Method and Device for Permanent Bonding of Wafers

Specification

This invention relates to a method for bonding of a first contact area of a first substrate to a second contact area of a second substrate and a device.

The objective in permanent or irreversible bonding of substrates is to produce an interconnection which is as strong and especially as irreversible as possible, therefore a high bond force, between the two contact areas of the substrates. There are various approaches and production methods for this purpose in the prior art.

The known production methods and the approaches which have been followed to date often lead to results which cannot be reproduced or can be poorly reproduced and which can hardly be applied in particular to altered conditions. In particular, production methods which are used at present often use high temperatures, especially > 400°C, in order to ensure reproducible results.

Technical problems such as high energy consumption and a possible destruction of structures which are present on the substrates result from the high temperatures of partially far above 300°C which have been necessary to date for a high bond force.

Other demands consist in the following:

- front-end-of-line compatibility.

  This is defined as the compatibility of the process during the production of the electrically active components. The bonding process must therefore be designed such that active components such as transistors, which are already present on the structure wafers, are neither adversely affected nor damaged during the processing. Compatibility criteria include

mainly the purity of certain chemical elements (mainly in CMOS structures) and mechanical loadability, mainly by thermal stresses.

- low contamination.
- no application of force.
- temperature as low as possible, especially for materials with different coefficients of thermal expansion.

The reduction of the bond force leads to more careful treatment of the structure wafer and thus to a reduction of the failure probability by direct mechanical loading.

Embodiments of this invention disclose a method and a device for careful production of a permanent bond with a bond force which is as high as possible at a temperature which is at the same time as low as possible.

According to a first aspect of the present invention, there is provided method for bonding of a first contact area of a first substrate to a second contact area of a second substrate, the second substrate or each of the substrates having at least one reaction layer, said method comprising the steps of: receiving the first and second substrates into a plasma chamber or a substrate chamber which is connected to a plasma chamber, the plasma chamber having at least first and second generators, generating alternating current at a first electrode with a first frequency with the first generator to produce plasma for forming a first reservoir in a first reservoir formation layer on the first contact area of the first substrate, generating alternating current at a second electrode with a second frequency with the second generator, the second frequency being different from the first frequency, at least partially filling the first reservoir with a first educt or a first group of educts, contacting the first contact area with the second contact area for formation of a pre-bond interconnection, and forming a permanent bond between the first and second contact areas, the permanent bond being at least partially strengthened by a reaction of the first educt with a second educt which is contained in the reaction layer of the second substrate.

According to a second aspect of the present invention, there is provided a method for

bonding of a first contact area of a first substrate to a second contact area of a second substrate, the second substrate or each of the substrates having a least one reaction layer, said method comprising the steps of: receiving the first and second substrates into an inductively coupled plasma chamber, forming a reservoir in a reservoir formation layer on the first contact area by exposing the first contact area to a plasma which has been produced by means of inductive coupling of the coil, a first frequency different from a second frequency of a second generator being applied on a first generator during plasma production, at least partially filling the first reservoir with a first educt or a first group of educts, contacting the first contact area with the second contact area for forming a pre-bond interconnection, and forming a permanent bond between the first and second contact area, the permanent bond being at least partially strengthened by a reaction of the first educt with a second educt which is contained in the reaction layer of the second substrate.

According to a third aspect of the present invention, there is provided a device for bonding of a first contact area of a first substrate to a second contact area of a second substrate, the second substrate or each of the substrates having a least one reaction layer, said device comprising: a bonding chamber, a first electrode and a second electrode which are located opposite, receiving means for receiving the first and second substrates between the first electrode and the second electrode, means for generating alternating current at a first electrode with a first frequency with a first generator to produce plasma for forming a first reservoir in a first reservoir formation layer on the first contact area of the first substrate, means for generating alternating current at a second electrode with a second frequency with a second generator, the second frequency being different from the first frequency, and means for making contact of the first contact area with the second contact area for forming a pre-bond interconnection.

According to a fourth aspect of the present invention, there is provided a device for bonding of a first contact area of a first substrate to a second contact area of a second substrate, the second substrate or each of the substrates having a least one reaction layer, said device comprising: a bonding chamber, a coil, receiving means for accommodating the first and second substrates within the coil, reservoir formation means for forming a first reservoir in a reservoir formation layer on the

first contact area by exposing the first contact area to a plasma which has been produced by means of inductive coupling of the coil, a first frequency which is different from a second frequency of a second generator being applied on a first generator during the plasma production, means for making contact of the first contact area with the second contact area for forming a pre-bond interconnection.

According to a fifth aspect of the present invention, there is provided a device for bonding of a first contact area of a first substrate to a second contact area of a second substrate, the second substrate having a least one reaction layer with the following features: a plasma chamber for producing a plasma, the plasma chamber having at least two generators, a bonding chamber which is connected to the plasma chamber, means for generating alternating current at a first electrode with a first frequency with a first generator to produce plasma for forming a first reservoir in a first reservoir formation layer on the first contact area of the first substrate, means for generating alternating current at a second electrode with a second frequency with a second generator, the second frequency being different from the first frequency, and means for making contact of the first contact area with the second contact area for forming a pre-bond interconnection.

All combinations of at least two of the features given in the specification, the claims and/or the figures also fall within the framework of the invention. At the given value ranges, values within the indicated limits will also be considered to be disclosed as boundary values and will be claimed in any combination.

The basic idea of embodiments of this invention is, using a capacitively coupled plasma or an inductively coupled plasma or a plasma from a remote plasma apparatus, to produce a plasma using which a reservoir for holding a first educt in one substrate is formed, which educt after making contact or producing a temporary bond between the substrates reacts with a second educt which is present in the other substrate, and which thus forms an irreversible or permanent bond between the substrates. Before or after forming the reservoir in a reservoir formation layer on the first contact area,

generally cleaning of the substrate or substrates, especially by a flushing step, occurs. This cleaning should generally ensure that there are no particles on the surfaces which would result in unbonded sites. The reservoir and the educt which is contained in the reservoir make it technically possible to induce directly on the contact areas after producing the temporary or reversible bond, in a dedicated manner, a reaction which increases the bonding speed and strengthens the permanent bond (first educt or first group with a second educt or a second group), especially by deformation of at least one of the contact areas by the reaction, preferably the contact area opposite the reservoir. On the opposing second contact area as per embodiments of the invention there is a growth layer in which the deformation as per embodiments of the invention takes place and the first educt (or the first group) reacts with the second educt (or the second group) which is present in the reaction layer of the second substrate. To accelerate the reaction between the first educt (or the first group) and the second educt (or the second group) it is provided as per embodiments of the invention in one advantageous embodiment that the growth layer which is located between the reaction layer of the second substrate and the reservoir be thinned before the substrates make contact, since in this way the distance between the reaction partners is reduced in an adjustable manner and at the same time the deformation/formation of the growth layer as per embodiments of the invention is promoted. The growth layer is removed at least partially, especially mostly, preferably completely, by the thinning. The growth layer grows again in the reaction of the first educt with the second educt even if it has been completely removed. The thinning of this growth layer could take place as per embodiments of the invention especially by means of etching, especially dry etching, polishing, sputtering or reduction of oxides. Preferably a combination of these methods, especially sputtering and oxide reduction, is conceivable.

As per embodiments of the invention there can be means for inhibiting the growth of the growth layer before the contact areas make contact, especially by passivation of the reaction layer of the second substrate, preferably by exposure to N_2, forming gas or an inert atmosphere or under a vacuum or by amorphization. In this connection, treatment with plasma which contains forming gas, especially consists largely of forming gas, has proven especially suitable. Here forming gas is defined as gases which contain at least 2%, better 4%, ideally 10% or 15% hydrogen. The remaining portion of the mixture consists of an inert gas such as for example nitrogen or argon.

When using forming gas it is possible in particular to thin the oxide layer by a process which is based on sputtering and oxide reduction.

Alternatively or in addition to this measure, it is advantageous as per embodiments of the invention to minimize the time between the thinning and the contact-making, especially < 2 hours, preferably < 30 minutes, even more preferably < 15 minutes, ideally < 5 minutes. Thus the oxide growth which takes place after thinning can be minimized.

The diffusion rate of the educts through the growth layer is increased by the growth layer which has been thinned and which is thus very thin at least at the beginning of the formation of the permanent bond or at the start of the reaction. This leads to a shorter transport time of the educts at the same temperature.

For the prebonding step, for producing a temporary or reversible bond between the substrates, there are various possibilities with the objective of producing a weak interaction between the contact areas of the substrates. The prebond strengths are below the permanent bond strengths, at least by a factor of 2 to 3, especially by a factor of 5, preferably by a factor of 15, still more preferably by a factor of 25. As guideline values the prebond strengths of pure, nonactivated,

hydrophilized silicon with roughly 100 mJ/m^2 and of pure, plasma-activated hydrophilized silicon with roughly 200 - 300 mJ/m^2 are mentioned. The prebonds between the molecule-wetted substrates arise mainly due to the van der Waals interactions between the molecules of the different wafer sides. Accordingly, mainly molecules with permanent dipole moments are suitable for enabling prebonds between wafers. The following chemical compounds are mentioned as interconnect agents by way of example, but not limited thereto

- water
- thiols
- AP3000
- silanes and/or
- silanols.

Suitable substrates as per embodiments of the invention are those whose material is able to react as an educt with another supplied educt to form a product with a higher molar volume, as a result of which the formation of a growth layer on the substrate is caused. The following combinations are especially advantageous, to the left of the arrow the educt being named and to the right of the arrow, the product/products, without the supplied educt or byproducts which react with the educt being named in particular:

- $Si \rightarrow SiO_2, Si_3N_4, SiN_xO_y$
- $Ge \rightarrow GeO_2, Ge_3N_4$
- α-$Sn \rightarrow SnO_2$
- $B \rightarrow B_2O_3, BN$
- $Se \rightarrow SeO_2$

- III-V: GaP, GaAs, InP, InSb, InAs, GaSb, GaN, AlN, InN, $Al_xGa_{1-x}As$, $In_xGa_{1-x}N$

- IV-IV: SiC, SiGe,

- III-VI: InAlP.

- nonlinear optics: $LiNbO_3$, $LiTaO_3$, KDP (KH_2PO_4)

- solar cells: CdS, CdSe, CdTe, $CuInSe_2$, $CuInGaSe_2$, $CuInS_2$, $CuInGaS_2$

- conductive oxides: $In_{2-x}SnxO_{3-y}$

As per embodiments of the invention, on at least one of the wafers and directly on the respective contact area there is the reservoir (or reservoirs) in which a certain amount of at least one of the supplied educts for the volume expansion reaction can be stored. Educts can therefore be for example O_2, O_3, H_2O, N_2, NH_3, H_2O_2, etc. Due to the expansion, especially dictated by oxide growth, based on the tendency of the reaction partners to reduce system energy, possible gaps, pores, and cavities between the contact areas are minimized and the bond force is increased accordingly by narrowing the distances between the substrates in these regions. In the best possible case the existing gaps, pores and cavities are completely closed so that the entire bonding area increases and thus the bond force as per embodiments of the invention rises accordingly.

The contact areas conventionally show a roughness with a quadratic roughness (R_q) of 0.2 nm. This corresponds to peak-to-peak values of the surfaces in the range of 1 nm. These empirical values were determined with atomic force microscopy (AFM).

The reaction as per embodiments of the invention is suitable for allowing the growth layer to grow by 0.1 to 0.3 nm for a conventional wafer surface of a circular wafer with a diameter from 200 to 300 mm with 1 monolayer (ML) of water.

As per embodiments of the invention it is therefore provided in particular that at least 2 ML,

preferably at least 5 ML, even more preferably at least 10 ML of fluid, especially water, be stored in the reservoir.

The formation of the reservoir by exposure to plasma is especially preferable, since plasma exposure moreover causes smoothing of the contact area and hydrophilization as synergy effects. The surface is smoothed by plasma activation predominantly by a viscous flow of the material of the reservoir formation layer and optionally of the reaction layer. The increase of the hydrophilicity takes place especially by the increase of the silicon hydroxyl compounds, preferably by cracking of Si-O compounds which are present on the surface, such as Si-O-Si, especially according to the following reaction:

$$Si\text{-}O\text{-}Si + H_2O \leftrightarrow 2SiOH$$

Another side effect, especially as a result of the aforementioned effects, consists in that the prebond strength is improved especially by a factor of 2 to 3.

The reservoir in the reservoir formation layer on the first contact area of the first substrate (and optionally of a reservoir formation layer on the second contact area of the second substrate) is formed for example by plasma activation of the first substrate which has been coated with a thermal oxide. The plasma activation is carried out in a vacuum chamber in order to be able to set the conditions necessary for the plasma. As per embodiments of the invention, for the plasma discharge, N_2 gas, O_2 gas or argon gas with ion energies in the range from 0 to 2000 eV is used, as a result of which a reservoir is produced with a depth of up to 20 nm, preferably up to 15 nm, more preferably up to 10 nm, most preferably up to 5 nm, of the treated surface, in this case the first contact area.

By setting a certain pressure in the vacuum chamber the average free path length for the plasma ions can be conceivably influenced or set as per embodiments of the invention.

Reproducible results in the production of the reservoir on the contact area/areas is possible by the inventive use of two different frequencies on the opposing electrodes to produce the plasma, which electrodes accelerate the plasma ions especially with application of an alternating current or an ac voltage, and/or by the use of an inductively coupled plasma source and/or remote plasma.

In the case of capacitive coupling it is advantageous if the electrodes are located within the plasma chamber.

Here optimum exposure of the contact areas and thus production of a reservoir which is defined exactly, especially in terms of volume and/or depth, are enabled by setting the parameters (different) the frequencies of the electrodes, the amplitudes, especially, preferably exclusively, the bias voltage applied on the second electrode and the chamber pressure.

The execution of the plasma activation apparatus as a capacitively coupled, double frequency plasma apparatus advantageously enables a separate setting of the ion density and the acceleration of the ions onto the wafer surface. Thus attainable process results can be set within a wide window and can be optimally matched to the demands of the application.

The bias voltage, especially in the form of a base voltage of the second, especially lower electrode, is used to influence the impact (speed) of the electrodes on the contact area of the substrate which is held on the second electrode, especially to attenuate or accelerate it.

In particular, the pore density distribution in the reservoir becomes adjustable by the aforementioned parameters, especially advantageous embodiments being described below.

In an inductively coupled plasma source, corresponding analogy considerations about the ac voltage of the capacitive coupling to alternating currents which are used to generate a magnetic field can be adopted. It is conceivable as per embodiments of the invention to manipulate the plasma of the

inductively coupled plasma source by an alternating current or alternating magnetic field of varied strength and/or frequency such that the plasma has the corresponding properties as per embodiments of the invention.

In a remote plasma, the plasma which is to actually be used is generated in an external source and is introduced into the sample space. In particular, components of this plasma, especially ions, are transported into the sample space. The passage of the plasma from the source space into the substrate space can be ensured by different elements such as locks, accelerators, magnetic and/or electrical lenses, diaphragms, etc. All considerations which apply to capacitively and/or inductively coupled plasma with respect to frequencies and/or strengths of the electrical and/or magnetic fields will apply to all elements which ensure the production and/or passage of the plasma from the source space into the substrate space. For example, it would be conceivable for the plasma to be produced by capacitive or inductive coupling by the parameters as per embodiments of the invention in the source space and afterwards for the aforementioned elements to penetrate into the substrate space.

As per embodiments of the invention any particle type, atoms and/or molecules which are suitable for producing the reservoir can be used. Preferably those atoms and/or molecules are used which the reservoir produces with the required properties. The relevant properties are mainly the pore size, the pore distribution and the pore density. Alternatively, as per embodiments of the invention gas mixtures such as for example air or forming gas consisting of 95% Ar and 5% H_2 can be used. Depending on the gas used, in the reservoir during the plasma treatment among others the following ions are present: $N+$, N_2+, $O+$, O_2+, $Ar+$. The first educt can be accommodated in the unoccupied free space of the reservoir/ reservoirs. The reservoir formation layer and accordingly the reservoir can extend

Figure 8 shows a representation of the concentration of injected nitrogen atoms by plasma as a function of the penetration depth into a silicon oxide layer. It was possible to produce two profiles by variation of the physical parameters. The first profile 11 was produced by more highly accelerated atoms more deeply in the silicon oxide, conversely the profile 12 was produced after altering the process parameters in a lower density. The superposition of the two profiles yields a sum curve 13 which is characteristic for the reservoir. The relationship between the concentration of the injected atom and/or molecule species is evident. Higher concentrations designate regions with a higher defect structure, therefore more space to accommodate the subsequent educt. A continuous change of the process parameters which is controlled especially in a dedicated manner during the plasma activation makes it possible to achieve a reservoir with a distribution of the added ions over depth, which distribution is as uniform as possible.

Alternatively to a reservoir which has been produced by plasma, the use of a TEOS (tetraethylorthosilicate) oxide layer on at least one of the substrates, at least the first substrate, is conceivable as a reservoir. This oxide is generally less dense than thermal oxide, for which reason as per embodiments of the invention compaction is advantageous. Compaction takes place by heat treatment with the objective of setting a defined porosity of the reservoir.

According to one embodiment of the invention, the filling of the reservoir can take place especially advantageously at the same time with the formation of the reservoir by the reservoir being applied as a coating to the first substrate, the coating already encompassing the first educt.

The reservoir is conceivable as a porous layer with a porosity in the nanometer range or as a layer which has channels with a channel thickness smaller than 10 nm, more preferably smaller than 5 nm, even more preferably smaller than 2 nm, most preferably smaller than 1 nm, most preferably

of all smaller than 0.5 nm.

For the step of filling of the reservoir with a first educt or a first group of educts, as per embodiments of the invention the following embodiments, also in combination, are conceivable:

- exposing the reservoir to the ambient atmosphere,
- flushing with especially deionized water,
- flushing with a fluid which contains the educt or which consists of it, especially H_2O, H_2O_2, NH4OH
- exposing the reservoir to any gas atmosphere, especially atomic gas, molecular gas, gas mixtures,
- exposing the reservoir to a water vapor-containing or hydrogen peroxide vapor-containing atmosphere and
- depositing a reservoir which has already been filled with the educt as a reservoir formation layer on the first substrate.

The following compounds are possible as educts: O_x^+, O_2, O_3, N_2, NH_3, H_2O, H_2O_2, and/or NH_4OH.

The use of the above cited hydrogen peroxide vapor is regarded as the preferred version, in addition to using water. Hydrogen peroxide furthermore has the advantage of having a greater oxygen to hydrogen ratio. Furthermore, hydrogen peroxide dissociates above certain temperatures and/or via the use of high frequency fields in the MHz range into hydrogen and oxygen.

On the other hand, H_2O offers the advantage of having a small molecule size. The size of the H_2O molecular is even smaller than that of the O_2 molecule, with which H_2O offers the advantage of being able to be more easily intercalated in the pores and being able to diffuse more

easily through the growth layer.

Mainly when using materials with different coefficients of thermal expansion the use of methods for dissociation of the aforementioned species which do not cause any noteworthy temperature increase or at best a local/specific temperature increase is advantageous. In particular there is microwave irradiation which at least promotes, preferably causes the dissociation.

According to one advantageous embodiment of the invention it is provided that the formation of the growth layer and strengthening of the irreversible bond take place by diffusion of the first educt into the reaction layer.

According to another advantageous embodiment of the invention it is provided that the formation of the irreversible bond takes place at a temperature of typically less than 300°C, advantageously less than 200°C, more preferably less than 150°C, even more preferably less than 100°C, most preferably at room temperature, especially during a maximum 12 days, more preferably a maximum 1 day, even more preferably a maximum 1 hour, most preferably a maximum 15 minutes. Another advantageous heat treatment method is dielectric heating by microwaves.

Here it is especially advantageous if the irreversible bond has a bond strength of greater than 1.5 J/m^2, especially greater than 2 J/m^2, preferably greater than 2.5 J/m^2.

The bond strength can be increased especially advantageously in that during the reaction, as per embodiments of the invention a product with a greater molar volume than the molar volume of the second educt is formed in the reaction layer. In this way growth on the second substrate is effected, as a result of which gaps between the contact areas can be closed by the chemical reaction as per embodiments of the invention. As a result, the distance between the contact areas, therefore the average

distance, is reduced, and dead spaces are minimized.

To the extent the formation of the reservoir takes place by plasma activation, especially with an activation frequency between 10 kHz and 20000 kHz, preferably between 10 kHz and 5000 kHz, even more preferably between 10 kHz and 1000 kHz, most preferably between 10 kHz and 600 kHz and/or a power density between 0.075 and 0.2 watt/cm^2 and/or with pressurization with a pressure between 0.1 and 0.6 mbar, additional effects such as smoothing of the contact area and also a clearly increased hydrophilicity of the contact area are caused.

Alternatively the formation of the reservoir as per embodiments of the invention can take place by using a tetraethoxysilane oxide layer which has been compacted in an especially controlled manner to a certain porosity as the reservoir formation layer.

According to another advantageous embodiment of the invention it is provided that the reservoir formation layer consists largely, especially essentially completely of an especially amorphous silicon dioxide, especially a silicon dioxide which has been produced by thermal oxidation, and the reaction layer consists of an oxidizable material, especially predominantly, preferably essentially completely, of Si, Ge, InP, GaP or GaN (or another material mentioned alternatively above). An especially stable reaction which especially effectively closes the existing gaps is enabled by oxidation.

Here it is provided as per embodiments of the invention that between the second contact area and the reaction layer there is a growth layer, especially predominantly of native silicon dioxide (or another material mentioned alternatively above). The growth layer is subject to growth caused by the reaction as per embodiments of the invention. The growth takes place proceeding from the transition Si-SiO2 (7) by re-formation of amorphous SiO2 and the deformation caused thereby, especially bulging, of

the growth layer, especially on the interface to the reaction layer, and especially in regions of gaps between the first and the second contact area. This causes a reduction of the distance or a reduction of the dead space between the two contact areas, as a result of which the bond strength between the two substrates is increased. A temperature between 200 and 400°C, preferably roughly 200°C and 150°C, more preferably a temperature between 150°C and 100°C, most preferably a temperature between 100°C and room temperature, is especially advantageous. The growth layer can be divided into several growth regions. The growth layer can at the same time be a reservoir formation layer of the second substrate in which another reservoir which accelerates the reaction is formed.

Here it is especially advantageous if the growth layer has an average thickness A between 0.1 nm and 5 nm prior to formation of the irreversible bond. The thinner the growth layer, the more quickly and easily the reaction takes place between the first and the second educt through the growth layer, especially by diffusion of the first educt through the growth layer to the reaction layer. The diffusion rate of the educts through the growth layer is increased by the growth layer which has been thinned and thus is very thin at least at the beginning of the formation of the permanent bond or at the start of the reaction. This leads to a shorter transport time of the educts at the same temperature.

Here the thinning as per embodiments of the invention plays a decisive part since the reaction can be further accelerated and/or the temperature can be further reduced by it. Thinning can be done especially by etching, preferably in a moist atmosphere, still more preferably in-situ. Alternatively the thinning takes place especially by dry etching, preferably in-situ. Here in-situ means performance in the same chamber in which at least one previous and/or one following step is/are carried out. A further apparatus arrangement which falls under the in-situ concept used here is an

according to one embodiment of the invention it is advantageous if the average distance B between the reservoir and the reaction layer immediately before formation of the irreversible bond is between 0.1 nm and 15 nm, especially between 0.5 nm and 5 nm, preferably between 0.5 nm and 3 nm. The distance B is influenced or produced as claimed in the invention by the thinning.

A device for executing the method is made as per embodiments of the invention with a chamber for forming the reservoir, a chamber provided especially separately from it for filling the reservoir, and an especially separately provided chamber for forming the prebond, all of which chambers are connected directly to one another via a vacuum system.

In another embodiment the filling of the reservoir can also take place directly via the atmosphere, therefore either in a chamber which can be opened to the atmosphere or simply on a structure which does not have jacketing, but can handle the wafer semiautomatically and/or completely automatically.

Other advantages, features and details of the invention will become apparent from the following description of preferred exemplary embodiments and using the drawings.

Figure 1a shows a first step of the method as claimed in the invention immediately after the first substrate makes contact with the second substrate,

Figure 1b shows an alternative first step of the method as claimed in the invention immediately after the first substrate makes contact with the second substrate,

Figure 2 shows a step of the method as claimed in the invention which takes place prior to contact-making, specifically the thinning of the second substrate,

Figures 3a and 3b show other steps of the method as claimed in the invention for forming a higher bond strength,