PROCESS AND EQUIPMENT FOR BONDING BY MOLECULAR ADHESION

The field of the invention is that of bonding by molecular adhesion of two substrates to one another.

The invention concerns a process and bonding equipment. It extends likewise to the formation of a structure comprising a thin layer made of a semiconductor material on a support substrate. To form such a structure, the typical procedure is to place a donor substrate in close contact with the support substrate, so as to effect bonding by molecular adhesion of the substrates to one another. This is then followed by transfer of a part of the donor substrate to the support substrate, so as to form the thin layer on the support substrate.

Bonding by molecular adhesion ('direct wafer bonding' or 'fusion bonding' according to English terminology) is a technique which enables two substrates having perfectly flat surfaces (polished mirror) to be stuck to one another, without the application of adhesive (gum type, glue, etc.).

The surfaces in question are generally those of substrates made of an insulating material (for example

quartz, glass) or a semiconductor material (for example Si, GaAs, SiC, Ge, etc).

Bonding is typically initiated by local application of light pressure to the two substrates placed in close contact. A bonding front then spreads over the entire extent of the substrates in a few seconds.

The bonding energy obtained at ambient temperature is generally low enough relative to that observed between two solids in covalent, ionic or metallic connection.

For numerous applications, bonding is thus reinforced by carrying out thermal annealing. In the case of a silicon surface stuck on another silicon or silicon oxide surface, the bonding energy reaches maximum after a bonding reinforcing annealing carried out at temperatures of the order of 1100°C to 1200°C.

In addition, to obtain satisfactory bonding of two substrates, the typical procedure prior to bonding is preparation of one and/or the other of the surfaces to be stuck. This means increasing the mechanical performance and/or to boost the quality of the bonding interface.

Preparation of the surfaces to be stuck with the aim of making them more hydrophilic is an example of such treatment for increasing the mechanical behaviour between the substrates during bonding. Within the scope of hydrophilic bonding, the following properties are preferred for the surfaces to be stuck.

- the absence of particles;
- the absence of hydrocarbons;

- the absence of metallic contaminants
- a low surface roughness, typically less than 5 Å RMS;
- strong hydrophily, that is, a substantial density of Si-OH silanol bonds terminating the surfaces to be stuck.

Preparation of the surfaces to be stuck is generally completed by utilising one or more chemical treatments. By way of example of chemical treatment prior to (hydrophilic) adhesion, the following can be mentioned:

- cleaning of RCA type, namely the combination of a SC1 (NH_4OH, H_2O_2, H_2O) bath adapted to shrinkage of the particles and the hydrocarbons and a SC2 (HCl, H_2O_2 H_2O) bath adapted to shrinkage of the metallic contaminants;
- cleaning with an ozone solution (O_3) adapted to shrinkage of the organic contaminants;
- cleaning with a solution containing a mixture of sulphuric acid and oxygenated water (or SPM solution, Sulphuric Peroxide Mixture).

Preparation of the surfaces to be stuck can likewise comprise mechanical preparation of the surfaces (light polishing, brushing), complementing or not the chemical treatment.

As a complement to conventional methods of bonding by molecular adhesion, strong bonding techniques at low temperature have been developed more recently to make heterostructures (adhesion of two materials of different type), to stick substrates comprising partially or totally manufactured electronic components

(aka patterned substrate and structured wafer), or even for sticking substrates capable of being altered during annealing at high temperature.

Bonding by molecular adhesion with plasma activation is an example of such a strong bonding technique carried out at low temperature.

Exposure, prior to the bonding of one and/or the other of the surfaces to be stuck to a plasma, allows strong bonding energy to be reached after relatively short reinforcing annealing of the bonding (around 2 hours) and conducted at low temperature (typically less than 600°C). For example the following articles can be mentioned:

- "Effects of plasma activation on hydrophilic bonding of Si and SiO_2" T. Suni et al., J. Electroch. Soc, Vol. 149. No. 6, p. 348 (2002);
- "Time-dependent surface properties and wafer bonding of O_2-plasma treated silicon (100) surfaces", M. Wiegand et al., J. Electroch. Soc. Vol. 147, No. 7, p. 2734 (2000).

It is evident that the different techniques for surface preparation mentioned earlier systematically incorporate at least one humid stage, that is, at least rinsing of the surfaces by deionised water.

The substrates are then dried, for example by centrifuging (dry spin). As a function of their degree of hydrophily, after drying the surfaces of the substrates have several monolayers of adsorbed water, these monolayers being at the origin of the intermolecular forces responsible for adhesion during contacting.

Bonding by molecular adhesion of substrates to one another generally causes defects. By way of example of defects caused by bonding, notable examples are defects of bubble type (or bubbles) at the level of the bonding interface between the two substrates, as well as defects of edge type (or edge voids) at the level of the thin layer of the final structure, "thin layer on support substrate", obtained after transfer.

Bubbles are understood as defects which result from gas and/or water combing at the bonding interface between the two substrates. Bubbles can appear after application of a low budget thermal to the adhered structure (for example after application of thermal annealing at 200°C over 2 hours) and are observable by inspection of the bonding interface using an infrared camera, or again by acoustic microscopy. The bubbles will be responsible for the presence of non-transferred zones at the level of the final structure obtained after transfer.

The article "Low-Temperature Wafer Bonding, Optimal O_2 Plasma Surface Pretreatment Time", by X. Zhang and J-P. Raskin in Electrochemical and Solid-State Letters, 7 (8) G 172-G174 (2004), illustrates the phenomenon of the formation of bubbles at the bonding interface.

Edge voids are understood to mean defects which result from bonding and which are typically observed at the periphery of the final structure (generally in the form of a circular plate).

An application of direct bonding is that carried out within the scope of producing structures of the

'semiconductor on insulator' SeOI type (Semiconductor On Insulator), and in particular 'silicon on insulator' SOI structures (Silicon On Insulator). Within this scope of application at least one of the substrates to be stuck has a surface layer of oxide; by way of example, Si/SiO_2 bonding or SiO_2/SiO_2 bonding is typically undertaken to form a SOI structure.

There are three main methods for producing SeOI structures by direct bonding: SMART CUT®, BSOI (and BESOI), and ELTRAN®. A description of the processes associated with each of these methods can be found in the work 'Silicon wafer bonding technology for VLSI and MEMS applications', S.S. Lyer and A.J. Auberton-Hervé, IEE (2002).

But defects of edge voids type, cause by the bonding step, are capable of appearing after transfer of the thin layer from the donor substrate to the support substrate.

As is schematically illustrated in Figure 1 in terms of forming a SOI structure, an edge void P is a hole (of a diameter typically between 100 m and 1 mm) in the thin transferred layer which corresponds to a zone of the donor substrate not transferred to the support substrate A.

The edge voids appear most often at the edge (peripheral zone) of the "thin layer on support substrate" structure (circular wafer); they are located at a distance of typically between 1 mm and 5 mm of the wafer edge.

The edge voids are macroscopic defects connected to poor bonding at the edge of the wafers. They can be

killer defects because, in the absence of a thin layer acting as an active layer for the formation of electronic components at the location of an edge void, no component can be manufactured at this location. Given the size of the edge voids, an electronic component comprising at least one edge void is necessarily defective.

In addition, a transfer process of the SMART CUT® type is notably interesting in that it allows for recycling of the donor substrate. So when adhesion of a recycled donor substrate is completed (that is, a donor substrate already having served for removal and transfer of a thin layer; known as 'refresh' wafer), a greater number of edge voids is observed than when bonding of an original donor substrate is completed (having never served to remove and/or transfer of a thin layer; known as 'fresh' wafer). This increased presence of edge voids tends to prohibit the recycling.

Since the presence of edge voids induces losses in terms of quality and yield, there is thus a need to prevent the formation of such defects.

It has been proposed in the document EP 1 566 830 to limit the number of defects of void type at the edge of a SOI wafer obtained as a result of molecular bonding. According to this document, these defects are always located at a specific position relative to the centre of the wafer, and seem to be due to the configuration of the edges of wafers. Therefore, to decrease the number of defects, this document proposes modifying the configuration of the edges of wafers during their manufacture. More precisely, this document

proposes modifying the curve of the edge drops, in regions ranging from 3 mm to 10 mm from the periphery of the wafer. This solution thus has the disadvantage of requiring previous mechanical intervention on the wafers.

Another application of direct bonding is that of Si/Si bonding of DSB type (Direct Si Bonding). As mentioned earlier, defects of bubble type are all the same capable of appearing at the bonding interface.

One solution for reducing the formation of bubbles consists of producing plasma activation of the surfaces to be stuck, so as to obtain good adhesion energy. This solution all the same does not prove satisfactory for reducing the number of bubbles at the bonding interface.

Embodiments of the present invention seek to provide a bonding technique which rectifies these disadvantages of the state of the art.

According to a first aspect of the present invention, there is provided a process for bonding by molecular adhesion of two substrates to one another, during which the surfaces of said substrates are placed in close contact and bonding occurs by propagation of a bonding front between said substrates, characterised in that it comprises, prior to bonding, a step consisting of modifying the surface state of one and/or the other of said substrates so as to regulate the propagation speed of the bonding front.

Certain preferred, though non-limiting, embodiments of this process are the following:

- modification of the surface state is a decrease in the thickness of a layer of water adsorbed on the surface of one and/or the other of the substrates to be stuck;
- modification of the surface state is completed by heating;
- heating is applied before the substrates are placed in close contact with one another and at least until initiation of bonding;
- heating is effected over a period of between 1 and 90 seconds, preferably for 30 seconds;
- heating is effected by thermal conduction via transmission of heat from a plate supporting one of the substrates to be stuck;
- heating is effected by radiation from a lamp lighting one of the substrates to be stuck;
- the lamp is a lamp radiating in the infrared range, with a wavelength of between 0.8 m and 5 m;
- heating is effected at a temperature of between 30°C and 90°C; preferably between 50°C and 60°C;
- heating is applied uniformly over the entire surface of the substrate to be stuck;
- heating is applied locally at a peripheral zone of the substrate to be stuck;
- adhesion being initiated in the centre, the peripheral covers the entire circumference of the substrate to be stuck;
- adhesion being initiated at the edge, the peripheral zone describes an arc of a circle diametrically opposed to the edge of initiation and limited by an angle at the centre of around 120°;

- before bonding, the process comprises a stage of plasma activation of one and/or the other of the surfaces to be stuck.
- modification of the surface state is effected by roughing the surface:
- the modification step of the surface state consists of forming a rough surface layer of one and/or the other of the substrates to be stuck;
- to form said rough layer, the process comprises a thermal oxidation operation of one and/or the other of the substrates so as to form a thermal oxide layer on the surface of one and/or the other of the substrates and an operation for treating the thermal oxide layer adapted to etch said oxide layer:
- treatment of the thermal oxide layer is chemical treatment;
- the layer of thermal oxide is a layer of SiO_2 and the chemical treatment is SC1 treatment conducted at a temperature of between 50°C and 80°C over a period of longer than three minutes, preferably over 10 minutes;
- to form said rough layer, the process comprises an operation for depositing a surface layer of oxide on the surface of one and/or the other of the substrates;
- the depositing operation consists of depositing a layer of TEOS oxide, a layer of LTO oxide, or a layer of nitride;

- the process comprises, before bonding and after said modification step of the surface state, a plasma activation stage of one and/or the other of the surfaces to be stuck.

According to a second aspect of the present invention, there is provided equipment for bonding by molecular adhesion of two substrates to one another following the propagation of a bonding front between said substrates, characterised in that it comprises means for modifying, prior to bonding, the surface state of one and/or the other of the substrates so as to regulate the propagation speed of the bonding front.

According to a third aspect of the present invention, there is provided a process for formation of a structure comprising a thin layer made of a semiconductor material on a support substrate, comprising the steps of placing a donor substrate in close contact with the support substrate so as to produce bonding by molecular adhesion of said substrates to one another following the propagation of a bonding front between said substrates, and transfer of part of the donor substrate to the support substrate so as to form said thin layer on the support substrate, characterised in that it comprises prior to bonding a step consisting of modifying the surface state of the donor substrate and/or of the support substrate so as to regulate the propagation speed of the bonding front.

Embodiments of the present invention also relate to the "thin layer on

support substrate" structures obtained from implementing this process.

Other aspects, aims and advantages of the present invention will emerge more clearly from reading the following detailed description of preferred embodiments of the latter, given by way of non-limiting example, and done in reference to the attached diagrams on which, other than Figure 1 already mentioned:

- Figure 2 illustrates the formation of edge voids as a function of the location of the point of initialisation of adhesion;
- Figure 3 represents different diagrams of equipment according to the second aspect of the invention;
- Figures 4 and 5 respectively show uniform heating and localised heating of two substrates to be placed in close contact to bring about their bonding by molecular adhesion;
- Figure 6 is a diagram illustrating the formation of edge voids as a function of the propagation speed of the bonding front;
- Figure 7 is a diagram showing an embodiment of the bonding process according to the first aspect of the invention.

According to a first aspect the invention concerns a process of bonding by molecular adhesion of two substrates to one another, during which said substrates are placed in close contact and bonding occurs by propagation of a bonding front between said substrates.

It is understood that the invention is not limited to bonding by molecular adhesion of two substrates to

one another, but extends likewise to the formation of a structure comprising a thin layer of semiconductor material on a support substrate, during which bonding by molecular adhesion is carried out of a donor substrate with the support substrate, followed by transfer of the thin layer from the donor substrate to the support substrate.

As mentioned earlier, the SMART CUT®, BSOI (and BESOI), and ELTRAN® processes are examples of processes utilising bonding by molecular adhesion.

According to the SMART CUT® process, prior to bonding an embrittlement zone will be formed by implantation of atomic or ionic species in the thickness of the donor substrate, and after bonding detachment of the donor substrate at the embrittlement zone to transfer the thin layer to the support substrate will be performed.

To carry out molecular adhesion, typical procedure is to place the donor substrate and the support substrate in close contact, then to initiate bonding by local application of light pressure on the two substrates placed in close contact. A bonding front then spreads over the entire extent of the substrates.

The origin of the defects resulting from bonding is not determined with certainty, these days.

Analysis by the applicant shows that, within the scope of Si/Si DSB type bonding, the bubble-type defects appear more particularly since no oxide layer (other than native) is present at the surface of the substrates to be stuck. The applicant estimates in effect that in the case of adhesion with the presence

of a layer of oxide (for example for Si/SiO_2 bonding, for example in view of formation of a SeOI structure), the water and gas encapsulated during bonding or appearing later (for example during thermal consolidation treatment of the bonding) preferably diffuse in the oxide layer and are thus less inclined to diffuse to the bonding interface. However, in the case of DSB bonding, in the absence of such a layer of oxide, the applicant estimates that the water and the gas encapsulated during bonding or appeared consequently have a tendency to diffuse to the bonding interface, where they will be combed and form bubbles.

With respect to the edge void-type defects, analysis by the applicant shows that these are defects forming with closing of the bonding, where the bonding front meets the edge of the stuck substrates.

The illustrations of Figure 2 show analysis undertaken by the applicant concerning the formation of edge voids. In Figure 2, the arrows represent the direction of propagation of the bonding front, the pointed lines represent the position of the bonding front at different instants, and the points represent the edge voids.

As is illustrated to the left in Figure 2, the applicant has effectively been able to determine that when bonding is initiated at the centre (by local application of pressure), edge voids are potentially found over the entire periphery of the support substrate. However, as is illustrated to the right in Figure 2, when bonding is initiated on board the wafer (typically at the level of a recess known as a 'notch'

made on board the wafer to facilitate its manipulation), edge voids can appear in a peripheral zone of the support substrate describing an arc of a circle diametrically opposed to the point of initiation, limited by an angle at the centre of around 120°.

In general, the invention proposes limiting the formation of defects caused by bonding, and even to completely prevent the formation of such defects, by regulating the propagation speed of the bonding front.

'Regulate' is understood to mean to control, maintain and conserve the command of evolution of a phenomenon. Within the scope of the present invention, the phenomenon is that of propagation of the bonding front, and evolution of the phenomenon corresponds to the propagation speed of the bonding front.

The speed of propagation is more precisely regulated so as to be reduced relative to the speed usually observed in the absence of such control.

To allow regulation of the propagation speed of the bonding front, the invention proposes carrying out, prior to bonding, a modification step of the surface state of one and/or the other of the surfaces to be stuck.

According to a first possible embodiment, this means in particular to control the quantity of water adsorbed at the surface, and more precisely to decrease, without completely eliminating all the same, the thickness of the layer of water adsorbed relative to the thickness of the layer of water normally

adsorbed. In other terms, this means to reduce the number of monolayers of water adsorbed at the surface.

Bonding by molecular adhesion is also known as direct bonding, because it concerns bonding not requiring the application of an adhesive (of gum or other glue type). It is really the water adsorbed on each of the surfaces (several monolayers of water) and placed in contact which acts as adhesive and ensures adhesion by means of Van der Waals force.

Within the scope of this first embodiment, the surface state of a substrate is modified, and the propagation speed of the bonding front is thus regulated, by playing on the temperature of said substrate prior to bonding.

Bonding by molecular adhesion is classically carried out at ambient temperature (20°C to 25°C), whether in the case of manual bonding or in the case of automatic bonding.

The applicant has been able to ascertain that the edge voids and the bubbles can be partially or totally eliminated when the substrates are pre-heated before and up until being placed in close contact. The heating actually causes modification of the surface state of the substrates placed in contact, enabling the propagation speed of the bonding front to be reduced. By controlling this heating, it is possible to regulate the propagation speed of the bonding front, that is, to control the reduction in the propagation speed of the bonding front.

Figure 6 illustrates a curve showing the number of edge voids Np observed after transfer as a function of

the propagation speed of the bonding front Vp (expressed in centimetres per second) for Si on SiO_2 bonding.

Figure 6 is only a diagram given purely by way of illustration. In addition, the different numerical examples obviously depend on the substrates utilised for adhesion (substrate originating from recycling 'refresh substrate', or not, 'fresh substrate'; type of material comprising the substrate, in particular its flexibility, etc.).

For low bonding speeds (typically less than 1.7 cm/s), the applicant has not recorded any edge voids. For a speed of 1.7 cm/s, the applicant has observed between 0 and 1 edge voids.

The number of edge voids then increases rapidly when the propagation speed of the bonding front rises. The applicant has thus been able to count 5 edge voids for a speed of the order of 2 cm/s and between 50 and 100 edge voids for a speed of the order of 3 cm/s.

When standard cleaning only (for example RCA) of the substrates to be stuck is carried out prior to bonding, the applicant has been able to observe a overall propagation speed of the bonding front of between 1 cm/s and 2.5 cm/s (G_N range in the figure). On average, there are no edge voids observed on all structures obtained after transfer when bonding is completed following RCA cleaning. But certain structures have a significant number of edge voids; these typically are those for which the bonding front has propagated at a speed greater than 1.7 cm/s.

It should be mentioned here that good bonding energy and rapid propagation of the bonding front are generally associated. The document US 6 881 596 proposes to determine the quality of the bonding interface by measuring the propagation speed of the bonding front.

The article "Dynamics of a Bonding Front" by Rieutord, Bataillou and Moriceau in Physical REview Letters, PRL 94, 236101 proposes a formula (see equation 5) indicating that the propagation speed increases if the bonding energy augments.

As already mentioned hereinabove, plasma activation can have been carried out as a complement to standard RCA cleaning. This plasma activation focuses especially on increasing the bonding energy.

The applicant has been able to ascertain that the propagation speed is more significant after plasma activation of the substrates to be stuck. Figure 6 schematically illustrates the propagation speed within the scope of RCA cleaning treatment + plasma activation (here activation of only one of the surfaces to be stuck). As can be noted, the increase in propagation speed is accompanied by the formation of a significant number of edge voids (see G_{N+P} range in the figure).

With reference to the description of the invention, prior to bonding the surface state of one and/or the other of the substrates to be stuck is modified so as to regulate the propagation speed of the bonding front. Within the scope of the example in Figure 6, this regulation is provided so that the speed of the bonding front is in the G_R range (typically

between 0.8 cm/s and 1.7 cm/s; or an overall bonding time of between 18 and 35 seconds for substrates in the form of wafers of 300 mm in diameter) so as to prevent the formation of edge voids.

A first application to be made of regulation by heating concerns the formation of a SeOI structure following bonding of two substrates, whereof one at least has a surface oxide layer.

In fact, by reducing the speed of the bonding front, better-quality bonding (in particular on the edge of the wafer) can be obtained, thus preventing the non-transfer of certain zones of the donor substrate to the support substrate and consequently the formation of edge voids. The applicant has ascertained that by using such hot contact, no edge void is observed, whereas as many as 80 to 100 edge voids can be counted on SOI structures originating from bonding by being placed in contact at ambient temperature. It will be noted that obtaining this good-quality bonding enables recycling, that is, the utilisation of substrates of the refresh type.

Within the scope of this first application, heating is conducted at a temperature of between 30°C and 90°C, preferably between 50°C and 60°C. This temperature range results from a compromise between the appearance of edge voids at a temperature close to 25°C (ambient temperature) and observation of a drop in bonding energy at excessive temperature.

If the substrates are heated to an excessive temperature, a majority of the water adsorbed at the surface (even all of it) will evaporate, and the

bonding force risks dropping sharply. Other types of defects are capable of being caused by excessively low bonding energy. At the extreme, molecular adhesion may not even be produced.

To illustrate the drop in bonding energy, reference can be made to the article by Suni et al. in J. Electrochem. Soc. Vol. 149 No. 6 pp. 348 to 351, 2002, entitled "Effects of Plasma Activation on Hydrophilic Bonding of Si and SiO_2", in which it is mentioned that the bonding energy drops from 2.5 J/m^2 (case of bonding at ambient temperature) to 1 J/m^2 (case of bonding conducted at 150°C), all this after bonding reinforcing annealing carried out at 200°C.

Within the scope of this first application, the invention proposes to use the lowest of the temperatures allowing the edge voids to disappear, so as not to cause a harmful drop in bonding energy.

In reference to the example in Figure 6, the aim is a propagation speed of the bonding front of not less than 0.8 cm/s so as not to cause a harmful drop in the bonding energy, and in any case less than 1.7 cm/s to avoid the formation of edge voids. Therefore, irrespective of the surface preparations made prior to bonding, the aim here is a speed in the G_R range, especially by reducing this speed by heating, in a controlled manner. Mention is made that plasma activation can likewise be utilised within the scope of regulating the speed of the bonding front, with plasma activation effectively causing acceleration of the propagation of the bonding front (or an increase in the propagation speed).

A first variant of this first possible embodiment consists of uniformly heating the whole of one and/or the other of the substrates to be stuck.

A second variant comprises conducting localised heating of one and/or the other of the substrates to be stuck, limited to the zone where the edge voids might disappear. As discussed hereinabove with respect to Figure 2, this is about the termination zone of the bonding front, localisation and the extent of this zone depending on the manner in which bonding has been initiated.

Accordingly, when the bonding of two circular substrates is initiated at the centre, the invention proposes heating the entire peripheral zone (that is, all of the circumference of the substrate). By way of purely illustrative example, this peripheral zone can be considered as occupying a peripheral band of 50 mm wide from the edge of a wafer 300 mm in diameter.

However, when the bonding of two circular substrates is initiated at the edge, the invention advantageously proposes to heat only the edge diametrically opposite to this point (in particular the peripheral zone delimited by an angle at the centre of around 120°).

By employing localised heating, the bonding front is uniquely slowed locally. This prevents the formation of edge voids without the rest of the bonding (non-heated zone) being altered and undergoing a loss in terms of bonding energy.

The heating (localised or extended to all of one and/or the other of the substrates) can be carried out

by thermal conduction. There can be provision for the plate on which repose one of the substrates to be stuck ("chuck" plate) to transmit its heat.

It can also be provided that heating is carried out by radiation, for example by using one or more halogen lamps illuminating all or part of the substrates to be heated.

Heating is completed before the surfaces to be stuck (the substrates then typically being placed opposite, separated by a few millimetres by means of spacers) are placed in close contact and at least until initiation of bonding (the substrates then having been placed in close contact). In particular, heating is carried out such that the zone where the edge voids are capable of appearing remains at the desired temperature until the substrates are adhered in this zone (by hypothesis, the water desorbed locally does not have to be able to condenser before the bonding is finished).

The duration of heating depends largely on the device utilised to raise then control the temperature of the heated zone. It is typically between 1 and 90 seconds.

By way of example, by means of a 500 W halogen lamp, the duration of heating is typically between 30 and 90 seconds.

It is noted that this time range likewise depends on other parameters, such as for example the distance between the lamp and the substrates.

The spectral distribution of the lamp utilised to heat and have the water desorbed is likewise a parameter influencing the duration of heating. In fact,

a lamp mainly emitting light in the infrared mode (length of average wave around 3 m, typically comprises between 0.8 μm and 5 μm) is particularly efficacious to effect desorption of water (the absorption band of the molecules of water are effectively close to 3 m) and thus leads to ultrarapid heating, quasi-instantaneously decreasing the thickness of the layer of water adsorbed. In addition, the utilisation of such infrared radiation helps to selectively heat the adsorbed water while heating the silicon wafer much less, a relatively transparent material in the infrared.

A second application from heating relates to carrying out adhesion of DSB type.

The applicant has effectively been able to determine that the bubbles can be partially or totally eliminated within the scope of Si/Si adhesion of DSB type when the substrates are heated uniformly before and until they are placed in close contact. IR observations have thus shown a significant reduction, even that the bubbles have disappeared.

Heating in effect diminishes the thickness of the layer of water adsorbed at the surface of the substrates. The quantity of water (and/or gas) capable of diffusing at the bonding interface is now reduced, which allows the appearance of bubbles at the bonding interface to disappear.

The previous discussion concerning the different ways of carrying out heating likewise applies to this second application, by noting all the same that uniform

heating of one and/or the other of the substrates to be stuck is preferably carried out here.

DSB bonding can especially be utilised to create Si/Si bonding of substrates having different crystalline orientations, or again substrates having different doping, or even substrates having different levels of constraints. Following transfer of part of one of the substrates to the other, to form a thin layer there, 'thin layer on support substrate' structures are produced, for which the thin layer on one side and the support substrate on the other have different properties.

In order to enable regulation of the propagation speed of the bonding front, the invention proposes to carry out, prior to adhesion, a modification step of the surface state of one and/or the other of the surfaces to be stuck. According to a second possible embodiment, the surface state of a substrate is modified by altering the surface roughness prior to bonding.

This second embodiment is more particularly adapted to the formation of a SeOI structure for which an insulating layer is interposed between the thin layer and the support substrate (also known as a buried layer). This insulating layer is normally formed by thermal oxidation of the donor substrate and/or of the support substrate or again by depositing a layer of oxide on the surface of the donor substrate and/or of the support substrate.

This embodiment proves especially advantageous for the formation of a SeOI structure having an ultra thin

insulating layer. In fact, it proves to be particularly difficult using techniques of the prior art to effect adhesion and/or transfer without defect with such a ultra thin layer interposed in between the thin layer and the support substrate.

By ultra thin insulating layer, it is generally understood here a layer which thickness is less than 500 Å, even less than 200 Å.

The propagation speed of the bonding front is sensitive to the surface state of the substrates put in contact. The different surface cleaning and/or treatment options made prior to bonding, but also the surface roughness, thus influence the rapidity with which the bonding front spreads. Within the scope of this second embodiment the applicant proposes controlling the surface roughness of a layer of oxide so as to regulate the propagation speed of the bonding front, that is, in such a way as to control the reduction in propagation speed of the bonding front. Since the bonding front is slowed, the result from this is a drop in the number of edge voids at the edge of the wafer.

A first variant to this second embodiment consists, prior to bonding, of modifying the surface state of a thermal oxide layer formed on the surface of one of the donor or support substrates and intended to form the buried layer by conducting 'aggressive' cleaning of the surface of said layer of oxide.

This cleaning is carried out prior to any plasma activation.

Of course, a thermal layer of oxide can be formed on each of the donor and support substrates and such 'aggressive' cleaning can be performed on one and/or the other of the surfaces of said thermal oxide layers.

For example, in the case of formation of a SOI structure comprising a buried, ultra thin thermal oxide layer of the order of 250 Å to 500 Å (such a layer is known as 'Ultra Thin BOX'), adapted chemical treatment can be carried out so as to lightly etch the surface of the oxide layer.

For example, SC1 treatment is applied according to conditions (temperature, duration) more significant than those respected during standard cleaning treatment. SC1 treatment can thus be applied within the scope of the invention at a temperature of between 50°C and 80°C, for example of the order of 70°C, with a treatment duration greater than 3 minutes, for example of the order of 10 minutes.

Figure 7 is a diagram illustrating the bonding process according to this variant to the first aspect of the invention. At stage 1, there are two substrates A and B. At stage B, procedure involves thermal oxidation of the substrate A to form a layer of oxide O at the surface of the substrate A. At stage 3, aggressive cleaning of the layer of oxide O is completed to obtain a rough layer O' at the surface of the substrate A. At stage 4, the substrates A and B are placed in close contact by way of the rough layer O', and bonding is initiated such that a bonding front spreads to the bonding interface.

A second variant of this second embodiment consists, prior to bonding, of modifying the surface state of one and/or the other of the donor and support substrates by depositing a rough layer on one and/or the other of said substrates.

Within the scope of the example of Figure 7, it is understood that according to this second variant steps 2 and 3 of Figure 3 are completed at the same time by deposit of a rough layer O' on surface of the substrate A.

It is required for example to deposit a TEOS layer of oxide (for example deposited by LPCVD - Low Pressure Chemical Vapor Deposition - or by PECVD - Plasma Enhanced Chemical Vapor Deposition), of a LTO layer of oxide (by chemical reaction of silane with the oxygen), or again a layer of nitride.

Depositing is effected according to adapted depositing conditions, as a function of the desired final thickness, to target a certain roughness, and in particular a roughness such that the surface state limits the propagation speed of the bonding front.

By way of example, a roughness of a TEOS layer of oxide of between 2 Å RMS and 5 Å RMS limits the propagation speed of the bonding front, at the same time as retaining good bonding energy.

It is specified here that the TEOS deposit is particularly adapted for the formation of ultra thin oxides (thickness less than 500 Å, or even less than 250 Å). In effect, the roughness of such deposited oxide is typically what is wanted, without requiring additional treatment.

Depositing conditions helping to target adequate roughness are for example the following: pressure of between 300 mT and 700 mT; temperature of between 650°C and 700°C. It is noted that the increase in pressure, as also the increase in temperature, results in a decrease in roughness.

It is noted that this second variant is applicable both to thick deposits of oxides and for deposits of ultra thin films, which subsequently undergo or not plasma activation treatment.

The invention also proposes, according to a second aspect, equipment enabling molecular adhesion of two substrates to one another.

Equipment for manual bonding by molecular adhesion usually comprises a support on which is placed a first substrate, the second substrate then being returned with respect to the first substrate. The initiation of bonding (local pressure) is assured manually by means of a stylus.

Automated equipment may comprise especially:

- an aligner for registering the centre and orientation of the wafer (in particular thanks to the presence of a recess known as 'notch');
- one or more station(s) for surface preparation prior to bonding (operations for cleaning, rinsing, drying, etc.);
- an adhesion support receiving the first substrate, then the second at the end of bonding. Spacers can likewise be provided to maintain the second substrate a few millimetres above the first before they are placed in contact;

- an automatic piston ensuring initiation of bonding;
- one or more loading ports receiving the cassettes of substrates to be stuck or already stuck;
- a robot ensuring transport of the wafers from one element of the equipment to another.

In general, the equipment according to the second aspect of the invention reprises the classical configuration of bonding equipment by molecular adhesion (manual or automated) but further comprises means for modifying, prior to adhesion, the surface state of one and/or the other of the substrates to be stuck. These are especially heating means for raising and controlling the temperature of one and/or the other of the donor and support substrates before they are placed in close contact and also during being placed in close contact (that is, also during propagation of the bonding front).

These heating means can dispense heat above and/or below the substrates ready to be stuck.

By way of example of devices for heating below, and in reference to Figure 3, a 'chuck' C can be provided, forming a 'heating wafer'. This is for example a chuck in the mass whereof one or more electrical resistors R are integrated (see illustration to the left in Figure 3), or a 'chuck' C in the mass whereof means F are integrated for circulating fluid whereof the temperature is regulated (at the centre in Figure 3). It is likewise possible to utilise (to the right in Figure 3) one or more heating lamps L which communicate their heat to the 'chuck' or directly

illuminate the rear face of one of the substrates through a transparent plate (at least transparent to IR radiation).

It is evident that in Figure 3 (as well as in Figures 4 and 5, to be mentioned hereinbelow) the donor and support substrates are shown as being opposite (typically separated by a few millimetres by spacers E), before being placed in close contact.

These different techniques can be utilised separately or in combination, locally or on the whole of the chuck. It is possible to produce temperature gradients over the extent of the surfaces, or again to create local control of the temperature.

By way of example of a device enabling heating from above, an arrangement of lamps radiating directly onto on the substrates can be provided, uniformly or deliberately localised (especially where the edge voids are capable of appearing).

So as to control the temperature of the heated zone (whether part or all of a substrate or the substrates) the equipment can also advantageously comprise a device for measuring the temperature in the heated zone (not shown; for example in the form of a pyrometer or a thermocouple).

Equipment can also be available in a manual or automatic version.

Hereinbelow two examples are provided for using the first embodiment of the process according to the first aspect of the invention for the formation of SOI structures, within the scope of the transfer process of SMART CUT® type.

A first example is that of uniform heating of the substrates by means of a heating chuck. The different stages are the following:

- preparation of the surfaces to be stuck according to humid cleaning combining RCA cleaning and treatment based on ozone;
- optional plasma activation (O_2) of the surface of the donor substrate;
- cleaning of the surfaces immediately prior to bonding, by brushing then rinsing with ultra-pure water and drying by centrifuging;
- uniform heating of the substrates to be stuck by means of a heating chuck on which are placed the substrates not yet in contact but placed opposite one another and separated by a few millimetres (see Figure 4). Heating is carried out for several seconds, according to the power of the heating device (from 1 to 90 seconds, typically 30 seconds),
- placing the substrates in close contact and initiation of bonding;
- termination of heating.

A second example is that of localised heating at the zone where edge voids are capable of appearing, and comprises the following stages:

- preparation of the surfaces to be stuck according to humid cleaning combining RCA cleaning and treatment based on ozone;
- optional plasma activation (O_2) of the surface of the donor substrate;

- cleaning of the surfaces immediately prior to adhesion, by brushing then rinsing with ultra-pure water and drying by centrifuging;
- heating of the substrates to be stuck only in the zone opposite the point of initiation using a lamp L placed above the substrates not yet placed in contact but opposite one another and separated by a few millimetres (cf. Figure 5). Heating is carried out for several seconds, according to the power of the heating device (from 1 to 90 seconds, typically 30 seconds);
- placing in contact and initiation of adhesion (I_C localised initiation at the wafer edge);
- termination of heating the wafers;

CLAIMS

1. A process for bonding by molecular adhesion of two substrates to one another during which the surfaces of said substrates are placed in close contact and bonding occurs by propagation of a bonding front between said substrates, characterised in that it comprises prior to bonding a step consisting of modifying the surface state of one and/or the other of the substrates so as to regulate the propagation speed of the bonding front.

2. The process as claimed in Claim 1, characterised in that modification of the surface state is a decrease in the thickness of a layer of water adsorbed at the surface of one and/or the other of the substrates to be bonded.

3. The process as claimed in any one of the preceding claims, characterised in that modification of the surface state is created by heating.

4. The process as claimed in the preceding claim, characterised in that heating is applied prior to

placing in close contact and at least up to initiation of bonding of the substrates to one another.

5. The process as claimed in one of the two preceding claims, characterised in that heating is carried out for a duration of between 1 and 90 seconds, preferably over 30 seconds.

6. The process as claimed in any one of Claims 3 to 5, characterised in that heating is carried out by thermal conduction via transmission of heat from a plate supporting one of the substrates to be bonded.

7. The process as claimed in any one of Claims 3 to 5, characterised in that heating is carried out by radiation from a lamp illuminating one of the substrates to be stuck.

8. The process as claimed in the preceding claim, characterised in that the lamp is a lamp radiating in the infrared range, at a wavelength of between 0.8 m and 5 m.

9. The process as claimed in any one of Claims 3 to 8, characterised in that heating is carried out at a temperature of between 30°C and 90°C, preferably between 50°C and 60°C.

10. The process as claimed in any one of Claims 3 to 9, characterised in that heating is applied uniformly over the extent of the surface of the substrate to be bonded.

11. The process as claimed in any one of Claims 3 to 9, characterised in that heating is applied locally at a peripheral zone of the substrate to be bonded.

12. The process as claimed in Claim 11, wherein adhesion is initiated at the centre, characterised in

that said peripheral zone covers the entire circumference of the substrate to be bonded.

13. The process as claimed in Claim 11, wherein adhesion is initiated at the edge, characterised in that said peripheral zone describes an arc of a circle diametrically opposed to the initiation edge and limited by an angle at the centre of around 120°.

14. The process as claimed in Claim 1, characterised in that modification of the surface state is created by roughening of the surface.

15. The process as claimed in the preceding claim, characterised in that the stage of modification of the surface state consists of forming a rough layer at the surface of one and/or the other of the substrates to be bonded.

16. The process as claimed in Claim 15, characterised in that to form said rough layer, it comprises an operation of thermal oxidation of one and/or the other of the substrates so as to form a thermal oxide layer at the surface of one and/or the other of the substrates and an operation for treatment of the thermal oxide layer adapted to etch said oxide layer.

17. The process as claimed in the preceding claim, characterised in that the treatment of the thermal oxide layer is chemical treatment.

18. The process as claimed in the preceding claim, characterised in that the thermal oxide layer is a layer of SiO_2, and the chemical treatment is SC1 treatment performed at a temperature of between 50°C

and 80°C for a duration greater than three minutes, preferably for 10 minutes.

19. The process as claimed in Claim 15, characterised in that to form said rough layer, it comprises an operation for depositing a layer of oxide on the surface of one and/or the other of the substrates.

20. The process as claimed in the preceding claim, characterised in that the depositing consists of carrying out deposit of a layer of TEOS oxide, a layer of LTO oxide, or a layer of nitride.

21. The process as claimed in any one of the preceding claims, characterised in that it further comprises prior to bonding a step of plasma activation of one and/or the other of the surfaces to be bonded.

22. The process as claimed in the preceding claim, characterized in that the plasma activation allows strong bonding energy to be reached after a reinforcing annealing of the bonding of around two hours.

23. The process as claimed in the preceding claim, characterized in that the annealing is conducted at a temperature less than 600°C.

24. The process as claimed in claims 21-23, in combination with any one of claims 3 to 13, characterised in that the plasma activation is performed prior to modification of the surface state by heating.

25. The process as claimed in claims 21-23, in combination with any one of claims 14 to 20, characterised in that the plasma activation is

performed after modification of the surface state by roughening.

26. A process for formation of a structure comprising a thin layer made of a semiconductor material on a support substrate, comprising the stages of:

- placing a donor substrate in close contact with the support substrate so as to produce bonding by molecular adhesion of said substrates to one another following propagation of a bonding front between said substrates;
- transfer of a part of the donor substrate to the support substrate so as to form said thin layer on the support substrate;

characterised in that it comprises prior to bonding a step consisting of modifying the surface state of the donor substrate and/or of the support substrate so as to regulate the propagation speed of the bonding front.

27. The process as claimed in the preceding claim, wherein the donor substrate is a refresh substrate originating from recycling.

28. Equipment for bonding by molecular adhesion of two substrates to one another following the propagation of a bonding front between said substrates, characterised in that it comprises means for modifying prior to bonding the surface state of one and/or the other of the substrates so as to regulate the propagation speed of the bonding front.

29. The equipment as claimed in the preceding claim, characterised in that the means for modification

of the surface state consist of heating means adapted to raise and control the temperature of one and/or the other of the substrates before being placed in close contact and at least up to initiation of bonding of said substrates to one another.

30. The equipment as claimed in Claim 29 comprising a plate on which one of the substrates to be stuck is placed, characterised in that the plate forms a heating wafer.

31. The equipment as claimed in Claim 30, characterised in that one or more electrical resistors are integrated into the mass of the plate.

32. The equipment as claimed in Claim 30, characterised in that means enabling circulation of fluid whereof the temperature is regulated are integrated into the mass of the plate.

33. The equipment as claimed in Claim 30, characterised in that it comprises one or more heating lamps illuminating the wafer for heating it.

34. The equipment as claimed in Claim 29, characterised in that the heating means are formed by one or more heating lamps radiating directly onto the substrates.

35. The equipment as claimed in the preceding claim, characterised in that the lamp is a lamp radiating in the infrared range, at a wavelength of between 0.8 m and 5 m.