

## DESCRIPTION

**TITLE: Method for directly bonding two substrates**

### TECHNICAL FIELD

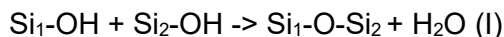
5       The invention relates to a method for directly bonding two substrates and a method for transferring a layer onto a support substrate comprising such a method for directly bonding two substrates.

### PRIOR ART

10       Direct bonding is a technique widely used in microelectronics to assemble substrates and form multilayer structures. It involves directly bringing the two surfaces to be bonded into contact, where they will spontaneously adhere to each other without the addition of any extra material, particularly without the use of a polymer adhesive. It is possible to have some monolayers of water adsorbed onto the surfaces to be bonded, in particular if they are  
15       hydrophilic, but the surfaces must be macroscopically dry.

      Spontaneous adhesion between the two surfaces to be bonded occurs under the influence of various attractive forces between the materials, for example, Van der Waals forces, capillary forces, and/or hydrogen bonds involving water molecules adsorbed onto the  
20       surfaces to be bonded. Covalent bonds can also form between the two surfaces to be bonded.

      For example, when the surfaces to be bonded are hydrophilic silicon surfaces or silicon oxide surfaces, the adhesion between the two surfaces results primarily from condensation reactions between, on the one hand, the silanols of the first surface to be bonded and, on the  
25       other hand, the silanols of the second surface to be bonded. More specifically, each condensation reaction generates a siloxane bond between the two surfaces to be bonded and releases a water molecule according to the following reaction (I):



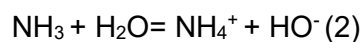
30       The attractive forces mentioned earlier act only over short ranges, and the formation of covalent bonds requires that the reagents be close enough for their molecular orbitals to overlap. Direct bonding therefore requires that the surfaces to be bonded be clean and flat, with very low roughness, for example, less than 0.5 nm. Typically, reaction (I) mentioned earlier  
35       can only occur at the points of contact between the two surfaces to be bonded. Furthermore, such reaction (I) is very slow and remains at equilibrium (it is not complete) at room temperature.

The quality of direct bonding can be assessed by a quantity called “bonding energy”, which corresponds to the energy required to separate the two surfaces once bonded. Due to the difficulties mentioned earlier, the bonding energy between two surfaces bonded by direct bonding at room temperature is insufficient to guarantee the mechanical strength of the resulting multilayer structure in subsequent applications of said multilayer structure, for example, if the multilayer structure is used in a method that induces high mechanical stresses on the bond interface. Indeed, the bonding energy between two surfaces following direct bonding at room temperature rarely reaches 200 mJ/m<sup>2</sup> when the two surfaces adhere under the effect of the attractive forces mentioned earlier. Furthermore, the condensation reaction (I) of silanols does not allow the energy to exceed 0.5 J/m<sup>2</sup>, even after several days.

One solution to increase the bonding energy is to heat the bonding interface after the two surfaces to be bonded have been contacted. For example, bringing two hydrophilic silicon or silicon oxide surfaces to be bonded into contact can be followed by heat treatment of the bonding interface at 200°C for 2 hours.

However, such high temperatures can induce the formation of gases and bubbles at the bonding interface, as well as significant thermal stress, particularly when the two substrates to be bonded have very different coefficients of thermal expansion. Indeed, in this latter case, the difference in behavior of the two substrates under the effect of temperature variations is such that it will cause the bonding interface to open before it has had time to strengthen.

Another solution involves treating at least one of the surfaces to be bonded with gas ammonia (NH<sub>3</sub>) or with an aqueous ammonia solution NH<sub>4</sub>OH. Since ammonia reacts partially with water to generate ammonium ions NH<sub>4</sub><sup>+</sup> and hydroxide ions, this solution is also often called an ammonium hydroxide solution. Ammonia is a weak base that will react with the water adsorbed onto the surface to be bonded, thus generating hydroxide ions OH<sup>-</sup> according to the following acid-base reaction (2):



The hydroxide ions generated by the acid-base reaction (2) act as catalysts for the condensation reaction (I) and therefore increase its kinetics.

However, ammonia NH<sub>3</sub> is extremely volatile: the evaporation of surface ammonia shifts the equilibrium of the acid-base reaction (2) towards the regeneration of ammonia NH<sub>3</sub> and therefore the consumption of catalytic hydroxide ions. In other words, it is difficult to maintain and control the amount of ammonia actually present on the surface to be bonded, even though

this maintenance is necessary for the proper functioning of the basic catalytic effect of the hydroxide ions as described above.

According to document US 7,109,093 B2, it is possible to obtain a bonding energy of the order of a few J/m<sup>2</sup> following direct bonding performed at room temperature between a first bonding layer of a first substrate and a second bonding layer of a second substrate, where the first and/or second bonding layers comprise a fluorinated oxide layer. To generate this fluorinated oxide layer within a bonding layer, for example, a silicon oxide layer, US 7,109,093 B2 describes a fluorination method comprising exposing the silicon oxide layer to hydrofluoric acid followed by annealing the layer thus exposed. During annealing, fluorine diffuses from the surface into the silicon oxide layer, thereby generating the fluorinated oxide layer.

The method described by US 7,109,092 B2 further comprises a step of finishing the surface of the silicon oxide layer, comprising the fluorinated oxide layer, prior to the actual direct bonding. This finishing step can be a rinse with water or ammonium hydroxide and allows for the generation or regeneration of the surface chemical functionalities necessary for surface adhesion according to the previously mentioned condensation reactions. According to US 7,109,092 B2, the fluorine that diffuses into the material during annealing breaks Si-O-Si bonds, making the fluorinated silicon oxide layer porous. When the direct bonding is carried out according to reaction (I) or reaction (II), this porosity allows the water or hydrogen generated by reactions (I) and (II) to diffuse into the porous fluorinated silicon oxide layer and to drive the condensation reaction to completion at room temperature.

However, in many cases, implementing the annealing process described in US 7,109,092 B2 for the formation of the fluorinated oxide layer is impossible. This is the case, for example, when the substrates to be bonded are multilayer structures comprising at least two layers with very different coefficients of thermal expansion. It is also the case when at least one of the two substrates to be bonded comprises temperature-sensitive circuits or components and/or a weakened area formed by the implantation of atomic or ionic species in a SmartCut™ process. Furthermore, the method described in US 7,109,092 B2 involves numerous steps, making it costly and complex to implement.

## **BRIEF DESCRIPTION OF THE INVENTION**

A purpose of the invention is to overcome the aforementioned disadvantages of the prior art.

To this end, the invention proposes a method for directly bonding two substrates, the method comprising the following steps:

a) providing a first substrate and a second substrate comprising, respectively, a first bonding surface made of hydrophilic silicon oxide and a second bonding surface made of hydrophilic silicon oxide,

b) adding fluoride ions to the first hydrophilic silicon oxide bonding surface;

5 c) bringing the first hydrophilic silicon oxide bonding surface into contact with the second hydrophilic silicon oxide bonding surface, so that the first substrate is adhered to the second substrate, by way of the fluoride ions at the bonding interface.

For the purposes of this invention, a hydrophilic silicon oxide bonding surface is defined  
10 as a silicon oxide surface containing silanol groups Si-OH. To be hydrophilic, the silicon oxide surface must, in particular, not comprise surface silicon hydride groups Si-H, or the ratio of the number of silicon hydride groups Si-H to the number of surface silanol groups must be less than 20%. Preferably, the silicon oxide surface must not comprise surface silicon hydride groups Si-H, for example, through reaction with water in a basic medium.

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Adding fluoride ions generates a hydrophilic silicon oxide surface onto which fluoride ions are physisorbed, for example, due to electrostatic interactions. It should be noted that the physisorbed fluoride ions may transiently add to the silicon atoms of the surface silanol groups, so that the hydrophilic silicon oxide bonding surface considered at a given instant may  
20 comprise some covalent bonds HO-Si-F resulting from a nucleophilic addition reaction as schematically represented in Figure 1. The hydrophilic silicon oxide bonding surface is therefore the result of a dynamic equilibrium between physisorbed and added fluoride ions. However, the pentacoordinated silicon atoms that result from the addition of fluoride ions are very unstable and have a very short lifetime, so that the hydrophilic silicon oxide bonding  
25 surface on which the fluoride ions were added consists essentially of physisorbed fluoride ions.

The method of the invention allows to obtain bonding energies exceeding  $1 \text{ J/m}^2$  with a low thermal budget. For example, the bonding energy can reach  $2500 \text{ J/m}^2$  after the addition of fluoride ions according to one embodiment of the invention and one hour of contact between  
30 the two surfaces at  $170^\circ\text{C}$ . By comparison, the bonding energy is only  $250 \text{ mJ/m}^2$  when there has been no addition of fluoride ions, all other parameters of the bonding method remaining unchanged. In other words, the addition of fluoride ions has increased the bonding energy tenfold. For example, after one hour of contact between the two surfaces at  $100^\circ\text{C}$ , the bonding energy is multiplied by 5 if fluoride ions have been added according to one embodiment of the  
35 invention.

The inventors attribute the achievement of the aforementioned high bonding energies at a low thermal budget to a nucleophilic catalytic effect of surface fluoride ions, which enhances

the kinetics of the condensation reaction (I) responsible for the adhesion between the first hydrophilic silicon oxide bonding surface of the first substrate and the second hydrophilic silicon oxide bonding surface of the second substrate. The inventors hypothesize that the introduction of fluoride ions onto the first hydrophilic silicon oxide bonding surface leads successively to the physisorption of said fluoride ions onto the first hydrophilic bonding surface, followed by the nucleophilic addition of at least some of said physisorbed fluoride ions to silicon atoms of the silanol groups of the first hydrophilic silicon oxide bonding surface, thereby generating the aforementioned pentacoordinated surface silicon atoms. Said pentacoordinated silicon atoms are highly reactive reaction intermediates: the electrophilicity of the silicon atoms of the first hydrophilic silicon oxide bonding surface is enhanced by the addition of fluoride ions, so that the oxygen of the silanol groups of the second hydrophilic silicon oxide bonding surface then easily substitutes for the fluoride ions.

The high bonding energies mentioned above are obtained in a single treatment step, and without thermal annealing of the hydrophilic silicon oxide bonding surfaces on which the addition of fluoride ions is carried out prior to the contact of the first substrate and the second substrate, which is particularly advantageous when one of these substrates comprises a weakened area and/or electronic components and/or several materials with different coefficients of thermal expansion.

The catalytic effect of fluoride ions is probably specific to the direct bonding between silicon oxide surfaces. However, the application of fluoride ions is easier to implement and requires fewer special precautions than the previously mentioned ammonia treatments, the beneficial effect of which on bonding energy is very difficult to observe in practice, particularly due to the volatility of ammonia.

According to other optional features of the invention taken alone or in combination where technically possible:

- the method further comprises, the addition of fluoride ions on the second hydrophilic silicon oxide bonding surface prior to bringing the first hydrophilic silicon oxide bonding surface into contact with the second hydrophilic silicon oxide bonding surface;
- the contacting of the first hydrophilic silicon oxide bonding surface with the second hydrophilic silicon oxide bonding surface is carried out at room temperature;
- during the entire duration between the addition of fluoride ions and the contacting of the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface, each hydrophilic silicon oxide bonding surface on which the addition of fluoride ions is implemented is maintained at room temperature and/or the addition of fluoride ions on the first hydrophilic silicon oxide bonding surface is implemented at room temperature;

- the method further comprises a consolidation annealing step d) carried out after step c) of bringing the first hydrophilic silicon oxide bonding surface into contact with the second hydrophilic silicon oxide bonding surface, the consolidation annealing being preferably carried out at a temperature comprised between 50°C and 250°C, even more preferably at a temperature comprised between 50°C and 100°C, for a duration preferably comprised between 15 min and 4 hours, even more preferably for a duration comprised between 15 min and 2 hours;
- the addition of fluoride ions on the first hydrophilic silicon oxide bonding surface comprises the deposition of a liquid comprising fluoride ions and/or fluoride ion donor species on the first hydrophilic bonding surface;
- the deposition of the liquid on the first hydrophilic silicon oxide bonding surface comprises: the deposition of a volume of the liquid comprising the fluoride ions and/or the fluoride ion donor species at the center of the first hydrophilic silicon oxide bonding surface, the spreading of said volume of liquid comprising the fluoride ions and/or the fluoride ion donor species by rotation of the first hydrophilic silicon oxide bonding surface, said first hydrophilic silicon oxide bonding surface being kept in rotation until ejection and evaporation of the volume of liquid comprising the fluoride ions and/or the fluoride ion donor species;
- the liquid comprising fluoride ions and/or fluoride ion donor species does not comprise hydrofluoric acid or ammonium fluoride;
- the liquid comprising fluoride ions and/or fluoride ion donor species is obtained from the dissolution of a fluoride ion salt and a counter-ion which is a neutral or basic cation;
- the addition of fluoride ions to the first hydrophilic silicon oxide bonding surface comprises: exposing said first hydrophilic silicon oxide bonding surface to a fluorinated plasma, rinsing with water, or exposing the first hydrophilic silicon oxide bonding surface previously exposed to the fluorinated plasma to a humid atmosphere;
- the addition of fluoride ions to the first hydrophilic silicon oxide bonding surface comprises exposing the first hydrophilic silicon oxide bonding surface to a gas containing fluorinated species;
- the gas containing fluorinated species does not comprise hydrofluoric acid;
- the gas comprises sulfur hexafluoride  $\text{SF}_6$  and/or tetrafluoromethane  $\text{CF}_4$ , mixed with ammonia  $\text{NH}_3$  or nitrogen trifluoride  $\text{NF}_3$  in a basic medium;
- the addition of fluoride ions on the first hydrophilic silicon oxide bonding surface comprises: implanting fluorine using an implanter on the first hydrophilic silicon oxide bonding surface, rinsing with water, or exposing the first previously implanted hydrophilic silicon oxide bonding surface to a humid atmosphere;
- the first hydrophilic silicon oxide surface and/or the second hydrophilic silicon oxide surface are made of chemical oxide, deposited oxide, thermal oxide and/or native oxide;

- the first substrate is a multilayer structure comprising a first layer made of a first material and a second layer made of a second material, the difference in coefficient of thermal expansion between the first material and the second material being greater than or equal to 10% or  $10^{-6}$  K<sup>-1</sup> in absolute value.

- 5    - the first substrate comprises elements of electronic components;  
      - the first substrate comprises a weakened area formed by the implantation of atomic or ionic species.

The invention extends to a method for transferring a layer onto a support substrate,  
 10    said method comprising the following steps:  
      a) providing a donor substrate comprising a first hydrophilic silicon oxide surface and a support substrate comprising a second hydrophilic silicon oxide surface,  
      b) forming a weakened area within the donor substrate so as to delimit a layer to be transferred between the first hydrophilic silicon oxide surface and the weakened area,  
 15    c) bonding the donor substrate and the support substrate, the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface being at the bonding interface and the bonding between the donor substrate and the support substrate being implemented by a bonding method as previously described,  
      d) detaching the donor substrate along the weakened area so as to transfer the layer to be  
 20    transferred onto the support substrate.

The invention also extends to an assembly comprising a first substrate and a second substrate, the first substrate being covered by a first hydrophilic silicon oxide surface and the second substrate by a second hydrophilic silicon oxide surface, the first hydrophilic  
 25    silicon oxide surface being directly bonded to the second hydrophilic silicon oxide surface, fluoride ions being disposed between the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface, wherein the surface concentration of fluoride ions at the bonding interface between the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface is comprised between  $10^{10}$  ions/cm<sup>2</sup> and  $10^{14}$  ions/cm<sup>2</sup>, and  
 30    wherein the fluoride ion concentration in the first substrate and in the second substrate at a distance greater than 1 nm from the bonding interface between the first substrate and the second substrate is less than  $10^{18}$  at/cm<sup>3</sup>.

Finally, the invention extends to a substrate having a first hydrophilic silicon oxide  
 35    surface on which fluoride ions are physisorbed, the surface concentration of fluoride ions physisorbed on said first hydrophilic silicon oxide surface being comprised between  $10^{10}$  ions/cm<sup>2</sup> and  $10^{14}$  ions/cm<sup>2</sup>, and in which the concentration of fluoride ions in said substrate at a distance greater than 1 nm from the first surface is less than  $10^{18}$  at/cm<sup>3</sup>.

## BRIEF DESCRIPTION OF THE FIGURES

Other features and advantages of the invention will become apparent from the detailed description that follows, with reference to the appended drawings, in which:

- Figure 1 illustrates the nucleophilic role of the fluoride ion in the condensation reaction of silanols which leads to the formation of a siloxane Si-O-Si bond between the two surfaces to be bonded;

- Figure 2 compares the bonding energy measured between two silicon oxide surfaces bonded by a direct bonding method, said direct bonding method comprising successively the deposition, centrifugation and evaporation of a cesium fluoride solution at a concentration of  $10^{-4}$  M on the surfaces, the contacting of the two surfaces then the implementation of a consolidation anneal at 220°C, with the bonding energy measured between two silicon oxide surfaces bonded by a direct bonding method not comprising the deposition of the cesium fluoride solution, the bonding energy being represented as a function of the duration of the consolidation anneal at 220°C;

- Figure 3 compares the bonding energy measured between two silicon oxide surfaces bonded by a direct bonding method, said direct bonding method comprising successively the deposition, centrifugation and evaporation of a cesium fluoride solution on the surfaces, the contacting of the two surfaces then the implementation of a consolidation anneal at 170°C, with the bonding energy measured between two silicon oxide surfaces bonded by a direct bonding method not comprising the deposition of the cesium fluoride solution, the bonding energy being represented as a function of the duration of the consolidation anneal at 220°C;

- Figure 4 shows the bonding energy measured between two silicon oxide surfaces bonded according to a direct bonding method, said direct bonding method comprising successively the deposition, centrifugation and evaporation of a cesium fluoride solution on the surfaces, the contacting of the two surfaces then the implementation of a consolidation anneal, depending on the consolidation annealing temperature, for different concentrations of the cesium fluoride solution;

- Figure 5 represents the bonding energy measured between two silicon oxide surfaces bonded according to a direct bonding method, said direct bonding method comprising exposing the surfaces to a dilute hydrofluoric acid vapor, contacting the two surfaces then the implementation of a consolidation anneal, depending on the consolidation annealing temperature (duration 2 h) for different times of exposure to this vapor.

- Figure 6 represents the bonding energy measured between two silicon oxide surfaces bonded using a direct bonding method, said direct bonding method comprising the immersion of the plates in a very dilute hydrofluoric acid solution (0.05%) for 1 minute, removing the plates followed by contacting the two surfaces then the implementation of a consolidation anneal,

depending on the consolidation annealing temperature. The reference value is obtained by soaking in DI water for the same duration.

## DETAILED DESCRIPTION OF EMBODIMENTS

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### Direct bonding method

The direct bonding method according to the invention comprises a first step of providing a first substrate comprising a first hydrophilic silicon oxide bonding surface and a second  
10 substrate comprising a second hydrophilic silicon oxide bonding surface.

**Providing a first substrate comprising a first hydrophilic silicon oxide bonding surface and a second substrate comprising a second hydrophilic silicon oxide bonding surface**

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#### *First substrate and second substrate*

The first substrate and/or the second substrate may, for example, be made of a material selected from silicon Si, germanium Ge, indium phosphide InP, gallium arsenide AsGa, alumina Al<sub>2</sub>O<sub>3</sub>, silicon oxide SiO<sub>2</sub>, silicon nitride Si<sub>3</sub>N<sub>4</sub>, silicon carbide SiC, gallium nitride GaN,  
20 copper, titanium, nickel, lithium niobate LiNbO<sub>3</sub> (known to the person skilled in the art as LNO) and lithium tantalate LiTaO<sub>3</sub> (known to the person skilled in the art as LTO).

Alternatively, the first substrate and/or the second substrate may be multilayer structures comprising at least two layers. For example, the first substrate - the second substrate  
25 respectively – comprises a first layer made of a first material and a second layer made of a second material. The first and second materials are, for example, selected from the materials previously mentioned. According to this embodiment, the step of supplying a first substrate comprising a first hydrophilic silicon oxide bonding surface and a second substrate comprising  
30 a second hydrophilic silicon oxide bonding surface may comprise one or more sub-steps of assembling said layers to form the first and/or the second substrate.

The direct bonding method according to the invention is particularly advantageous when the first and/or second substrates comprise layers made of materials having a large difference  
35 in coefficient of thermal expansion. A large difference in coefficient of thermal expansion is defined as a difference of 10% or more between the values of said coefficients of thermal expansion.

Indeed, under the effect of a rapid temperature increase, and due to the previously mentioned differences in coefficients of thermal expansion and the low elasticity of these structures, significant stresses can arise. These stresses can locally exceed the breaking strength of the material or assembly and cause cracking or delamination.

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Such cracking or delamination typically occurs when stresses exceed 10 MPa, meaning that the product of the temperature variation and the difference in coefficients of thermal expansion between the first and second materials is greater than  $10^{-4}$ . Since the bonding method avoids temperature variations exceeding 100°C, the difference in coefficients of thermal expansion between the first and second materials can be greater than  $10^{-6} \text{ K}^{-1}$  in absolute value or 10 % in relative values. The annealing temperature is limited according to the differences in coefficients of thermal expansion.

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Furthermore, the first and/or second substrate may comprise one or more electronic component elements. For example, the first and/or second substrate comprise metallic parts such as copper lines and insulating parts made of silicon oxide (hybrid bonding). Similarly, the step of supplying a first substrate comprising a first hydrophilic silicon oxide bonding surface and a second substrate comprising a second hydrophilic silicon oxide bonding surface may in this case comprise one or more sub-steps of forming said electronic component elements.

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The direct bonding method according to the invention is particularly advantageous when the first and/or second substrates comprise such electronic components, as these materials are inherently inhomogeneous, since they contain, for example, metallic parts, insulating oxides, or specific semiconductors. Therefore, they cannot tolerate excessive temperature variations, as these variations can lead to high stresses that may result in the formation of defects (such as delamination). A temperature of 200°C thus appears to be an upper limit that should not be exceeded for extended periods.

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Finally, the first substrate and/or the second substrate may also comprise a weakened area formed for example by the implantation of atomic and/or ionic species.

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The direct bonding method according to the invention is particularly advantageous when the first and/or second substrates comprise such a weakened area, as the material is then locally weakened to prepare for a future thermal fracture step, and it is therefore desirable to strengthen the remainder of the structure (i.e., the bonding interface) without mechanically stressing the weakened implanted area. Typically, implantation fracture temperatures are above 300°C, but it is necessary to avoid exceeding 200°C to prevent damage to the weakened structure.

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The first substrate and the second substrate may be of the same nature or they may be different. The direct bonding method according to the invention is particularly advantageous when the first substrate (or a layer of said first substrate) and the second substrate (or a layer of the second substrate) are made of materials having a large difference in coefficient of thermal expansion for the same reasons as previously stated.

*First hydrophilic silicon oxide bonding surface and second hydrophilic silicon oxide bonding surface*

As previously mentioned, the first substrate and the second substrate comprise, respectively, a first hydrophilic silicon oxide bonding surface and a second hydrophilic silicon oxide bonding surface. A hydrophilic bonding surface is defined as one with a strong affinity for water, such that at least a monolayer of water remains naturally adsorbed onto the hydrophilic bonding surface. The contact angle of a hydrophilic surface is typically less than ten degrees.

For example, the first hydrophilic silicon oxide bonding surface and/or the second hydrophilic silicon oxide bonding surface can be native silicon oxide surfaces. In other words, if the first and/or second substrate comprises a material that naturally forms a silicon oxide layer on its surface - called a native silicon oxide layer - (typically silicon Si or silicon carbide SiC, which naturally form a silicon oxide layer), the first hydrophilic silicon oxide bonding surface and/or the second hydrophilic silicon oxide bonding surface can be the surface of said native oxide layer. If the first and/or second substrate is/are silicon oxide or comprise(s) a silicon oxide layer, the first hydrophilic silicon oxide bonding surface and/or the second hydrophilic silicon oxide bonding surface may be directly the surface of said silicon oxide.

For example, the first hydrophilic silicon oxide bonding surface and/or the second hydrophilic silicon oxide bonding surface can be thermal silicon oxide surfaces. According to this embodiment, the step of supplying a first substrate comprising a first hydrophilic silicon oxide bonding surface and a second substrate comprising a second hydrophilic silicon oxide bonding surface can comprise a sub-step of forming a first thermal silicon oxide layer on the first substrate and/or a sub-step of forming a second thermal silicon oxide layer on the second substrate, a surface of the first, respectively, of the second, thermal silicon oxide layer forming the first, respectively, the second, hydrophilic silicon oxide bonding surface.

A thermal oxide is understood to be an oxide formed by direct oxidation of a material by exposure of said material, at high temperature, to dioxygen (dry oxidation), to water (wet oxidation) or optionally to other oxidants (for example  $N_2O$ ).

5 A thermal silicon oxide layer can be formed on the surface of a silicon or silicon carbide substrate. For this purpose, the silicon or silicon carbide substrate is, for example, heated to a temperature preferably comprised between  $800^{\circ}\text{C}$  and  $1200^{\circ}\text{C}$ , then a surface of said silicon or silicon carbide substrate is exposed to an atmosphere of dioxygen or water vapor. The oxidation temperature determines the growth rate of the thermal silicon oxide layer from the  
10 surface of the silicon or silicon carbide substrate exposed to the dioxygen or water vapor atmosphere. In the case of wet oxidation, the formation of the thermal oxide layer may involve the combustion of dihydrogen with dioxygen in a torch and the exposure of the silicon or silicon carbide substrate to the water vapor produced by said combustion, the heat generated by the combustion of dihydrogen may also be used to raise the silicon or silicon carbide substrate to  
15 the chosen oxidation temperature.

The thickness of the thermal silicon oxide layer is, for example, comprised between 1 nm and  $1\text{ }\mu\text{m}$ .

20 For example, the first hydrophilic silicon oxide bonding surface and/or the second hydrophilic silicon oxide bonding surface may be chemical silicon oxide surfaces. According to this embodiment, the step of supplying a first substrate comprising a first hydrophilic silicon oxide bonding surface and a second substrate comprising a second hydrophilic silicon oxide bonding surface may comprise a sub-step of forming a first chemical silicon oxide layer on the  
25 first substrate and/or a sub-step of forming a second chemical silicon oxide layer on the second substrate, a surface of the first, respectively, of the second, chemical silicon oxide layer forming the first, respectively, the second, hydrophilic silicon oxide bonding surface.

A chemical oxide is defined as an oxide formed by the oxidation of a material at low  
30 temperature (preferably at room temperature) in the presence of water or certain oxidants such as hydrogen peroxide  $H_2O_2$  or ozone  $O_3$ . A chemical silicon oxide layer can be formed in this way on the surface of a silicon, silicon carbide, or silicon nitride substrate by exposing said surface, at low temperature, to water or an oxidant such as those mentioned above. The thickness of the chemical silicon oxide layer on the surface of the silicon substrate is, for  
35 example, comprised between 0.5 nm and 3 nm.

For example, the first hydrophilic silicon oxide bonding surface and/or the second hydrophilic silicon oxide bonding surface can be deposited silicon oxide surfaces. According

to this embodiment, the step of supplying a first substrate comprising a first hydrophilic bonding surface and a second substrate comprising a second hydrophilic bonding surface can comprise a sub-step of depositing a first silicon oxide layer on the first substrate and/or a sub-step of depositing a second silicon oxide layer on the second substrate, a surface of the first, respectively, of the second, deposited oxide layer forming the first, respectively, the second, hydrophilic silicon oxide bonding surface.

A deposited oxide is defined as an oxide formed by the chemical addition of material, for example, in the form of vapor or plasma. A silicon oxide layer can be deposited on virtually any type of material, including IV/IV, III/V, and II/VI semiconductors, as well as oxides such as  $\text{LiTaO}_3$  or  $\text{LiNbO}_3$ . The thickness of the deposited silicon oxide layer is for example comprised between 1 nm and 10  $\mu\text{m}$ .

For the deposition of a silicon oxide layer, the precursor providing the silicon is typically silane ( $\text{SiH}_4$ ), while the precursor providing the oxygen is, for example,  $\text{N}_2\text{O}$  or  $\text{O}_2$ . For example, the substrate on which the silicon oxide layer is to be deposited is placed in a plasma chamber. Then, a carrier gas, for example dihydrogen, comprising the silicon and oxygen precursors, such as  $\text{SiH}_4$  and  $\text{N}_2\text{O}$ , is introduced into the plasma chamber. Under the effect of the plasma, the precursors decompose and react, forming a silicon oxide layer on the surface of the substrate exposed to the plasma.

If the first substrate and/or the second substrate are made of silicon oxide or comprise a silicon oxide layer and/or if the first substrate and/or the second substrate are made of a material that naturally forms a silicon oxide layer on the surface or comprise such a material, the supply of the first substrate comprising a first hydrophilic silicon oxide bonding surface and of the second substrate comprising a second hydrophilic silicon oxide bonding surface may nevertheless comprise the formation of a first deposited thermal or chemical silicon oxide layer, on the first substrate and/or the formation of a second deposited thermal or chemical silicon oxide layer, on the second substrate so that a surface of the first, respectively of the second, deposited thermal or chemical silicon oxide layer forms the first, respectively the second, hydrophilic silicon oxide bonding surface.

The first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface may be of the same or different types. For example, the first hydrophilic silicon oxide bonding surface may be a chemical silicon oxide surface, and the second hydrophilic silicon oxide bonding surface may be a native silicon oxide surface. In this case, the step of providing a first substrate comprising a hydrophilic silicon oxide bonding surface and a second substrate comprising a second hydrophilic silicon oxide bonding surface may

comprise a sub-step of forming a chemical silicon oxide layer on the first substrate. For example, the first hydrophilic silicon oxide bonding surface may be a thermal silicon oxide surface, and the second hydrophilic silicon oxide bonding surface may be a deposited silicon oxide surface. In this case, the step of supplying a first substrate comprising a hydrophilic silicon oxide bonding surface and a second substrate comprising a second hydrophilic silicon oxide bonding surface may comprise a sub-step of forming a thermal silicon oxide layer on the first substrate and a sub-step of forming a deposited silicon oxide layer on the second substrate.

Such combinations are mentioned by way of example and are in no way limiting the scope of the invention. Any combination of native, chemical, thermal, and deposited silicon oxide surfaces of the first substrate and the second substrate remains covered by the present invention.

Furthermore, depending on the nature of the first, respectively the second, substrate to be obtained (monolithic substrate, or multilayer structure comprising materials with very different coefficients of thermal expansion, possibly comprising elements of electronic components and/or a weakened area) and the application considered for the assembly resulting from the bonding between the first substrate and the second substrate (manufacture of SOI substrate for advanced microelectronics, substrate for RF, substrate for photonics) the person skilled in the art is able to choose the nature of the silicon oxide most suitable for the first, or second, substrate, as well as the order of the sequence of the different sub-steps previously mentioned allowing to provide the first, or second, expected substrate.

### **Addition of fluoride ions to at least the first hydrophilic bonding surface**

The method further comprises a step of adding fluoride ions to the first hydrophilic silicon oxide bonding surface, or to both the first hydrophilic silicon oxide bonding surface and on the second hydrophilic silicon oxide bonding surface. As previously mentioned, following the addition of fluoride ions, the fluoride ions are essentially physisorbed on the hydrophilic silicon oxide surface.

#### *Addition in liquid form*

According to a particular embodiment, the addition of fluoride ions comprises the deposition of a liquid comprising fluoride ions and/or fluoride ion donor species on the hydrophilic bonding surface.

For example, the liquid comprising fluoride ions is a solution of a fluoride salt, preferably an aqueous solution. The dissolved salt is selected, for example, from ammonium fluoride, lithium fluoride, sodium fluoride, potassium fluoride, cesium fluoride, magnesium fluoride, calcium fluoride, and barium fluoride. Cesium fluoride advantageously has better solubility in water than sodium fluoride or potassium fluoride. The concentration of the fluoride salt solution deposited on the first hydrophilic bonding surface is preferably comprised between  $10^{-5}$  mol/L and  $10^{-3}$  mol/L to prevent crystal formation during evaporation.

For example, the liquid comprising fluoride ions and/or fluoride ion donor species is a dilute hydrofluoric acid solution, and the fluoride ion donor species is hydrofluoric acid. The hydrofluoric acid concentration is preferably chosen to be less than 0.5% in order to limit oxide etching.

Preferably, however, the liquid comprising fluoride ions and/or fluoride ion donor species is not a hydrofluoric acid solution, an ammonium fluoride solution, or any other liquid having the effects of hydrofluoric acid and ammonium fluoride.

Indeed, hydrofluoric acid and ammonium fluoride are acid species that donate protons ( $H^+$ ) and tend to counteract the desired catalytic effect. Furthermore, hydrofluoric acid and ammonium fluoride have the ability to react with silicon oxide and thereby etch the layer. Such etching damages the silicon dioxide layer, particularly its dielectric properties, and is undesirable. The desired catalytic effect, on the contrary, requires maintaining the fluoride ions physisorbed on the surface at the bonding interface.

Thus, in a preferred embodiment, the liquid comprising the fluoride ions is a solution of a fluoride ion salt and a counterion that is neutral or basic. The counterion may, in particular, be an alkali or alkaline earth cation. For example, the liquid comprising the fluoride ions is a solution of ammonium fluoride, lithium fluoride, sodium fluoride, potassium fluoride, cesium fluoride, magnesium fluoride, calcium fluoride, and/or barium fluoride. Even more preferably, the counterion is also non-metallic. The counterion may, in particular, be a polyatomic cation, for example, a derivative of the ammonium ion  $NH_4^+$  by substitution of one or more protons. For example, the liquid comprising the fluoride ions is a solution of dimethylammonium fluoride.

The deposition of the liquid comprising fluoride ions and/or fluoride ion donor species can be carried out for example by coating, by spraying or by spin-coating.

Spraying refers to the dispensing of droplets of solution in aerosol form.

Coating refers to the process of dipping and removing a substrate from the solution.

Preferably, the deposition of the liquid comprising fluoride ions and/or fluoride ion donor species is carried out using a rotating device. In other words, the deposition of the liquid comprising fluoride ions and/or fluoride ion donor species involves rotating the first hydrophilic silicon oxide bonding surface and depositing a volume of the liquid comprising the fluoride ions and/or fluoride ion donor species at the center of the first rotating hydrophilic silicon oxide bonding surface, for example, using a pipette, the rotation of the first hydrophilic silicon oxide bonding surface allows said volume of the liquid comprising the fluoride ions and/or fluoride ion donor species to be spread over the entire first hydrophilic silicon oxide bonding surface.

The volume of the liquid comprising the fluoride ions and/or fluoride ion donor species is preferably comprised between 1 cm<sup>3</sup> and 100 cm<sup>3</sup> for a first substrate of 300mm diameter, while the rotation speed of the first bonding surface during deposition is preferably comprised between 100 rpm and 3000 rpm.

Following the deposition of the volume of liquid comprising fluoride ions and/or fluoride ion donor species, the first hydrophilic silicon oxide bonding surface is then kept in rotation until the volume of liquid comprising fluoride ions and/or fluoride ion donor species is ejected and evaporated.

Preferably, the first hydrophilic silicon oxide bonding surface is kept rotating at a rotational speed comprised between 100 rpm and 3000 rpm for a duration comprised between 1 s and 1 min.

The deposition of the liquid comprising fluoride ions and/or fluoride ion donor species using a rotating tray is highly advantageous because it can be implemented in machines commonly used for bonding substrates in the microelectronics industry. Indeed, these machines already incorporate, for the purposes of cleaning and preparing surfaces for bonding, the equipment that allows for the deposition of the volume of liquid comprising fluoride ions and/or fluoride ion donor species and the spreading of said volume as described above. Therefore, the person skilled in the art does not need to invest in new equipment to implement the invention according to this embodiment.

Keeping the first hydrophilic silicon oxide bonding surface rotating until the volume of liquid comprising fluoride ions and/or fluoride ion donor species is ejected and evaporated allows the first hydrophilic silicon oxide bonding surface to dry, while retaining a sufficient amount of fluoride ions on the first hydrophilic silicon oxide bonding surface.

The choice of rotation speed allows, to some extent, for the modulation of the amount of fluoride ions remaining on the surface during bonding by adjusting the proportion of the liquid volume comprising fluoride ions and/or fluoride ion donor species that is ejected relative to the proportion that evaporates. A high speed allows for more efficient removal of excess solution and prevents the formation of droplets, and increases the evaporation rate. However, if the rotation speed exceeds 3000 rpm, too large a proportion of the liquid volume comprising fluoride ions and/or fluoride ion donor species is ejected, resulting in insufficient fluoride ions remaining on the surface. Conversely, if the speed is below 100 rpm, too large a proportion of the liquid volume comprising fluoride ions and/or fluoride ion donor species is evaporated, resulting in an excess of fluoride ions on the surface.

Furthermore, said amount of fluoride ions and/or fluoride ion donor species deposited and maintained on the surface can be adjusted using various parameters, such as the concentration of fluoride ions and/or fluoride ion donor species in the liquid comprising the fluoride ions and/or fluoride ion donor species and the pH of said liquid which affects the surface charge of the oxide.

According to this embodiment of fluoride ion addition, the method does not comprise any additional finishing steps on the hydrophilic silicon oxide bonding surfaces, for example no RCA cleaning, between the addition of fluoride ions and the contacting of the two substrates to be bonded. Indeed, it is important not to remove the physisorbed fluoride ions from the first, and possibly the second, hydrophilic silicon oxide bonding surface so that these fluoride ions are located close to the bonding interface when the two substrates are contacted and can act as a catalyst.

As previously mentioned, the method according to the invention is particularly advantageous when the substrates to be bonded are substrates comprising a weakened area formed by implantation of ions or atoms or comprising elements of electrical components and/or comprising several layers of distinct materials, in particular materials having very different coefficients of thermal expansion, for example coefficients of thermal expansion differing by more than 10%.

Indeed, the addition of fluoride ions to each hydrophilic silicon oxide bonding surface to be treated can be very advantageously carried out at room temperature, typically at a temperature comprised between 18°C and 25°C. Furthermore, the method does not require annealing each of the substrates to whose surface the fluoride ions have been added. Annealing the hydrophilic silicon oxide bonding surfaces after adding fluoride ions would result

in the diffusion of fluoride ions from the first, and possibly the second, hydrophilic silicon oxide bonding surface into the interior of the first, and possibly the second, substrate, thus generating a porous subsurface layer. However, as previously mentioned, the desired effect is the catalysis, by fluoride ions physisorbed on the first hydrophilic silicon oxide bonding surface and possibly on the second hydrophilic silicon oxide bonding surface, of the condensation reactions that lead to adhesion between the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface when said first and second hydrophilic silicon oxide bonding surfaces are contacted. This effect differs from that induced by the presence of a porous layer within the first and possibly the second substrate, which would be generated by annealing the substrates to which the fluoride ions have been added, namely shifting the equilibrium of said condensation reactions towards adhesion between the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface by allowing the diffusion of water produced in the direction of the reaction, away from the bonding interface.

Thus, the fluoride ion addition is preferably carried out at room temperature, and each hydrophilic silicon oxide bonding surface to which the fluoride ions have been added is preferably maintained at room temperature for the entire duration between the addition of fluoride ions and the contacting of the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface. In this way, the method is also more economical, less energy-intensive, and easier to implement.

According to a specific embodiment of fluoride ion addition in liquid form, the deposition of the liquid comprising fluoride ions or fluoride ion donor species can be preceded by activation of the hydrophilic silicon oxide bonding surface using a plasma. Indeed, plasma activation of a silicon oxide bonding surface is known to the person skilled in the art to have a beneficial effect on the bonding energy: indeed, plasma breaks numerous bonds, in particular Si-O-Si bonds, and generates highly reactive species. Upon exposure of the plasma-activated surface to water or a humid atmosphere, these reactive species react with the water to form new surface Si-OH silanols. Thus, plasma activation ultimately increases the number of surface silanol groups that can then react in the condensation reactions when the substrates are contacted for bonding. The inventors have highlighted a beneficial effect of combining plasma activation and the addition of fluoride ions or fluoride ion donor species in liquid form, since such a combination, with all other parameters unchanged, allows to increase the bonding energy compared to simple plasma activation or the sole addition of fluoride ions or fluoride ion donor species in liquid form.

Plasma, for example, is formed from a gas such as dioxygen, dinitrogen, helium, or argon. Advantageously, the plasma does not comprise fluoride ion donor species, and the addition of fluoride ions or fluoride ion donor species is implemented in a separate second step using a liquid comprising the fluoride ions or fluoride ion donor species. This embodiment advantageously allows to optimize the amounts of fluoride ions and/or fluoride ion donor species used and to avoid excessive fluorination, and thus altering, the silicon oxide layer.

Each hydrophilic silicon oxide bonding surface to be fluorinated can be exposed to said plasma for a duration comprised between 1 s and 1 min.

#### *Addition in gas form*

Alternatively, the addition of fluoride ions may comprise exposure to a gas comprising fluoride ion donor species.

Upon contact with water adsorbed on the hydrophilic silicon oxide bonding surface, molecules of the fluoride ion donor species will adsorb onto the hydrophilic silicon oxide bonding surface and dissociate in order to release fluoride ions.

For example, the fluoride ion donor species is gas hydrofluoric acid or gas boron trifluoride  $\text{BF}_3$ .

Preferably, however, the fluoride ion donor species is not hydrofluoric acid or any other acid or etching gas that could damage the silicon oxide layer. Gas boron trifluoride  $\text{BF}_3$ , for example, when adsorbed onto the surface, reacts with water to form hydrofluoric acid. Furthermore, it is a highly toxic gas.

Thus, in preferred embodiments, the fluoride ion donor species is sulfur hexafluoride  $\text{SF}_6$  and/or tetrafluoromethane  $\text{CF}_4$ , mixed with ammonia  $\text{NH}_3$  to basify the surface and avoid producing hydrofluoric acid, or the fluoride ion donor species is gas nitrogen trifluoride  $\text{NF}_3$  in a medium which, in a basic medium, gives nitrites and fluoride ions.

The gas comprising the fluoride ion donor species is selected from argon or nitrogen. Alternatively, the gas can be directly the vapors of the fluoride ion donor species.

The partial pressure in fluoride ion donor species is, for example, comprised between 0.1 mbar and 1 bar.

Each hydrophilic silicon oxide bonding surface to be fluorinated is exposed to said gas for a duration preferably comprised between 1 s and 1 min.

According to this embodiment as well, the addition of fluoride ions can be very advantageously carried out at low temperatures. More precisely, the gas temperature can be comprised between 18°C and 25°C. Furthermore, each hydrophilic silicon oxide bonding surface can be maintained at room temperature after the addition of fluoride ions until the two substrates to be bonded are contacted.

According to a particular embodiment of the addition of fluoride ions in gas form, the exposure of the hydrophilic silicon oxide bonding surface to a gas comprising fluoride ion donor species can be preceded by activation of the hydrophilic silicon oxide bonding surface using a plasma. Such plasma activation can be implemented as previously described for the addition in liquid form and allows for an increase in bonding energy compared to simple plasma activation or the sole addition of fluoride ions or fluoride ion donor species in gas form.

Advantageously, the plasma does not comprise fluoride ion donor species, and the addition of fluoride ions or fluoride ion donor species is implemented in a separate second step using the gas comprising the fluoride ion donor species. This embodiment advantageously allows to optimize the amounts of fluoride ion donor species used and to avoid fluorinating, and thus altering, the silicon oxide layer as little as possible.

On the other hand, when the addition of fluoride ions is carried out in gas form, the method also does not comprise an additional step of finishing the hydrophilic silicon oxide bonding surfaces, for example no cleaning, between the addition of fluoride ions in gas form and the contacting of the two substrates to be bonded in order not to remove the fluoride ions physisorbed on the hydrophilic silicon oxide bonding surface on which the addition of fluoride ions has been carried out.

#### *Addition via a plasma*

Alternatively, the addition of fluoride ions may successively comprise:

- exposing the hydrophilic silicon oxide bonding surface to a fluorinated plasma, in other words to a plasma comprising fluoride ion donor species, so as to obtain a fluorinated plasma activated hydrophilic silicon oxide bonding surface;
- rinsing the fluorinated plasma activated hydrophilic silicon oxide bonding surface with water or exposing said surface to a humid atmosphere, for example to air, so as to achieve the addition of fluoride ions within the meaning of the present invention.

Fluoride ion donor species comprised in the plasma are typically selected from  $\text{SF}_6$ ,  $\text{CF}_4$  and  $\text{CH}_2\text{F}_2$ .

5 Fluoride plasma is, for example, a plasma formed from a gas such as dioxygen, dinitrogen, helium or argon into which said fluoride ion donor species have been incorporated.

The concentration of fluoride ion donor species in the plasma is preferably comprised between 0.1% and 10% in order to optimize the interaction between the major species in the  
10 plasma and the fluorinated molecules.

Each hydrophilic silicon oxide bonding surface to be fluorinated is preferentially exposed to the fluorinated plasma for a duration comprised between 1 s and 1 min.

15 Water rinsing of the fluorinated plasma activated hydrophilic silicon oxide bonding surface is typically carried out by rinsing with deionized water.

Exposure of the hydrophilic silicon oxide bonding surface to fluorinated plasma results in the breaking of many bonds and the formation on the surface of highly reactive species such  
20 as Si-F, Si-HF or Si-OH.

During rinsing or exposure to a humid atmosphere of the activated hydrophilic silicon oxide bonding surface, said highly reactive species will react with water to create numerous surface silanols and release physisorbed mobile fluoride ions in the vicinity of said surface  
25 silanols, thus generating the addition of fluoride ions within the meaning of the present invention.

Thus, as previously mentioned, exposure to a fluorinated plasma has the major disadvantage of physically altering the silicon oxide layer and therefore its properties, such as  
30 its dielectric constant. Therefore, plasma addition is not the preferred addition method.

According to this embodiment as well, the addition of fluoride ions can very advantageously be implemented at low temperatures. More precisely, despite the fact that the plasma temperature (defined by the kinetic energy of the electrons) is very high (typically  
35 between  $10^4$  and  $10^5$  K), the substrate temperature remains comprised between 18 °C and 30 °C.

Finally, each hydrophilic silicon oxide bonding surface exposed to fluorinated plasma and rinsed can then be kept at room temperature until the two substrates to be bonded are contacted.

## 5        *Addition via implantation*

Alternatively, the addition of fluoride ions may successively comprise:

- the implantation of low-energy fluorine through the silicon oxide bonding surface, so as to obtain an implanted hydrophilic silicon oxide bonding surface,
- 10    - the rinsing of the implanted hydrophilic silicon oxide bonding surface with water or the exposure of said surface to a humid atmosphere, for example to air, so as to carry out the addition of fluoride ions within the meaning of the present invention.

Low energy implantation is understood to mean implantation at implantation energies  
15    below 25 keV in  $\text{SiF}_3$  or below 5 keV for fluoride ions, which corresponds to an implantation depth of the order of 5 nm to 10 nm.

Just like exposure to fluorinated plasma, fluorine implantation results in the breaking of many bonds and the formation on the surface of highly reactive species such as Si-F, Si-HF  
20    or Si-OF.

During rinsing or exposure to a humid atmosphere of the implanted hydrophilic silicon oxide bonding surface, said highly reactive species will react with water to create numerous surface silanols and release physisorbed mobile fluoride ions in the vicinity of said surface  
25    silanols, thus generating the addition of fluoride ions within the meaning of the present invention.

Thus, as previously mentioned, the major disadvantage of implantation is that it physically alters the silicon oxide layer and therefore its properties, such as its dielectric  
30    constant. Therefore, addition via implantation is not the preferred addition method.

According to this embodiment as well, the addition of fluoride ions can very advantageously be implemented at low temperatures. More precisely, the substrate temperature during implantation can be comprised between 10°C and 50°C, with regulation of  
35    the temperature of the implanted substrate.

Finally, each hydrophilic silicon oxide bonding surface, after the addition of fluoride ions by implantation then rinsing, can then be kept at room temperature until the two substrates to be bonded are contacted.

#### 5      *Hydrophilic silicon oxide bonding surface after the addition of fluoride ions*

After the addition of fluoride ions according to any of the embodiments described above, the surface concentration of fluoride ions on each hydrophilic silicon oxide bonding surface is preferably comprised between  $10^{10}$  ions/cm<sup>2</sup> and  $10^{14}$  ions/cm<sup>2</sup>. Such a surface concentration  
10 remains sufficiently low so as not to disrupt the interface properties while allowing efficient catalysis.

The measurement of the surface concentration of fluoride ions on the first hydrophilic silicon oxide bonding surface can be done by spectroscopic techniques such as XPS or mass  
15 spectrometry.

#### **Bringing the first hydrophilic silicon oxide bonding surface into contact with the second hydrophilic silicon oxide bonding surface**

In the case where only an addition of fluoride ions has been implemented on the first hydrophilic silicon oxide bonding surface, the direct bonding method further comprises a step of bringing the first hydrophilic silicon oxide bonding surface into contact with the second hydrophilic silicon oxide bonding surface, so as to obtain the adhesion of the first substrate with the second substrate, the fluoride ions physisorbed on the first hydrophilic silicon oxide  
20 bonding surface being at the bonding interface.  
25

In other words, the fluoride ions were not removed from the first hydrophilic silicon oxide bonding surface between the fluoride ion addition step and the contacting step, for example due to an additional cleaning step.  
30

In the case where an addition of fluoride ions has also been implemented on the second hydrophilic silicon oxide bonding surface, contact is made between the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface, so as to obtain the adhesion of the first substrate with the second substrate, the fluoride ions physisorbed on  
35 the first hydrophilic silicon oxide bonding surface and on the second hydrophilic silicon oxide bonding surface being at the bonding interface.

In other words, the fluoride ions were not removed from the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface between the fluoride ion addition step and the contacting step, for example due to an additional cleaning step.

5        The addition of fluoride ions to both surfaces to be bonded can be advantageous in order to provide a greater amount of fluoride ions to the interface, while using less concentrated solutions and thus reducing the risk of crystal formation during drying.

10       The contact between the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface (if applicable) is preferably carried out at room temperature.

15       Bringing the bonding surfaces into contact may comprise applying localized pressure to generate a point of contact between the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface. The bonding wave propagates from this point of contact over the entire bonding interface within a few seconds. Alternatively, contact may be achieved without applying pressure. According to this embodiment, the first substrate and the second substrate can remain in contact for several tens of seconds until the evacuation of air between the two substrates results in the formation of a point of contact and the initiation of the bonding wave propagation. The vapor pressure when bringing the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface into contact is preferably comprised between 1 Pa and  $10^5$  Pa.

25       Adding fluoride ions to at least one of the two hydrophilic silicon oxide bonding surfaces, followed by bringing the two hydrophilic silicon oxide bonding surfaces into contact by way of the fluoride ions at the bonding interface, and maintaining the resulting assembly at room temperature (after the bonding wave has ceased to propagate), allows bonding energies of the order of  $1 \text{ J/m}^2$  to  $2 \text{ J/m}^2$  to be reached after a few tens of hours. By comparison, such a bonding energy is only reached after several days without the addition of fluoride ions and with all other experimental parameters remaining unchanged. Thus, adding fluoride ions increases the bonding kinetics.

35       To further increase said bonding kinetics, the direct bonding method may further comprise a subsequent step of consolidation annealing of the assembly obtained after bringing the first substrate and the second substrate into contact.

For example, annealing consists of applying a temperature comprised between  $50^\circ\text{C}$  and  $250^\circ\text{C}$ , more preferably comprised between  $50^\circ\text{C}$  and  $100^\circ\text{C}$ , for a duration preferably

comprised between 15 minutes and 4 hours, and even more preferably comprised between 15 minutes and 2 hours. Consolidation annealing temperatures below 100°C would not allow bonding energies of the order of 1 J/m<sup>2</sup> or 2 J/m<sup>2</sup> to be reached in less than two hours without the addition of fluoride ions.

5

The annealing temperature is chosen according to the nature of the first substrate and the second substrate and their ability or inability to withstand a given temperature.

### **Method for transferring a layer onto a support substrate**

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The invention extends to a method for transferring a layer onto a support substrate.

The method for transferring a layer onto a support substrate comprises a step of supplying a donor substrate comprising a first hydrophilic silicon oxide surface and a support substrate comprising a second hydrophilic silicon oxide surface.

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The donor substrate and the support substrate are such as the first substrate and the second substrate previously described.

20

For example, the donor substrate and/or the support substrate comprise silicon Si, germanium Ge, indium phosphide InP, gallium arsenide AsGa, alumina Al<sub>2</sub>O<sub>3</sub>, silicon oxide SiO<sub>2</sub>, silicon nitride Si<sub>3</sub>N<sub>4</sub>, silicon carbide SiC, gallium nitride GaN, copper, titanium, nickel, LNO and/or LTO.

25

The donor substrate and/or the support substrate can be multilayer structures comprising at least two layers. For example, the donor substrate is a pseudo-donor substrate comprising a first layer of LTO and a second layer of silicon. For example, the support substrate is silicon.

Furthermore, the donor substrate and/or the support substrate may comprise one or more electronic component elements. For example, the donor substrate and/or the support substrate may comprise copper connections insulated by silicon oxide sections.

30

Thus, the step of supplying a donor substrate comprising a first hydrophilic silicon oxide surface and a support substrate comprising a second hydrophilic silicon oxide surface may comprise one or more sub-steps of layer arrangement and formation of electronic component elements as previously described.

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As previously mentioned, the donor substrate and the support substrate comprise, respectively, a first hydrophilic silicon oxide surface and a second hydrophilic silicon oxide surface. The first hydrophilic surface and/or the second hydrophilic surface are typically native, thermal, chemical, or deposited oxide surfaces as previously described. Thus, the step of supplying a donor substrate comprising a first hydrophilic silicon oxide surface and a support substrate comprising a second hydrophilic silicon oxide surface may comprise the formation of said native, thermal, chemical, or deposited silicon oxide surfaces according to any of the embodiments previously described.

The first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface may be of the same nature (native, thermal, chemical, or deposited). Alternatively, the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface may be of different natures.

The method for transferring a layer onto a support further comprises a step of forming a weakened area within the donor substrate so as to delimit a layer to be transferred between the first hydrophilic surface and the weakened area. In a preferred embodiment, the weakened area is formed by implanting atomic species into the donor substrate, the implantation being carried out through the first hydrophilic surface. The atomic species are implanted at a predetermined depth, this depth determining the thickness of the layer to be transferred. The implanted atomic species are preferably hydrogen and/or helium.

Subsequently, the method for transferring a layer onto a support substrate further comprises bonding between the donor substrate and the support substrate, with the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface being at the bonding interface. The bonding between the donor substrate and the support substrate is achieved by a direct bonding method according to any of the previously described embodiments. The addition of fluoride ions can be carried out on the first hydrophilic silicon oxide surface of the donor substrate, on the second hydrophilic silicon oxide surface of the support substrate, or simultaneously on both the first hydrophilic silicon oxide surface of the donor substrate and the second hydrophilic silicon oxide surface of the support substrate.

The layer transfer method ultimately comprises detaching the donor substrate along the weakened area to transfer the layer to be transferred onto the support substrate. Detachment along the weakened area can be initiated by mechanical action and/or the application of thermal energy. In a particular embodiment, the consolidation annealing and the step of detachment along the weakened area can be coupled within the same temperature ramp, for example, by implementing temperature plateaus.

### **Substrate**

The invention also relates to a substrate having a first hydrophilic silicon oxide surface on which fluoride ions are physisorbed, the surface concentration of fluoride ions physisorbed on said first hydrophilic silicon oxide surface being comprised between  $10^{10}$  ions/cm<sup>2</sup> and  $10^{14}$  ions/cm<sup>2</sup>.

The first substrate and the first hydrophilic silicon oxide bonding surface can be according to any of the embodiments previously described.

As previously mentioned, the measurement of the surface concentration of fluoride ions on the first hydrophilic silicon oxide bonding surface can be done by spectroscopic techniques such as XPS or mass spectrometry.

In a preferred embodiment, the substrate does not comprise an embedded porous fluorinated silicon oxide layer. In other words, the fluoride ion concentration in the silicon oxide layer of the substrate, other than at the interface, is less than  $10^{18}$ /cm<sup>3</sup>. Such a substrate can advantageously be obtained by avoiding embodiments of the addition of fluoride ions and/or fluoride ion donor species that have an acidifying, etching, or altering effect on the silicon oxide layer as previously mentioned (e.g., plasma, implantation, exposure to liquid or vapor hydrofluoric acid, and exposure to an ammonium fluoride solution).

### **Assembly comprising a first substrate and a second substrate**

The invention finally relates to an assembly comprising a first substrate and a second substrate, the first substrate being covered by a first hydrophilic silicon oxide surface and the second substrate being covered by a second hydrophilic silicon oxide surface, the first hydrophilic silicon oxide surface being directly bonded to the second hydrophilic silicon oxide surface, fluoride ions being at the bonding interface.

The first substrate, the first hydrophilic silicon oxide bonding surface, the second substrate and the second hydrophilic silicon oxide bonding surface can be according to any of the embodiments previously described.

Preferably, the surface concentration of fluoride ions at the bonding interface between the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface is comprised between  $10^{10}$  ions/cm<sup>2</sup> and  $10^{14}$  ions/cm<sup>2</sup>.

The measurement of the surface concentration of fluorine at the bonding interface between the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface can be performed using high-resolution electron microscopy techniques coupled with  
5 EELS (Electron Energy Loss Spectroscopy) or EDX (X-ray spectroscopy) spectroscopies. Other direct quantification techniques can be employed by opening the interface.

In a preferred embodiment, the assembly does not comprise a buried fluorinated porous silicon oxide layer. In other words, the fluoride ion concentration in each silicon oxide layer of  
10 the first substrate and the second substrate, from the first atomic layers (for example, the first nanometer below the surface), is less than  $10^{18}$  at/cm<sup>3</sup>. The oxides are therefore not altered in volume and retain their properties (for example, their dielectric constants and refractive indices) up to their surface.

Such an assembly can advantageously be obtained by avoiding embodiments of the  
15 addition of fluoride ions and/or fluoride ion donor species which have an acidifying, etching or modifying effect on the silicon oxide layer as previously mentioned (e.g. plasma, implantation, exposure to liquid or vapor hydrofluoric acid and exposure to an ammonium fluoride solution).

## 20 **Examples**

A series of examples of the implementation of a method according to particular embodiments of the invention is described below.

### 25 *Example 1*

10mL of a cesium fluoride solution at a concentration of  $10^{-4}$  M is dispensed onto a first silicon substrate of 200 mm in diameter having a 100 nm thick first hydrophilic silicon oxide bonding surface of the thermal oxide type. The system is rotated at a speed of 2000 rpm until  
30 the thickness of the deposited solution film is uniform. This uniformity can be conventionally observed through the appearance of colored Newton fringes, which move across the surface as the film thins due to the combined effect of centrifugal flow and evaporation, until they disappear when the film thickness is less than half the wavelength of visible light (that is to say, typically less than 200 nm). Then the substrate is kept rotating for about ten more  
35 seconds, so as to evacuate the excess of the aqueous cesium fluoride solution and to dry the first hydrophilic silicon oxide bonding surface.

Provision is made of second silicon substrate of 200 mm in diameter having a 100 nm thick second hydrophilic silicon oxide bonding surface of the thermal oxide type, and the same treatment as previously described for the first silicon substrate is applied.

The first hydrophilic silicon oxide bonding surface is then brought into contact with the second hydrophilic silicon oxide bonding surface at room temperature to achieve direct bonding between the first substrate and the second substrate. Optionally, the newly formed structure, comprising the first substrate and the second substrate, is annealed at 220°C for a duration of 10 to 250 minutes to consolidate it.

Finally, the bonding energies obtained are measured as a function of the duration of said consolidation anneal using the conventional blade insertion method, known as the “Maszara method”, in an anhydrous atmosphere. The results are represented by square symbols in Figure 2.

#### *Comparative example 1*

The same operation as in Example 1 is performed, replacing the cesium fluoride solution with deionized water (DIW). The results are represented by circular symbols in Figure 2.

This shows the effect of dispensing a solution containing fluoride ions.

#### *Example 2*

10 mL of a cesium fluoride solution at a concentration of  $10^{-4}$  M is dispensed onto a first silicon substrate of 200 mm in diameter having a 100 nm thick first hydrophilic silicon oxide bonding surface. The system is rotated at 2000 rpm until Newton fringes disappear. The substrate is then kept rotating for approximately ten additional seconds to remove excess cesium fluoride solution and dry the hydrophilic silicon oxide bonding surface.

Provision is made of a second silicon substrate of 200 mm in diameter having a 100 nm thick second hydrophilic silicon oxide bonding surface of the thermal oxide type, and the same treatment as previously described for the first silicon substrate is applied.

The first hydrophilic silicon oxide bonding surface is then brought into contact with the second hydrophilic silicon oxide bonding surface at room temperature to achieve direct bonding between the first substrate and the second substrate. Optionally, the newly formed

structure, comprising the first substrate and the second substrate, is annealed at 170°C for a duration of 10 to 250 minutes to consolidate it.

Finally, the bonding energies obtained are measured as a function of the duration of said consolidation anneal using the conventional blade insertion method, known as the “Maszara method”, in an anhydrous atmosphere. The results are represented by square symbols in Figure 3.

#### *Comparative example 2*

The same operation as in Example 2 is performed, replacing the cesium fluoride solution with deionized water (DIW). The results are represented by circular symbols in Figure 3.

#### *Example 3*

10 mL of a cesium fluoride solution at a concentration of  $10^{-4}$  M is dispensed onto a first silicon substrate of 200 mm in diameter having a 100 nm thick first hydrophilic silicon oxide bonding surface. The system is rotated at 2000 rpm until Newton fringes disappear. The substrate is then kept rotating for approximately ten additional seconds to remove excess cesium fluoride solution and dry the hydrophilic silicon oxide bonding surface.

Provision is made of a second silicon substrate of 200 mm in diameter having a 100 nm thick second hydrophilic silicon oxide bonding surface of the thermal oxide type, and the same treatment as previously described for the first silicon substrate is applied.

The first hydrophilic silicon oxide bonding surface is then brought into contact with the second hydrophilic silicon oxide bonding surface at room temperature to achieve direct bonding between the first substrate and the second substrate. Optionally, the newly formed structure, comprising the first substrate and the second substrate, is annealed at a temperature comprised between 100°C and 300°C for 2 hours to consolidate it.

Finally, the bonding energies obtained are measured as a function of the consolidation annealing temperature and the concentration of the deposited cesium fluoride solution. The results are represented in Figure 4 using diamond symbols (concentration of the deposited cesium fluoride solution of  $10^{-3}$  mol/L), square symbols (concentration of  $10^{-4}$  mol/L), and triangle symbols (concentration of  $10^{-5}$  mol/L).

#### *Comparative example 3*

The same operation as in Example 3 is performed, replacing the cesium fluoride solution with deionized water (DIW). The results are represented by circular symbols in Figure 4.

5        *Example 4*

Provision is made of a first silicon substrate of 200 mm in diameter having a 100 nm thick first hydrophilic silicon oxide bonding surface of the thermal oxide type. Provision is made of a second substrate, identical to the first substrate.

10

The first substrate and the second substrate are placed in a chamber through which dilute hydrofluoric acid vapor is circulated, so as to expose the first hydrophilic silicon oxide bonding surface to the hydrofluoric acid vapor for a duration of 10, 30 or 60 seconds.

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The gas is then purged, and the first hydrophilic silicon oxide bonding surface is contacted with the second hydrophilic silicon oxide bonding surface immediately upon removal from the chamber, at room temperature, to achieve direct bonding between the first substrate and the second substrate. Optionally, the newly formed structure, comprising the first substrate and the second substrate, is annealed at a temperature comprised between 100°C and 500°C for a duration of 2 hours to consolidate it.

20

The bonding energies obtained are then measured as a function of this consolidation annealing temperature. The results are shown in Figure 5 using triangles (for 10 s exposure), squares (30 s exposure), or pentagons (60 s exposure). The reference value corresponds to bonding performed without introducing HF gas into the chamber.

25

*Example 5*

Example 5 shows the effect of exposure to a 0.05% hydrofluoric acid solution for 1 minute. The solution is applied by coating, that is to say, by simply dipping the plates into a very dilute HF solution. The plates are then slowly withdrawn from the solution. They appear “dry” upon removal. They are immediately bonded together. A consolidation annealing is then carried out for 2 hours at various temperatures, from 100°C to 500°C. The curve shown in solid circles in Figure 6 represents the energies obtained after these different annealing cycles. The reference curve corresponds to the same experimental protocol, but with the hydrofluoric acid solution replaced by pure water (deionized water).

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## CLAIMS

1. A method for directly bonding two substrates, the method comprising the following steps:

- 5 a) providing a first substrate and a second substrate comprising, respectively, a first bonding surface made of hydrophilic silicon oxide and a second bonding surface made of hydrophilic silicon oxide,  
b) adding fluoride ions to the first hydrophilic silicon oxide bonding surface;  
c) bringing the first hydrophilic silicon oxide bonding surface into contact with the second  
10 hydrophilic silicon oxide bonding surface, so that the first substrate is adhered to the second substrate, by way of the fluoride ions at the bonding interface.

2. The method according to claim 1, further comprising the addition of fluoride ions on the second hydrophilic silicon oxide bonding surface prior to bringing the first hydrophilic  
15 silicon oxide bonding surface into contact with the second hydrophilic silicon oxide bonding surface.

3. The method according to claim 1 or 2, wherein the contacting of the first hydrophilic silicon oxide bonding surface with the second hydrophilic silicon oxide bonding surface is  
20 carried out at room temperature.

4. The method according to any one of claims 1 to 3, wherein, during the entire duration between the addition of fluoride ions and the contacting of the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface, each hydrophilic silicon oxide  
25 bonding surface on which the addition of fluoride ions is implemented is maintained at room temperature and/or, wherein the addition of fluoride ions on the first hydrophilic silicon oxide bonding surface is implemented at room temperature.

5. The method according to any one of claims 1 to 4, further comprising a  
30 consolidation annealing step d) carried out after step c) of bringing the first hydrophilic silicon oxide bonding surface into contact with the second hydrophilic silicon oxide bonding surface, the consolidation annealing being preferably carried out at a temperature comprised between 50°C and 250°C, even more preferably at a temperature comprised between 50°C and 100°C, for a duration preferably comprised between 15 min and 4 hours, even more preferably for a  
35 duration comprised between 15 min and 2 hours.

6. The method according to any one of claims 1 to 5, wherein the addition of fluoride ions on the first hydrophilic silicon oxide bonding surface comprises the deposition of a liquid

comprising fluoride ions and/or fluoride ion donor species on the first hydrophilic bonding surface.

7. The method according to claim 6, wherein the deposition of the liquid on the first hydrophilic silicon oxide bonding surface comprises:

- the deposition of a volume of the liquid comprising the fluoride ions and/or the fluoride ion donor species at the center of the first hydrophilic silicon oxide bonding surface,
- the spreading of said volume of the liquid comprising the fluoride ions and/or the fluoride ion donor species by rotation of the first hydrophilic silicon oxide bonding surface, said first hydrophilic silicon oxide bonding surface being kept in rotation until ejection and evaporation of the volume of liquid comprising the fluoride ions and/or the fluoride ion donor species.

8. The method according to any one of claims 6 or 7, in the liquid comprising fluoride ions and/or fluoride ion donor species does not comprise hydrofluoric acid or ammonium fluoride.

9. The method according to any one of claims 6 to 8, wherein the liquid comprising fluoride ions and/or fluoride ion donor species is obtained from the dissolution of a fluoride ion salt and a counter-ion which is a neutral or basic cation.

10. The method according to any one of claims 1 to 5, wherein the addition of fluoride ions to the first hydrophilic silicon oxide bonding surface comprises:

- exposing said first hydrophilic silicon oxide bonding surface to a fluorinated plasma,
- rinsing with water, or exposing the first hydrophilic silicon oxide bonding surface previously exposed to the fluorinated plasma to a humid atmosphere.

11. The method according to any one of claims 1 to 5, wherein the addition of fluoride ions to the first hydrophilic silicon oxide bonding surface comprises exposing the first hydrophilic silicon oxide bonding surface to a gas containing fluorinated species.

12. The method according to claim 11, wherein the gas containing fluorinated species does not comprise hydrofluoric acid.

13. The method according to any one of claims 11 or 12, wherein the gas comprises sulfur hexafluoride  $\text{SF}_6$  and/or tetrafluoromethane  $\text{CF}_4$ , mixed with ammonia  $\text{NH}_3$  or nitrogen trifluoride  $\text{NF}_3$  in a basic medium.

14. The method according to any one of claims 1 to 5, wherein the addition of fluoride ions to the first hydrophilic silicon oxide bonding surface comprises:

- implanting fluorine using an implanter on the first hydrophilic silicon oxide bonding surface,

- rinsing with water, or exposing the first previously implanted hydrophilic silicon oxide bonding surface to a humid atmosphere.

15        15. The method according to any one of claims 1 to 14, wherein the first hydrophilic silicon oxide surface and/or the second hydrophilic silicon oxide surface are made of chemical oxide, deposited oxide, thermal oxide and/or native oxide.

10        16. The method according to any one of claims 1 to 15, wherein the first substrate is a multilayer structure comprising a first layer made of a first material and a second layer made of a second material, the difference in coefficient of thermal expansion between the first material and the second material being greater than or equal to 10% or  $10^{-6} \text{ K}^{-1}$  in absolute value.

15        17. The method according to any one of claims 1 to 16, wherein the first substrate comprises elements of electronic components.

18. The method according to any one of claims 1 to 17, wherein the first substrate comprises a weakened area formed by the implantation of atomic or ionic species.

20        19. A method for transferring a layer onto a support substrate, said method comprising the following steps:

- a) providing a donor substrate comprising a first hydrophilic silicon oxide surface and a support substrate comprising a second hydrophilic silicon oxide surface,
- b) forming a weakened area within the donor substrate so as to delimit a layer to be transferred
- 25        between the first hydrophilic silicon oxide surface and the weakened area,
- c) bonding the donor substrate and the support substrate, the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface being at the bonding interface and the bonding between the donor substrate and the support substrate being implemented by a bonding method according to any one of claims 1 to 17,
- 30        d) detaching the donor substrate along the weakened area so as to transfer the layer to be transferred onto the support substrate.

20. An assembly comprising a first substrate and a second substrate, the first substrate being covered by a first hydrophilic silicon oxide surface and the second substrate by a second hydrophilic silicon oxide surface, the first hydrophilic silicon oxide surface being directly bonded

35        to the second hydrophilic silicon oxide surface, fluoride ions being disposed between the first hydrophilic silicon oxide bonding surface and the second hydrophilic silicon oxide bonding surface, wherein the surface concentration of fluoride ions at the bonding interface between the first hydrophilic silicon oxide surface and the second hydrophilic silicon oxide surface is

40        comprised between  $10^{10} \text{ ions/cm}^2$  and  $10^{14} \text{ ions/cm}^2$ , and wherein the fluoride ion

concentration in the first substrate and in the second substrate at a distance greater than 1 nm from the bonding interface between the first substrate and the second substrate is less than  $10^{18}$  at/cm<sup>3</sup>.

- 5            21. A substrate having a first hydrophilic silicon oxide surface on which fluoride ions are physisorbed, the surface concentration of fluoride ions physisorbed on said first hydrophilic silicon oxide surface being comprised between  $10^{10}$  ions/cm<sup>2</sup> and  $10^{14}$  ions/cm<sup>2</sup>, and in which the concentration of fluoride ions in said substrate at a distance greater than 1 nm from the first surface is less than  $10^{18}$  at/cm<sup>3</sup>.