environment, including high temperature and/or vacuum processing, for example. Still further yet, in alternative embodiments, some surface modification layers may be used on a carrier having a glass bonding surface to controllably bond a thin sheet having a polymer bonding surface. The polymer bonding surface may be part of a polymer thin sheet on which electronic or other structures are formed or, alternatively, the polymer bonding surface may be part of a composite sheet comprising a glass layer on which the electronic or other structures are formed.

[0011a] In an aspect, there is provided a method of controllably bonding a thin sheet to a carrier, comprising:

obtaining a thin sheet having a thin sheet bonding surface;

obtaining a carrier having a carrier bonding surface;

depositing a carbonaceous surface modification layer onto at least one of the thin sheet bonding surface and the carrier bonding surface;

incorporating polar groups with the surface modification layer; and

bonding the thin sheet bonding surface to the carrier bonding surface via the surface modification layer.

[0011b] In another aspect, there is provided a thin sheet removably bonded to a carrier article, comprising:

a thin sheet having a thin sheet bonding surface;

a carrier having a carrier bonding surface;

a surface modification layer, wherein the surface modification layer comprises a plasma-polymerized hydrocarbon bonding the thin sheet bonding surface to the carrier bonding surface.

[0011c] In another aspect, there is provided a thin sheet removably bonded to a carrier article, comprising:

a thin sheet having a thin sheet bonding surface;

a carrier having a carrier bonding surface;

a surface modification layer, wherein the surface modification layer comprises a bulk carbonaceous layer having a first polar group concentration and a surface layer having a second polar group concentration, wherein the second polar group concentration is higher than the first polar group concentration, the surface modification layer bonding the thin sheet bonding surface to the carrier bonding surface.

[0012] 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.

[0013] 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 appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a schematic side view of an article having carrier bonded to a thin sheet with a surface modification layer therebetween.

[0015] FIG. 2 is an exploded and partially cut-away view of the article in FIG. 1.

[0016] FIG. 3 is a graph of surface hydroxyl concentration on silica as a function of temperature.

[0017] FIG. 4 is a graph of the surface energy of an SC1-cleaned sheet of glass as a function annealing temperature.

[0018] 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.

[0019] FIG. 6 is a schematic top view of a thin sheet bonded to a carrier by bonding areas.

[0020] FIG. 7 is a schematic side view of a stack of glass sheets

[0021] FIG. 8 is an exploded view of one embodiment of the stack in FIG. 7.

sheets and have < 10 ppm, and even < 5 ppm in dimension change (as compared to their size after the first heat treatment) after a second heat treatment.

[00248] Although the furnace in the above-described annealing example was purged with nitrogen, annealing furnaces may also be purged with other gasses including, air, argon, oxygen, CO2, or combinations thereof, depending upon the annealing temperature, and the stability of the surface modification layer material at those temperatures in a particular environment. Alternatively to an inert atmosphere, the furnace in the above-described annealing could be a vacuum environment.

[00249] Additionally, although not shown, the glass may be annealed in a spool, instead of sheet, form. That is, a suitable surface modification layer may be formed on one or both sides of a glass ribbon, and the ribbon then rolled. The entire roll could be subject to the same treatment as noted above for sheets, whereupon the glass of the entire spool would be annealed without sticking one wrap of the glass to an adjacent one. Upon un-rolling, the surface modification layer may be removed by any suitable process.

[00250] Outgassing

[00251] 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.

[00252] A first manner of measuring small amounts of outgassing (outgassing test #1) is based on surface energy measurements, and will be described with reference to FIG. 9. To carry out this test, a setup as shown in FIG. 9 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

[00265] Material #7 is a is CH4-H2 plasma deposited polymer sequentially treated with brief N2-O2 and N2 plasmas. This material is similar to the surface modification layer in the examples of Table 11, above. As shown in FIG. 10, lines 7001 and 7002 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 7003 and 7004, the surface energy of the cover did not significantly change either, i.e., the change is ≤ 5mJ/m2. Accordingly, there was no outgassing associated with this material from 450°C to 600°C.

[00266] Significantly, for Materials #1-4, and 7 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. 10 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.

[00267] A second manner of measuring small amounts of outgassing (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 ≤ 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 ≥ 5 is significant, indicative of outgassing, and is not desirable. On the other hand a change in % bubble area of ≤ 1 is insignificant and an indication that there has been no outgassing.

[00268] 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

What is Claimed is:

1. A method of controllably bonding a thin sheet to a carrier, comprising:

obtaining a thin sheet having a thin sheet bonding surface;

obtaining a carrier having a carrier bonding surface;

depositing a carbonaceous surface modification layer onto at least one of the thin sheet bonding surface and the carrier bonding surface;

incorporating polar groups with the surface modification layer; and

bonding the thin sheet bonding surface to the carrier bonding surface via the surface modification layer.

2. The method of claim 1, wherein the at least one of the thin sheet bonding surface and the carrier bonding surface has a surface energy including a polar component, and wherein the incorporation of the polar groups increases the polar component of the surface energy by at least 20 mJ/m^2.

3 The method of claim 1 or claim 2, wherein the surface modification layer is deposited by plasma polymerization of a carbon-containing gas.

4. The method of claim 3, further comprising flowing hydrogen together with the carbon-containing gas during the plasma polymerization.

5. The method of claim 3 or claim 4, further comprising using a diluent gas during the plasma polymerization to control the mole fraction of deposition gas.

6. The method any one of claims 3-5, further comprising flowing a reactive gas during the plasma polymerization.

7. The method of any one of claims 1-6, wherein depositing the surface modification layer is performed prior to the incorporation of polar groups and provides a first surface energy on the at least one of the thin sheet bonding surface and the carrier bonding surface; and wherein the incorporation of polar groups is performed after the deposition of the surface modification layer and changes the first surface energy to a second surface energy, wherein the second surface energy is greater than the first.

8. The method of ~~claim~~any one of claims 1-7, wherein the polar group incorporation is performed by one of:

treatment of the surface modification layer with a nitrogen-containing gas;

sequential treatment of the surface modification layer with a first treatment gas then a second treatment gas, wherein the first treatment gas is one of a nitrogen-containing gas and a hydrogen-containing gas, and where the second treatment gas is the other one of the nitrogen-containing gas and the hydrogen-containing gas;

treatment of the surface modification layer with an oxygen-containing gas;

plasma treatment of the surface modification layer with a nitrogen-and-oxygen-containing gas;

sequential plasma treatment of the surface modification layer with a first treatment gas then a second treatment gas, wherein the first treatment gas is a nitrogen-and-oxygen-containing gas and wherein the second treatment gas is a nitrogen-containing gas.

9. The method of claim 1, wherein the at least one of the thin sheet bonding surface and the carrier bonding surface has an average surface roughness Ra of ≤ 1 nm prior to deposition of the surface modification layer, and wherein the at least one of the thin sheet bonding surface and the carrier bonding surface has an average surface roughness Ra of ≤ 1 nm after deposition and subsequent removal of the surface modification layer by O2 plasma cleaning.

10. The method of any one of claims 1-9, wherein the at least one of the thin sheet bonding surface and the carrier bonding surface comprises glass, and further wherein the surface modification layer achieves on the at least one bonding surface a surface energy of 37 to 74 mJ/m^2 prior to bonding with the other one of the thin sheet bonding surface and the carrier bonding surface.

11. The method of any one of claims 1-10, wherein the thin sheet comprises at least one via therein.

12. A thin sheet removably bonded to a carrier article, comprising:

a thin sheet having a thin sheet bonding surface;

a carrier having a carrier bonding surface;

a surface modification layer, wherein the surface modification layer comprises a plasma-polymerized hydrocarbon bonding the thin sheet bonding surface to the carrier bonding surface.

13. A thin sheet removably bonded to a carrier article, comprising:

a thin sheet having a thin sheet bonding surface;

a carrier having a carrier bonding surface;

a surface modification layer, wherein the surface modification layer comprises a bulk carbonaceous layer having a first polar group concentration and a surface layer having a second polar group concentration, wherein the second polar group concentration is higher than the first polar group concentration, the surface modification layer bonding the thin sheet bonding surface to the carrier bonding surface.

14. The article of claim 12 or claim 13, wherein the at least one of the thin sheet bonding surface and the carrier bonding surface has an average surface roughness Ra of ≤ 1 nm prior to deposition of the surface modification layer.

15. The article of any one of claims 12-14 ~~or claim 13~~, wherein the surface modification layer bonds the carrier bonding surface with the thin sheet bonding surface so that after subjecting the

bonded sheet and carrier 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 thin sheet do not separate from one another if one is held and the other subjected to the force of gravity, and the thin sheet may be separated from the carrier without breaking the thinner one of the carrier and the sheet into two or more pieces.

16. The article of any one of claims 12-15 ~~or claim 13~~, wherein the surface modification layer is configured so that when the carrier bonding surface is bonded with the thin sheet bonding surface with the surface modification layer therebetween to form an article, after subjecting the article to an outgassing temperature cycle by heating in an chamber cycled from room temperature to 450°C at a rate of 9.2 °C per minute, held at a temperature of 450°C for 10 minutes, and then cooled at furnace rate to 200 °C, and then removing the article from the chamber and allowing the article to cool to room temperature, the surface modification layer does not outgas during the outgassing temperature cycle.

17. The article of claim 16, wherein outgassing is defined as a change in % bubble area that is ≥ 5, according to ~~outgassing test #2~~a second manner of measuring outgassing.

18. The article of claim 16, wherein outgassing is defined as a change in surface energy of the cover ≥ 15 mJ/m^2 at a test limit temperature of 450°C according to ~~outgassing test #1~~a first manner of measuring outgassing.

19. The article of any one of claims 12-18 ~~or claim 13~~, wherein the portion of the surface modification layer in direct contact with the bonding surface comprises up to 3% fluorine.

20. The article of any one of claims 12-19 ~~or claim 13~~, wherein the thin sheet comprises at least one via therein.