming a gap of 0.63 mm between surfaces 902 and 912. During this testing, the chamber 930 was incorporated in MPT-RTP600s rapid thermal processing equipment that was cycled from room temperature to the test limit temperature at a rate of 9.2°C per minute, held at the test limit temperature for varying times as shown in the graphs as "Anneal Time", and then cooled at furnace rate to 200°C. After the oven had cooled to 200°C, the test article was removed, and after the test article had cooled to room temperature, the surface energies of each surface 902 and 912 were again measured. Thus, by way of example, using the data for the change in cover surface energy, tested to a limit temperature of 450°C, for Material #1, line 1003, the data

was collected as follows. The data point at 0 minutes shows a surface energy of 75 mJ/m2 (milli-Joules per square meter), and is the surface energy of the bare glass, i.e., there has been no time-temperature cycle yet run. The data point at one minute indicates the surface energy as measured after a time-temperature cycle performed as follows: the article 901 (having Material #1 used as a surface modification layer on the carrier 900 to present surface 902) was placed in a heating chamber 930 at room temperature, and atmospheric pressure; the chamber was heated to the test-limit temperature of 450°C at a rate of 9.2°C per minute, with a N2 gas flow at two standard liters per minute, and held at the test-limit temperature of 450°C for 1 minute; the chamber was then allowed to cool to 300°C at a rate of 1°C per minute, and the article 901 was then removed from the chamber 930; the article was then allowed to cool to room temperature (without N2 flowing atmosphere); the surface energy of surface 912 was then measured and plotted as the point for 1 minute on line 1003. The remaining data points for Material #1 (lines 1003, 1004), as well as the data points for Material #2 (lines 1203, 1204), Material #3 (lines 1303, 1304), Material #4 (lines 1403, 1404), Material #5 (lines 1503, 1504), and Material #6 (lines 1603, and 1604), were then determined in a similar manner with the minutes of anneal time corresponding to the hold time at the test-limit temperature, either 450°C, or 600°C, as appropriate. The data points for lines 1001, 1002, 1201, 1202, 1301, 1302, 1401, 1402, 1501, 1502, 1601, and 1602, representing surface energy of surface 902 for the corresponding surface modification layer materials (Materials #1-6) were determined in a similar manner, except that the surface energy of the surface 902 was measured after each time-temperature cycle.

[00140] The above assembly process, and time-temperature cycling, were carried out for six different materials as set forth below, and the results are graphed in FIG. 7. Of the six materials, Materials #1-4 correspond to surface modification layer materials described above. Materials #5 and #6 are comparative examples.

[00141] Material #1 is a CHF3-CF4 plasma polymerized fluoropolymer. This material is consistent with the surface modification layer in example 3b, above. As shown in FIG. 7, lines 1001 and 1002 show that the surface energy of the carrier did not significantly change. Thus, this material is very stable at temperatures from 450°C to 600°C. Additionally, as shown by the lines 1003 and 1004, the surface energy of the cover did not significantly change either, i.e., the change is $\leq$ 5mJ/m2. Accordingly, there was no outgassing associated with this material from 450°C to 600°C.

[00142] Material #2 is a phenylsilane, a self-assembled monolayer (SAM) deposited form 1% toluene solution of phenyltriethoxysilane and cured in vacuum oven 30 minutes at 190°C. This material is consistent with the surface modification layer in example 4c, above. As shown in FIG. 7, lines 1201 and 1202 indicate some change in surface energy on the carrier. As noted above, this indicates some change in the surface modification layer, and comparatively, Material #2 is somewhat less stable than Material #1. However, as noted by lines 1203 and 1204, the change in surface energy of the carrier is ≤ 5mJ/m2, showing that the changes to the surface modification layer did not result in outgassing.

[00143] Material #3 is a pentafluorophenylsilane, a SAM deposited from 1% toluene solution of pentafluorophenyltriethoxysilane and cured in vacuum oven 30 minutes at 190°C. This material is consistent with the surface modification layer in example 4e, above. As shown in FIG. 7, lines 1301 and 1302 indicate some change in surface energy on the carrier. As noted above, this indicates some change in the surface modification layer, and comparatively, Material #3 is somewhat less stable than Material #1. However, as noted by lines 1303 and 1304, the change in surface energy of the carrier is ≤ 5mJ/m2, showing that the changes to the surface modification layer did not result in outgassing.

[00144] Material #4 is hexamethyldisilazane (HMDS) deposited from vapor in a YES HMDS oven at 140°C. This material is consistent with the surface modification layer in Example 2b, of Table 2, above. As shown in FIG. 7, lines 1401 and 1402 indicate some change in surface energy on the carrier. As noted above, this indicates some change in the surface modification layer, and comparatively, Material #4 is somewhat less stable than Material #1. Additionally, the change in surface energy of the carrier for Material #4 is greater than that for any of Materials #2 and #3 indicating, comparatively, that Material #4 is somewhat less stable than Materials #2 and #3. However, as noted by lines 1403 and 1404, the change in surface energy of the carrier is ≤ 5mJ/m2, showing that the changes to the surface modification layer did not result in outgassing that affected the surface energy of the cover. However, this is consistent with the manner in which HMDS outgasses. That is, HMDS outgasses ammonia and water which do not affect the surface energy of the cover, and which may not affect some electronics fabrication equipment and/or processing. On the other hand, when the products of the outgassing are trapped between the thin sheet and carrier, there may be other problems, as noted below in connection with the second outgassing test.

[00145] Material #5 is Glycidoxypropylsilane, a SAM deposited from 1% toluene solution of glycidoxypropyltriethoxysilane and cured in vacuum oven 30 minutes at 190°C. This is a comparative example material. Although there is relatively little change in the surface energy of the carrier, as shown by lines 1501 and 1502, there is significant change in surface energy of the cover as shown by lines 1503 and 1504. That is, although Material #5 was relatively stable on the carrier surface, it did, indeed outgas a significant amount of material onto the cover surface whereby the cover surface energy changed by ≥ 10mJ/m2. Although the surface energy at the end of 10 minutes at 600°C is within 10 mJ/m2, the change during that time does exceed 10mJ/m2. See, for example the data points at 1 and 5 minutes. Although not wishing to be bound by theory, the slight uptick in surface energy from 5 minutes to 10 minutes is likely do to some of the outgassed material decomposing and falling off of the cover surface.

[00146] Material #6 is DC704 a silicone coating prepared by dispensing 5 ml Dow Corning 704 diffusion pump oil tetramethyltetraphenyl trisiloxane (available from Dow Corning) onto the carrier, placing it on a 500°C hot plate in air for 8 minutes. Completion of sample preparation is noted by the end of visible smoking. After preparing the sample in the above manner, the outgassing testing described above was carried out. This is a comparative example material. As shown in FIG. 7, lines 1601 and 1602 indicate some change in surface energy on the carrier. As noted above, this indicates some change in the surface modification layer, and comparatively, Material #6 is less stable than Material #1. Additionally, as noted by lines 1603 and 1604, the change in surface energy of the carrier is ≥ 10mJ/m2, showing significant outgassing. More particularly, at the test-limit temperature of 450°C, the data point for 10 minutes shows a decrease in surface energy of about 15 mJ/m2, and even greater decrease in surface energy for the points at 1 and 5 minutes. Similarly, the change in surface energy of the cover during cycling at the 600°C test-limit temperature, the decrease in surface energy of the cover was about 25 mJ/m2 at the 10 minute data point, somewhat more at 5 minutes, and somewhat less at 1 minute. Altogether, though, a significant amount of outgassing was shown for this material over the entire range of testing.

[00147] Significantly, for Materials #1-4, the surface energies throughout the time-temperature cycling indicate that the cover surface remains at a surface energy consistent with that of bare glass, i.e., there is collected no material outgassed from the carrier surface. In the case of Material #4, as noted in connection with Table 2, the manner in which the

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

removing scanner artifacts (by using a calibration reference scan performed without a sample in the scanner). The bonded area is then analyzed using standard image processing techniques such as thresholding, hole filling, erosion/dilation, and blob analysis. The newer Epson Expression 11000XL Photo may also be used in a similar manner. In transmission mode, bubbles in the bonding area are visible in the scanned image and a value for bubble area can be determined. Then, the bubble area is compared to the total bonding area (i.e., the total overlap area between the thin sheet and the carrier) to calculate a % area of the bubbles in the bonding area relative to the total bonding area. The samples are then heat treated in a MPT-RTP600s Rapid Thermal Processing system under N2 atmosphere at test-limit temperatures of 300°C, 450°C, and 600°C, for up to 10 minutes. Specifically, the time-temperature cycle carried out included: inserting the article into the heating chamber at room temperature and atmospheric pressure; the chamber was then heated to the test-limit temperature at a rate of 9°C per minute; the chamber was held at the test-limit temperature for 10 minutes; the chambe9 was then cooled at furnace rate to 200°C; the article was removed from the chamber and allowed to cool to room temperature; the article was then scanned a second time with the optical scanner. The % bubble area from the second scan was then calculated as above and compared with the % bubble area from the first scan to determine a change in % bubble area (Δ% bubble area). As noted above, a change in bubble area of ≥ 5% is significant and an indication of outgassing. A change in % bubble area was selected as the measurement criterion because of the variability in original % bubble area. That is, most surface modification layers have a bubble area of about 2% in the first scan due to handling and cleanliness after the thin sheet and carrier have been prepared and before they are bonded. However, variations may occur between materials. The same Materials #1-6 set forth with respect to the first outgassing test method were again used in this second outgassing test method. Of these materials, Materials #1-4 exhibited about 2% bubble area in the first scan, whereas Materials #5 and #6 showed significantly larger bubble area, i.e., about 4%, in the first scan.

[00150] The results of the second outgassing test will be described with reference to FIGS. 8 and 9. The outgassing test results for Materials #1-3 are shown in FIG. 8, whereas the outgassing test results for Materials #4-6 are shown in FIG. 9.

[00151] The results for Material #1 are shown as square data points in FIG. 8. As can be seen from the figure, the change in % bubble area was near zero for test-limit temperatures of

300°C, 450°C, and 600°C. Accordingly, Material # 1 shows no outgassing at these temperatures.

[00152] The results for Material #2 are shown as diamond data points in FIG. 8. As can be seen from the figure, the change in % bubble area is less than 1 for test-limit temperatures of 450°C and 600°C. Accordingly, Material #2 shows no outgassing at these temperatures.

[00153] The results for Material #3 are shown as triangle data points in FIG. 8. As can be seen from the figure, similar to the results for Material #1, the change in % bubble area was near zero for test-limit temperatures of 300°C, 450°C, and 600°C. Accordingly, Material # 1 shows no outgassing at these temperatures.

[00154] The results for Material #4 are shown as circle data points in FIG. 9. As can be seen from the figure, the change in % bubble area is near zero for the test-limit temperature of 300°C, but is near 1% for some samples at the test-limit temperatures of 450°C and 600°C, and for other samples of that same material is about 5% at the test limit temperatures of 450°C and 600°C. The results for Material #4 are very inconsistent, and are dependent upon the manner in which the thin sheet and carrier surfaces are prepared for bonding with the HMDS material. The manner in which the samples perform being dependent upon the manner in which the samples are prepared is consistent with the examples, and associated discussion, of this material set forth in connection with Table 2 above. It was noted that, for this material, the samples having a change in % bubble area near 1%, for the 450°C and 600°C test-limit temperatures, did not allow separation of the thin sheet from the carrier according to the separation tests set forth above. That is, a strong adhesion between the thin sheet and carrier may have limited bubble generation. On the other hand, the samples having a change in % bubble area near 5% did allow separation of the thin sheet from the carrier. Thus, the samples that had no outgassing had the undesired result of increased adhesion after temperature treatment which sticking the carrier and thin sheet together (preventing removal of the thin sheet from the carrier), whereas the samples that allowed removal of the thin sheet and carrier had the undesired result of outgassing.

[00155] The results for Material #5 are shown in FIG. 9 as triangular data points. As can be seen from the figure, the change in % bubble area is about 15% for the test-limit temperature of 300°C, and is well over that for the higher test-limit temperatures of 450°C and 600°C. Accordingly, Material # 5 shows significant outgassing at these temperatures.

[00156] The results for Material #6 are shown as square data points in FIG. 9. As can be seen from this figure, the change in % bubble area is over 2.5% for the test-limit temperature of 300°C, and is over 5% for the test limit-temperatures of 450°C and 600°C. Accordingly, Material #6 shows significant outgassing at the test-limit temperatures of 450°C and 600°C.

[00157] For Making Electronic Devices

[00158] One use of the controlled bonding as described herein is to make articles—including those having a carrier and a thin sheet bonded thereto—which are, in turn, used to make electronic devices, for example, TFTs, OLEDs (including an organic light emitting material), PV devices, touch sensors, interposers, integrated circuits, resistor-capacitor circuits, and displays.

[00159] In any event, electronic device processing equipment as is currently designed for thicker sheets may be used to process the glass article so as to dispose an electronic-device component, or part of the electronic device, onto the sheet of the article. The electronic device component should be disposed on the portion(s) of the thin sheet that are bonded to the carrier via the controlled bonding described above, whereby the thin sheet remains separable from the carrier even after processing to the temperatures necessary to make the electronic device. The device processing may include processing at temperatures of $\geq 400^{\circ}C$, $\geq 500^{\circ}C$, $\geq 600^{\circ}C$, or up to 650°C, and in some instances, up to 700°C, for example. As described above, suitable surface modification layers may be chosen so that the thin sheet remains removable from the carrier—even after processing to such temperatures—without damage to at least the thin sheet, and preferably without damage to both the thin sheet and the carrier. Any number of electronic-device components may be disposed in any number of steps for doing so, until the electronic device is complete or at a suitable intermediate stage. The article may be assembled before the electronic device processing, or may be assembled as a part of the electronic device making process.

[00160] The device processing may include keeping the article intact throughout the entire device processing, or may include dicing the article at one or more points in the process. For example, the device processing may include forming one electronic-device component on the article, and then dicing the article into two or more portions that are then subject to further processing, i.e., disposing an additional component of the electronic device onto the sheet or onto the electronic-device component existing on the sheet from disposition in a prior step. The dicing step may be done so that each portion of the article includes a portion of the thin

sheet that remains bonded to the carrier, or so that only a subset of the diced portions include such an arrangement. Within any of the diced portions, the entire area of the thin sheet in that portion may remain bonded to the entire area of the carrier in that portion.

[00161] After the device processing, either to completion or to an intermediate stage, the device and the portion of the thin sheet on which it is disposed, may be removed from the carrier. The thin sheet may be removed in its entirety, or a portion thereof may be separated from a remaining portion and that portion removed from the carrier. The removal may take place from the article in its entirety, or from one or more of the portions diced therefrom.

[00162] Use to process thin wafers in semiconductor and/or interposer processing

[00163] Another use of controlled bonding via surface modification layers (including materials and the associated bonding surface heat treatment) is to provide for use of a thin sheet on a carrier to process the thin sheet in processes requiring a temperature ≥ 400°C (for example ≥ 450°C, ≥ 500°C, ≥ 550°C, ≥ 600°C), as in FEOL processing, for example. That is, the thin sheet may be a wafer that is processed at thickness without having to thin it later on. Surface modification layers (including the materials and bonding surface heat treatments), as exemplified by the examples 2e, 3a, 3b, 4c, 4d, and 4e, above, may be used to provide reuse of the carrier under such temperature conditions. Specifically, these surface modification layers may be used to modify the surface energy of the area of overlap between the bonding areas of the thin sheet and carrier, whereby the entire thin sheet may be separated from the carrier after processing. The thin sheet may be separated all at once, or may be separated in sections as, for example, when first removing devices produced on portions of the thin sheet and thereafter removing any remaining portions to clean the carrier for reuse, for example. In the event that the entire thin sheet is removed from the carrier, as by removal of the thin sheet as a whole, or as by removing diced sections of the thin sheet the sum of which add to the entire thin sheet, the carrier can be reused as is by simply by placing another thin sheet thereon. Alternatively, the carrier may be cleaned and once again prepared to carry a thin sheet by forming a surface modification layer anew. Because the surface modification layers prevent permanent bonding of the thin sheet with the carrier, they may be used for processes wherein temperatures are ≥ 600°C. Of course, although these surface modification layers may control bonding surface energy during processing at temperatures ≥ 600°C, they may also be used to produce a thin sheet and carrier combination that will withstand processing at lower temperatures, for example temperatures ≥ 400°C (for example ≥ 450°C, ≥

500°C, ≥ 550°C), and may be used in such lower temperature applications to control bonding, without outgassing (in the case of materials of examples 3a, 3b, 4c, 4d, and 4e), for example in BEOL processing. Moreover, where the thermal processing of the article will not exceed 400°C, surface modification layers as exemplified by the examples 2c, 2d, 4b may also be used in this same manner. The thin sheet may be a polysilicon or single crystal silicon wafer, silicon wafer, glass, ceramic, glass-ceramic, quartz, sapphire, having a thickness of ≤ 200 microns, and may be processed at, for example temperatures ≥ 500°C to form RC circuits, ICs, or other electronic devices thereon in FEOL processing. After FEOL processing, the wafer may easily be removed from the carrier without damaging the electronic devices. Before removal, however, the wafer may undergo further, lower temperature processing, as in BEOL processing, for example.

[00164] A second use of controlled bonding via surface modification layers (including materials and the associated bonding surface heat treatments) is to fabricate an interposer. More specifically, with the use of the surface modification layers an area of controlled bonding can be formed wherein a sufficient separation force can separate the thin sheet (or a portion thereof) from the carrier without damage to either the thin sheet or the carrier caused by the bond, yet there is maintained throughout processing a sufficient bonding force to hold the thin sheet relative to the carrier. In this case, the thin sheet is an interposer, which may be a wafer made from any suitable material including silicon, polysilicon, single crystal silicon, glass, ceramic, glass-ceramic, quartz, sapphire, for example, and which may have a thickness of ≤200 microns, for example.

[00165] An example of an interposer, and the fabrication thereof, will now be described with reference to FIGS. 10-12.

[00166] With reference to FIG. 10, a thin sheet 20 may be bonded to a carrier 10 by a controlled bonding area 40.

[00167] In this embodiment, the carrier 10, may be a glass substrate, or another suitable material having a similar surface energy as glass, for example, silicon, polysilicon, single crystal silicon, ceramic, glass-ceramic, sapphire, or quartz. An advantage of using a glass substrate is that flat sheets having minimal thickness variation can be obtained at a relatively low cost, avoiding the need for expensive carrier substrates. Additionally, with glass, a high quality can be achieved in a cost effective manner. That is, a very uniform thickness glass substrate can be made very cheaply, and used as a carrier. However, with the surface

modification layers of the present disclosure, the carrier need not be a high precision carrier having a low total thickness variation as in the case where the wafer will be thinned to final thickness. That is, when a wafer on a carrier will be thinned, the carrier must have a very tight control on total thickness variation because any variation in the carrier will be present in the thinned wafer upon thinning. With the surface modification layers of the present disclosure, which allow forming devices on the wafer when the wafer is already at final thickness, the total thickness variation of the carrier is much less important.

[00168] In this embodiment, the thin sheet 20 is used to form interposers 56. The sheet may be silicon, including polysilicon or a single crystal silicon wafer, quartz, sapphire, ceramic, or glass, for example. The sheet 20 may have a thickness of ≤200 microns. The interposers 56 each having a perimeter 52 and an array 50 of vias, wherein the array 50 has a perimeter 57. Although ten interposers 56 are shown, any suitable number—including one— may be disposed on one thin sheet 20. For convenience of illustration, each interposer 56 is shown as having only one array 50 of vias, but such need not be the case; instead any interposer 56 may have more than one array 50. Further, although each interposer is shown as having the same number of arrays 50, such need not be the case; any number (including zero) of the interposers may have the same number of arrays 50. Additionally, although the arrays 50 will typically have the same number and pattern of vias, such need not be the case. For convenience of illustration, vias 60 are shown on only one of the arrays 50 of one of the interposers 56, but such need not be the case, i.e., any one or more of the remaining interposers 56 may have one or more arrays 50 of vias 60.

[00169] Reference will now be made to FIG. 11, which is a cross-sectional view as taken along line 11-11 in FIG. 10. The vias 60 may include through vias or blind vias, i.e., vias that end within the thickness of the sheet 20. Vias 60 have a diameter 62, and are spaced at a pitch 64. Although the diameters 62 are shown as being the same, such need not be the case, i.e., there may be different diameter vias in one array 50 or in different arrays 50 on one interposer 56. The diameter 62 may be from 5 microns to 150 microns, for example. Similarly, although the vias 62 are spaced at the same pitch 64, such need not be the case, i.e., different pitches may be present in one array 50, or in different arrays 50 on one interposer 56 or in different interposers 56 on one thin sheet 20. The pitch may be such that there are from 1 to 20 vias per square millimeter, for example, and will depend upon the design and application of the interposer. Additionally, material 61 may be present in any one or more of

the vias 60. The material 61 may be an electrically conductive material, an electrically insulating material, or a combination thereof. For example, a conductive material may be formed on the perimeter of the via, i.e., at its outside diameter 62, and either a different conductive material or an insulating material may be used to fill in the remainder of the via.

[00170] Reference will now be made to FIG. 12, which is a view similar to that in FIG. 11, but with devices/structures disposed on the interposer 56 and connected to via(s) 60. As shown in FIG. 12, a device 66 may be disposed over, and connected with, a plurality of vias 60. Device 66 may include integrated circuits; MEMS; microsensors; power semiconductors; light-emitting diodes; photonic circuits; CPU; SRAM; DRAM, eDRAM; ROM, EEPROM; flash memory; interposers; embedded passive devices; and microdevices fabricated on or from silicon, silicon-germanium, gallium arsenide, and gallium nitride. Although only one device 66 is shown, there may be any suitable number of devices 66 on one interposer 56, including an array of devices 56. Alternatively, a structure 68 may be disposed over and connected with only one via 60. Structures 68 may include: 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 (for example, Cu, Al, W), low k dielectrics, polymer dielectrics, metal nitrides, and metal silicides. Although only one structure 68 is shown, there may be any suitable number of structures 68 on one interposer 56, including array(s) of structures 56. Further, one or more structures 68 may be disposed on a device 66.

[00171] In the controlled bonding area 40, the carrier 10 and thin sheet 20 are bonded to one another so that over the entire area of overlap, the carrier 10 and thin sheet 20 are connected, but may be separated from one another, even after high temperature processing, e.g. processing at temperatures $\geq 400°C$, for example $\geq 450°C$, $\geq 500°C$, $\geq 550°C$, $\geq 600°C$, and on up to about 650°C, or in some cases to 700°C.

[00172] The surface modification layers 30, including the materials and bonding surface heat treatments, as exemplified by the examples 2a, 2e, 3a, 3b, 4c, 4d, and 4e, above, may be used to provide the controlled bonding areas 40 between the carrier 10 and the thin sheet 20. Specifically, these surface modification layers may be formed within the perimeters 52 of the arrays 50 either on the carrier 10 or on the thin sheet 20. Accordingly, when the article 2 is processed at high temperature during device processing, there can be provided a controlled bond between the carrier 10 and the thin sheet 20 within the areas bounded by perimeters 52

whereby a separation force may separate (without catastrophic damage to the thin sheet or carrier) the thin sheet and carrier in this region, yet the thin sheet and carrier will not delaminate during processing, including ultrasonic processing. Additionally, because of the very small thickness of the surface modification layer, i.e., less than 100 nanometers, less than 40 nanometers, less than 10 nanometers, and in some instances about 2 nanometers, there is no effect on the wafer due to CTE mismatch between the wafer and the surface modification layer (as there is in the case of thicker adhesive layers, i.e., on the order of 40-60 microns or more). Additionally, when there is a need to limit outgassing between the thin sheet and carrier, the surface modification layer materials of examples 3b, 4c, and 4e may be used.

[00173] Then, during extraction of the interposers 56 (each having an array 50 of vias 60) having perimeters 52, the portions of thin sheet 20 within the perimeters 52 may simply be separated from the carrier 10 after processing and after separation of the thin sheet along perimeters 52. Alternatively, the thin sheet 20 (and alternatively both the thin sheet 20 and the carrier 10) may be diced along lines 5, whereby a section of the thin sheet 20 larger than the interposer 56 perimeter 52 may be removed from the carrier 10, or sections of the carrier 10 as in the event that the carrier is diced together with the thin sheet 20. Because the surface modification layers control bonding energy to prevent permanent bonding of the thin sheet with the carrier, they may be used for processes wherein temperatures are $\geq 600^{\circ}C$. Of course, although these surface modification layers may control bonding surface energy during processing at temperatures $\geq 600^{\circ}C$, they may also be used to produce a thin sheet and carrier combination that will withstand processing at lower temperatures for example $\geq 400^{\circ}C$ (for example $\geq 450^{\circ}C$, $\geq 500^{\circ}C$, $\geq 550^{\circ}C$), and may be used in such lower temperature applications. Moreover, where the thermal processing of the article will not exceed $400^{\circ}C$, surface modification layers as exemplified by the examples 2c, 2d, 4b may also be used—in some instances, depending upon the other process requirements—in this same manner to control bonding surface energy. Moreover, as noted above, the surface modification layer materials of examples 3b, 4c, and 4e, may be used in instances were outgassing between the thin sheet and carrier is a concern.

[00174] Conclusion

[00175] It should be emphasized that the above-described embodiments of the present invention, particularly any "preferred" embodiments, are merely possible examples of

implementations, merely set forth for a clear understanding of various principles of the invention. Many variations and modifications may be made to the above-described embodiments of the invention without departing substantially from the spirit and various principles of the invention. All such modifications and variations are intended to be included herein within the scope of this disclosure and the present invention and protected by the following claims.

[00176] For example, although the surface modification layer 30 of many embodiments is shown and discussed as being formed on the carrier 10, it may instead, or in addition, be formed on the thin sheet 20. That is, the materials as set forth in the examples 4 and 3 may be applied to the carrier 10, to the thin sheet 20, or to both the carrier 10 and thin sheet 20 on faces that will be bonded together.

[00177] Further, although some surface modification layers 30 were described as controlling bonding strength so as to allow the thin sheet 20 to be removed from the carrier 10 even after processing the article 2 at temperatures of 400°C, or of 600°C, of course it is possible to process the article 2 at lower temperatures than those of the specific test the article passed and still achieve the same ability to remove the thin sheet 20 from the carrier 10 without damaging either the thin sheet 20 or the carrier 10.

[00178] Still further, although the controlled bonding concepts have been described herein as being used with a carrier and a thin sheet, in certain circumstances they are applicable to controlling bonding between thicker sheets of glass, ceramic, or glass ceramic, wherein it may be desired to detach the sheets (or portions of them) from each other.

[00179] Further yet, although the controlled bonding concepts herein have been described as being useful with glass carriers and glass thin sheets, the carrier may be made of other materials, for example, ceramic, glass ceramic, or metal. Similarly, the sheet controllably bonded to the carrier may be made of other materials, for example, ceramic or glass ceramic.

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.