Method for Permanent Bonding of Wafers

Specification

This invention relates to a method for bonding of a first contact surface of a first substrate to a second contact surface of a second substrate ~~as claimed in Claim 1~~.

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 surfaces of the substrates. There are various approaches and production methods for this 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 especially to altered conditions. In particular production methods which used at present often use high temperatures, especially > 400°C in order to ensure reproducible results.

Technical problems such as high energy consumption and 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 the chemical elements (mainly in CMOS structures) and mechanical

loadability, mainly by thermal stresses.

- low contamination.

- no application of force.

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.

~~The object~~Embodiments of this invention ~~is therefore to~~ devise a method for careful production of a permanent bond with a bond force which is as high as possible.

~~This object is achieved with the features of Claim 1. Advantageous developments of the invention are given in the dependent claims.~~

According to an aspect of the present invention, there is provided a method for bonding of a first contact surface of a first substrate to a second contact surface of a second substrate said method comprising: forming a reservoir in a surface layer on the first contact surface, at least partially filling of the reservoir with a first educt or a first group of educts, contacting the first contact surface with the second contact surface for formation of a prebond connection and forming a permanent bond between the first and second contact surface, said permanent bond at least partially strengthened by the reaction of the first educt with a second educt contained in a reaction layer of the second substrate.

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 disclosed as boundary values and will be claimed in any combination.

The basic idea of embodiments of this invention is to devise a reservoir for holding a first educt at least on one of the substrates, to react it after making contact or producing a temporary

bond between the substrates with a second educt which is present in the other substrate, and thus to form an irreversible or permanent bond between the substrates. Before or after forming the reservoir in one surface layer on the first contact surface, 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 contained in the reservoir form a technical possibility for inducing a reaction which strengthens the permanent bond and which increases the bond speed in a controlled manner directly on the contact surfaces after producing the temporary or reversible bond, especially by deforming at least one of the contact surfaces by the reaction, preferably the contact surface which is opposite the reservoir.

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 surfaces 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, mainly due to the van-der-Waals interactions between the molecules of the different 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 ~~claimed in~~ 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

- Te $\rightarrow$ TeO_2, TeO_3

- Mg $\rightarrow$ MgO, Mg_3N_2

- Al $\rightarrow$ Al_2O_3, AlN

- Ti $\rightarrow$ TiO_2, TiN

- V $\rightarrow$ V_2O_5

- Mn $\rightarrow$ MnO, MnO_2, Mn_2O_3, Mn_2O_7, Mn_3O_4

- Fe $\rightarrow$ FeO, Fe_2O_3, Fe_3O_4

- Co $\rightarrow$ CoO, Co_3O_4,

- Ni $\rightarrow$ NiO, Ni_2O_3

- Cu $\rightarrow$ CuO, Cu_2O, Cu_3N

- Zn → ZnO

- Cr → CrN, $Cr_{23}C_6$, Cr_3C, Cr_7C_3, Cr_3C_2

- Mo → Mo_3C_2

- Ti → TiC

- Nb → Nb_4C_3

- Ta → Ta_4C_3

- Zr → ZrC

- Hf → HfC

- V → V_4C_3, VC

- W → W_2C, WC

- Fe → Fe_3C, Fe_7C_3, Fe_2C

The following mixed forms of semiconductors as substrates are also conceivable:

- 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-IV: 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 ~~claimed in~~ per embodiments of the invention, on at least one of the wafers and directly on the respective contact surface there is a reservoir 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, N2, NH3, 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 surfaces 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 surface increases and thus the bond force as ~~claimed in~~ per embodiments of the invention rises accordingly.

The contact surfaces 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 ~~claimed in~~ 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 of 200 to 300 mm with 1 monolayer (ML) of water.

As ~~claimed in~~ per embodiments of the invention it is therefore provided in particular that at least 2 ML, preferably at least 5 ML, even more preferably 10 ML fluid, especially water, is 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 surface and hydrophilization as synergy effects. The surface is smoothed by plasma activation predominantly by a viscous flow of the material of the surface layer. The increase of the hydrophilicity takes place especially by the increase of the silicon hydroxyl compounds, preferably by cracking of Si-O compounds 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 surface layer on the first contact surface of the first 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 adjust the conditions necessary for the plasma. As ~~claimed in~~ 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 surface. As ~~claimed in~~ per embodiments of the invention each 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, pore distribution and pore density. Alternatively, as ~~claimed in~~ 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.

The reservoir is formed based on the following considerations: The pore size is smaller than 10 nm, preferably smaller than 5 nm, more preferably smaller than 1 nm, even more preferably smaller than 0.5 nm, most preferably smaller than 0.2 nm.

The pore density is preferably directly proportional to the density of the particles which produce the pores by striking action, most preferably can even be varied by partial pressure of the striking species, and depending on the treatment time and the parameter, especially of the plasma system used.

The pore distribution preferably has at least one region of greatest pore concentration under the surface, by variation of the parameters of several such regions which are superimposed into a

preferably plateau-shaped region (see Figure 7). The pore distribution decreases toward zero with increasing thickness. The region near the surface during bombardment has a pore density which is almost identical to the pore density near the surface. After the end of plasma treatment the pore density on the surface can be reduced as a result of stress relaxation mechanisms. The pore distribution in the thickness direction with respect to the surface has one steep flank and with respect to the bulk a rather flatter, but continuously decreasing flank (see Figure 7).

For the pore size, the pore distribution and pore density, similar considerations apply to all methods not produced with plasma.

The reservoir can be designed by controlled use and combination of process parameters. Figure 7 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 atoms and/or molecule species is evident. Higher concentrations designate regions with higher defect structure, therefore more space to accommodate the subsequent educt. A continuous change of the process parameters which is controlled in a dedicated manner during the plasma activation makes it possible to achieve a reservoir with a distribution of the added ions over the depth, which is as uniform as possible.

As a reservoir, alternatively to a reservoir produced by plasma, the use of a TEOS (tetraethyl orthosilicate)-oxide layer on at least one of the substrates, at least the first substrate, is conceivable. This oxide is generally less dense than thermal oxide, for which reason compaction is

advantageous as ~~claimed in~~ per embodiments of the invention. The 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 density 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 ~~claimed in~~ 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- or hydrogen peroxide vapor-containing atmosphere and
- depositing a reservoir already filled with the educt as a surface layer on the first substrate.

The following compounds are possible as educts: 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.

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 educts 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.

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 ~~claimed in~~ 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 surfaces can be closed by the chemical reaction as ~~claimed in~~ per embodiments of the invention. As a result, the distance between the contact surfaces, 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 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 surface and also a clearly increased hydrophilicity of the contact

surface are effected.

Alternatively thereto, the formation of the reservoir as ~~claimed in~~ per embodiments of the invention can take place by using a tetraethoxy silane-oxide layer as the surface layer, compacted especially in a controlled manner to a certain porosity.

According to another advantageous embodiment of the invention it is provided that the surface layer consists predominantly, especially essentially completely of an especially amorphous, especially silicon oxide 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. An especially stable reaction which especially effectively closes the existing gaps is enabled by oxidation.

Here it is especially advantageous as ~~claimed in~~ per embodiments of the invention if between the second contact surface and the reaction layer there is a growth layer, especially predominantly of native silicon dioxide. The growth layer is subject to growth caused by the reaction as ~~claimed in~~ 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 surface. This causes a reduction of the distance or a reduction of the dead space between the two contact surfaces, 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.

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 thorough the growth layer to the reaction layer.

According to one embodiment of the invention it is advantageously provided that the formation of the reservoir is carried out in a vacuum. Thus contamination of the reservoir with unwanted materials or compounds can be avoided.

In another embodiment of the invention, it is advantageously provided that filling of the reservoir takes place by one or more of the steps cited below:

- exposing the first contact surface to the atmosphere, for filling the reservoir with atmospheric humidity and/or oxygen contained in the air,
- exposing the first contact surface to a fluid consisting especially predominantly, preferably almost completely, of especially deionized H_2O and/or H_2O_2,
- exposing the first contact surface to N_2 gas and/or O_2 gas and/or Ar gas and/or forming gas, especially consisting of 95% Ar and 5% H_2, especially with an ion energy in the range from 0 to 2000 eV,
- vapor deposition for filling the reservoir with any already named educt.

It is especially effective for the process sequence if the reservoir is formed preferably in a thickness R between 0.1 nm and 25 nm, more preferably between 0.1 nm and 15 nm, even more preferably between 0.1 nm and 10 nm, most preferably between 0.1 nm and 5 nm. Furthermore, 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.

A device for executing the method is as ~~claimed in~~ per embodiments of the invention formed with a chamber for forming the reservoir and a chamber provided especially separately 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 1 shows a first step of the method as claimed in the invention immediately after the first substrate makes contact with the second substrate,

Figures 2a and 2b show other steps of the method as claimed in the invention for forming a higher bond strength,

Figure 3 shows another step of the method as claimed in the invention which follows the steps according to Figure 1, Figure 2a and Figure 2b, with substrate contact surfaces which are in contact,

Figure 4 shows a step as claimed in the invention for formation of an irreversible/permanent bond between the substrates,

Figure 5 shows an enlargement of the chemical/physical processes which proceed on the two contact surfaces during the steps according to Figure 3 and Figure 4,