Method for Bonding of Substrates

Specification

This invention relates to a method for bonding of a first contact area of a first substrate which is largely transparent at least to a certain wavelength range to a second contact area of a second substrate which is largely transparent at least to a certain wavelength range, a method for producing a first substrate and a method for producing a second substrate.

The generic methods are used especially to produce multilayer semiconductor, glass or ceramic composites. One especially important application relates to the production of multilayer photovoltaic cells.

One of the main limitations in the production of multilayer cells is the incompatibility of the lattice structures of the individual semiconductor materials with respect to their dimension and shape. In the production of the individual layers by direct growth of layers on one another this leads to defects in the semiconductor layer which has been implemented with it. These defects adversely affect the quality of the produced layer and especially the attainable efficiency for the conversion of light into electrical energy. Limitations with respect to the following parameters result from this in practice:

a) the number of attainable active layers in the structure. This is limited at present to 2 to a maximum three layers due to the above described problems.

b) optimization of the individual layers with respect to the optimum wavelength range. In practice it is not currently possible to optimize the individual layers completely freely with respect to the optimum wavelength range and associated conversion characteristics for the conversion of light into electrical energy, since compromises must always be reached with respect to the compatibility of the lattice structure.

c) use of more favorable materials: For certain wavelengths it would be desirable to use for example silicon or germanium since these materials would allow an ideal compromise between efficiency and costs. Often the use of these materials is however not possible since the lattice structure is not adequately compatible with the other structures which are used in the cell.

Embodiments of this invention disclose a method with which the production of the aforementioned multilayer composites more efficiently and with more diverse parameters is enabled.

According to a first aspect of the present invention, there is provided a method for bonding of a first contact area of a first at least largely transparent substrate to a second contact area of a second at least largely transparent substrate, on at least one of the contact areas an oxide being used for bonding, from which an at least largely transparent interconnection layer is formed with: an electrical conductivity of at least 10e1 S/cm (measurement: four point method, relative to temperature of 300K) and an optical transmittance greater than 0.8 for a wavelength range from 400 nm to 1500 nm on the first and second contact area, application of a first oxide layer with the aforementioned electrical conductivity and the aforementioned optical transmittance to the first substrate, application of a second oxide layer to the second substrate, plasma activating at least one of the substrates, and bonding of the substrates at room temperature.

According to a second aspect of the present invention, there is provided a method for producing a first substrate with a first contact area for bonding to a second contact area of a second substrate, wherein an upper surface of the first contact area comprises a first oxide layer with: an electrical conductivity of at least $10e^{1}$ S/cm (measurement: four point method, relative to temperature of 300K) and an optical transmittance greater than 0.8for a wavelength range from 400 nm to 1500 nm being applied to the first substrate, application of a first oxide layer with the

aforementioned electrical conductivity and the aforementioned optical transmittance to the first substrate, application of a second oxide layer to the second substrate, plasma activating at least one of the substrates, and bonding of the substrates at room temperature.

According to a third aspect of the present invention, there is provided a method for producing a second substrate with a second contact area for bonding to a first contact area of a first substrate, with the following steps, especially the following sequence: application of a second oxide layer to the second substrate, application of a third oxide layer to the second oxide layer, the third oxide layer having an oxygen volume S_1 which is smaller than 70% of the maximum oxygen volume S_{max} of the third oxide layer and application of a fourth oxide layer to the third oxide layer, application of a first oxide layer with the electrical conductivity and the optical transmittance of claim 1 to the first substrate, plasma activating at least one of the substrates, and bonding of the substrates at room temperature.

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 invention is based on the idea of bonding two substrates instead of growing two layers and being able to provide several layers with different (especially optical) properties by the bonding.

The invention is based especially on the approach of producing the individual layers located in the cell structure, especially the interconnection layer which is intended for bonding, on separate

substrates before making contact and only later stacking/bonding them. Thus the individual layers can be produced on growth substrates which have been optimized for this purpose. This is possible especially by means of growing by MOCVD.

One especially original aspect of this invention is how these layers can be stacked in an electrically conductive and optically transparent form with a simultaneously economical process. Moreover the preparation of the substrates which is necessary for this purpose is described.

The described method is preferably suitable for stacking of multilayer solar cells. Alternatively however the method can also be used to produce any other structures and components in which optically transparent and electrically conductive interconnections between any (especially optical) materials, especially semiconductor materials, glasses and ceramics are necessary. In this sector more applications are increasingly arising due to the greatly increased importance of solid state light sources such as LEDs and lasers in a host of applications such as lighting, communications, and working of materials. In the display production sector new innovative product technologies are also becoming increasingly important since additional functions such as contact detection (feedback in the area of touch screens, etc.) are to be integrated into displays.

Advantages of the invention are mainly the following:

- electrically conductive, optically transparent bonding interface (interconnection layer),
- very thin, durable layer(s) which are stable over the long term,
- temperature-resistant layer(s) and
- high efficiency (fast and economical in production).

A central, especially original aspect of this invention is the use of transparent conductive oxides for producing the electrically conductive and optically transparent interconnection layer

between the substrates. The interconnection is produced especially by means of wafer bonding, preferably with a direct bonding method and even more preferably a direct bonding method with plasma activation.

Especially indium-tin-oxide (ITO) is used as the transparent conductive oxides (TCO). The abbreviation ITO will be used below for indium-tin-oxide. ITO is widely used in the production of LCD displays, where it is used as an optically transparent electrical conductor. Alternatively the following materials are used:

- doped zinc oxide, especially aluminum doped zinc oxide (AZO), gallium doped zinc oxide (GZO),
- fluorine [doped] tin oxide (FTO), and
- antimony tin oxide (ATO).

Basically any material which can be oxidized and which especially with appropriate doping has the desired properties, especially electrical conductivity and optical transparency, can be used.

In this connection, as claimed in the invention electrical conductivity is addressed when the material has a conductivity of > 10e1 S/cm, preferably 10e2 S/cm, more preferably 10e3 S/cm (measured with the four point method which is conventional in semiconductor technology, relative to a temperature of 300 K). The optical transmission (transmittance) defined as that percentage of light of a certain wavelength range, which the layer is designed to pass according to the application, should be at least > 80%, advantageously > 87%, preferably > 93% and even more preferably > 96% by a film with a thickness according to the application.

As claimed in the invention wavelength ranges which extend from 300 nm to 1800 nm are preferred for photovoltaic applications. This means that the relevant wavelength range is in any case

larger than the wavelength range visible to humans. This is intended to ensure that the UV portion in the light and the IR portion in the light can also be converted into electrical energy. Since in a multilayer solar cell the uppermost layer is already processing a part of the spectrum and thus converting it into electrical energy, it is acceptable if the bond interconnection has somewhat smaller wavelength range in which it allows transmission. In particular therefore the aforementioned transmission values will apply at least to wavelengths > 600 nm, advantageously > 500 nm, more advantageously > 400 nm, and most advantageously > 350 nm. Furthermore the transmission values should also apply especially to the entire wavelength range proceeding from the minimum wavelength range to a maximum 1300 nm, advantageously up to a maximum 1500 nm, more advantageously up to a maximum 1700 nm, and most advantageously up to a maximum 1800 nm.

The oxides are applied to the substrates which are to be interconnected as claimed in the invention especially by means of the following methods:

- MO CVD, metal organic molecular beam deposition,
- spray pyrolysis, pulsed laser deposition (PLD) or
- sputtering.

To ensure the desired properties of the layers, it is critical as claimed in the invention to ensure the correct mixing ratio. In particular the proportion of oxygen can improve the optical transparency in some of these oxides, its having to be ensured that the oxygen portion is not too high since otherwise the electrical conductivity is reduced.

Generally the bond interconnection (interconnection layer, also bonding interface) is produced by a precursor laminar structure being deposited on the substrates to be bonded. Then the

layers are plasma-activated and joined especially at room temperature, as a result of which a prebond (temporary bond) is formed. During the subsequent heat treatment process (annealing) the precursor laminar structure is converted into a layer consisting of transparent electrically conductive oxide, the bond interconnection being strengthened at the same time.

One especially original embodiment of the method as claimed in the invention is described using two semiconductor wafers (first and second substrate). The method can however also be applied analogously to any other optically specific combination of materials.

In a first module (coating apparatus) the first semiconductor layer is grown on a first carrier which is formed especially by the substrate itself (later back-thinning) which due to its crystal structure and its surface is suited for growing a first semiconductor layer (first substrate). Thereupon, one layer (first oxide layer) of the selected TCO is deposited in-situ, i.e. without removing the substrate from the coating apparatus which has been used for the growth of the semiconductor layer. The in-situ process ensures that this TCO can adhere directly to the semiconductor without its being able to form an oxide which would influence the electrical conductivity. This is especially ensured when the substrate in-situ is transported in the apparatus (consisting of other modules) in a protective atmosphere which is as free as possible of oxidizing elements in the atmosphere. This is especially ensured in atmospheres which are largely free of oxygen and water. Preferably this is ensured by the configuration of the apparatus with a high vacuum atmosphere in which the pressure is less than $1*e^{-5}$ mbar, preferably less than $1*e^{-6}$ mbar, and most preferably less than $1*e^{-7}$ mbar.

The second semiconductor layer is grown on a second carrier which with respect to the crystal structure and surface is optimized for the growth of a second semiconductor layer (second

substrate). In-situ a TCO layer (second oxide layer) consisting of a selected TCO material is optionally deposited on this layer.

Then a precursor layer (third oxide layer) with a layer thickness D3 is deposited on this TCO layer 2". This precursor layer is chosen such that here the material is not yet completely oxidized, but compared to the already deposited TCO layer (second oxide layer) has an oxygen deficiency. In particular at least > 30%, preferably at least > 45%, more preferably at least > 60%, and most preferably > 75% of the oxygen volume S_{max} which would be necessary for complete oxidation are absent.

Then a TCO layer (fourth oxide layer) consisting of the selected TCO material with a thickness D4 is optionally deposited on this precursor layer.

D3 is chosen to be so large that there is enough volume to later ensure during the reaction a relatively large volumetric growth so that a complete closing of the defects in the bonding interface is ensured. At the same time the layer thickness is chosen to be so small that preferably all the material contained in this layer is completely oxidized during the process. This is especially ensured for layer thicknesses with a thickness from 1 to 10 nm. Preferably the layer thickness is between 1 to 7 nm. Even more preferably the layer thickness is between 1 and 5 nm.

D4 is chosen such that the layer thickness is large enough to protect the underlying layer D3 from a reaction in the ambient atmosphere. In particular the precursor layer will be largely prevented from reacting with oxygen or moisture from the ambient atmosphere, especially from oxidizing. In this connection largely means that when the substrate is exposed to the ambient atmosphere at room temperature for a duration of a maximum 2 hours, advantageously less than 20% of the precursor layer will react. Even more preferably less than 10% of this precursor layer

react. Most preferably less than 5% of the precursor layer react. This is especially ensured for layer thicknesses of the precursor layer of at least 0.5 to 1 nm. At the same time the layer however will be thin enough to later allow diffusion of the educts/educt from the reservoir (see farther below). Therefore the maximum thickness of this layer is advantageously a maximum 2 to 3 nm. Even more advantageously the maximum layer thickness is at most 1.5 to 2 nm. Most advantageously the maximum layer thickness is a maximum 1 to 1.5 nm.

Then the first substrate is subjected to a plasma activation process to produce a reservoir (see farther below for reservoir formation).

Then the substrates are bonded at room temperature. In doing so van der Waals forces ensure that the substrates adhere to one another at room temperature. During a subsequent annealing process a first educt intercalated in the reservoir, especially H_2O, diffuses through the optional fourth oxide layer (especially likewise exposed beforehand to plasma) and oxidizes the third oxide layer. This increases the volume of the oxidized material; this leads to closing of the defects in the surface (growth layer).

Then one or both of the carriers, if present, can optionally be removed. Alternatively one of the carriers can likewise be a semiconductor layer which later becomes part of the final structure.

Another especially original aspect of this invention is, using a capacitively coupled plasma or an inductively coupled plasma or a plasma from the 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 an oxide 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 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 claimed in the invention there is a growth layer in which the deformation as claimed in the invention takes place and the first educt (or the first group) reacts with the second educt (or the second group) 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 claimed in the invention in one advantageous embodiment that the growth layer which lies 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 claimed in 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 the layer had been completely removed. The thinning of this growth layer could take place as claimed in 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, also is conceivable.

As claimed in 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 claimed in 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 interconnection agents by way of example, but not limited thereto

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

Suitable substrates as claimed in 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 → MgO, Mg_3N_2

- Al → Al_2O_3, AlN

- Ti → TiO_2, TiN

- V → V_2O_5

- Mn → MnO, MnO_2, Mn_2O_3, Mn_2O_7, Mn_3O_4

- Fe → FeO, Fe_2O_3, Fe_3O_4

- Co → CoO, Co_3O_4,

- Ni → NiO, Ni_2O_3

- Cu → 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

- In → In_2O_3

- Sn → Sn_2O_2

- Sn → SnO

- Zn → ZnO

- Al → Al_2O_3

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

- 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 claimed in 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 claimed in 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 claimed in 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 claimed in 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 oxide 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 present on the surface, such as Si-O-Si, especially according to the following reaction:

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

For other surfaces it can generally be stated that an increase of the density of the isolated OH compounds occurs; this results in improved hydrophilicity.

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 oxide layer on the first contact area of the first substrate (and optionally of an oxide 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 claimed in 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 (amplitude) 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 claimed in the invention.

Reproducible results in the production of the reservoir on the contact area/surfaces 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 the (different) 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 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 claimed in 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 claimed in the invention.

In a remote plasma, the plasma which is to actually be used is generated in an external source and introduced into the sample space. In particular the 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 claimed in the invention in the source space and afterwards for the aforementioned elements to penetrate into the substrate space.

As claimed in 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, pore distribution and pore density. Alternatively, as claimed in 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, during the plasma treatment among others the following ions are present in the reservoir: N+, N_2+, O+, O_2+, Ar+. The first educt can be accommodated in the unoccupied free space of the reservoir/reservoirs. The oxide layer and accordingly the reservoir can extend into the reaction layer.

Advantageously there are different types of plasma species which can react with the reaction layer and which consist at least partially, preferably mostly of the first educt. To the extent the second educt is Si/Si, an O_x plasma species would be advantageous.

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 mm, 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 the partial pressure of the striking species, and depending on the treatment time and the parameters, 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 8). The pore distribution decreases toward zero with increasing thickness. The near-surface region 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 8).

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 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 deeper 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 the depth, which distribution is as uniform as possible. These considerations likewise apply analogously to layers other than silicon oxide in which the reservoir can be formed in the case of other material combinations. In particular these considerations can also be applied to TCO layers.

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 claimed in 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 claimed in 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 already filled with the educt as an oxide 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 moreover has the advantage of having a greater oxygen to hydrogen ratio. Furthermore, hydrogen peroxide dissociates into hydrogen and oxygen above certain temperatures and/or via the use of high frequency fields in the MHz range.

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 claimed in 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 claimed in 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 a smoothing of the contact area and also a clearly increased hydrophilicity of the contact area are caused.

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

According to another advantageous embodiment of the invention it is provided that the oxide 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 claimed in 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 claimed in 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 an oxide 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 claimed in the invention plays a decisive part since the reaction can be further accelerated and/or the temperature 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 apparatus in which the transport of the substrates takes place between individual process chambers in an atmosphere which can be adjusted in a controlled manner, for example using inert gases, but especially in a vacuum environment. Wet etching takes place with chemicals in the vapor phase, while dry etching takes place with chemicals in the liquid state. To the extent the growth layer consists of silicon dioxide, etching with hydrofluoric acid or diluted hydrofluoric acid can be done. To the extent the growth layer consists of pure Si, etching can be done with KOH.

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 area to the atmosphere, for filling the reservoir with atmospheric humidity and/or the oxygen contained in the air,
- exposing the first contact area to a fluid consisting especially predominantly, preferably almost completely, of especially deionized H_2O and/or H_2O_2,

- exposing the first contact area 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. The distance B is influenced or produced as claimed in the invention by the thinning.

A device for executing the method is made as claimed in 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.

The use of solar energy by means of photovoltaic systems is becoming increasingly important since fossil fuels are becoming scarce in the medium term and moreover constitute a major environmental problem in recovery and use, especially by the contribution to the greenhouse

effect. To strengthen the competitiveness of photovoltaics from a purely economic standpoint, it is necessary to improve the efficiency of conversion of light into electrical energy at the same cost or an at most moderate cost increase. But there are limits on the possible efficiency. These limits result primarily from the restriction that a single semiconductor material can process only light with a limited wavelength range and convert it into electrical energy.

One application of this invention for producing multilayer solar cells or as in English "multi-junction solar cells" is therefore especially advantageous.

In them the individual layers are stacked vertically on top of one another in the solar cell. Incident light first strikes the uppermost layer which is optimized for converting light with a certain first wavelength range into electrical energy. Light with a wavelength range which can largely not be processed in this layer penetrates this first layer and is incident on the underlying second layer which is optimized for processing a second wavelength range and thus producing electrical energy. In these multilayer cells it is optionally possible that light with a wavelength range which also can largely not be processed in this second layer is incident on the underlying third layer which is optimized for processing light with a third wavelength range and thus producing electrical energy. It can be imagined that a plurality (n) of these layers is purely theoretically possible. In practice these cells are structured such that the uppermost layer which incident light penetrates first processes that wavelength range with the shortest wavelength. The second layer, the next shorter wavelength range, and so forth. Here as claimed in the invention not only is a two-layer structure conceivable, but three or more layers can be implemented. Here it is provided that the layers be interconnected vertically in an electrically conductive manner, i.e. with a resistance as small as possible and in an optically transparent manner. The layers are deposited especially by so-called "metal organic

chemical vapor deposition" abbreviated "MO CVD" processes, the deposition of the two active layers of the multiple cell taking place especially "in-situ", i.e. without exposing the substrates to the normal ambient atmosphere between the deposition processes. Preferably between the active layers also blocking layers (second or fourth oxide layer) and/or buffer layers (second or fourth oxide layer) are placed which improve the quality of the resulting cell.

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 schematic view of one embodiment of this invention briefly before the first substrate makes contact with the second substrate.

The same or equivalent features are identified with the same reference numbers.

The situation in Figure 1 shows only one cross sectional segment of a first contact area 3 of a first substrate 1 and a second contact area 4 of a second substrate 2. The surfaces of the contact areas 3, 4 are terminated with polar OH groups and are accordingly hydrophilic. The first substrate 1 and the second substrate 2 are held by the force of attraction of the hydrogen bridges between the OH groups which are present on the surface and the H_2O molecules and also between the H_2O molecules alone, among others by van der Waals forces and/or hydrogen bridges. The hydrophilicity of at least the first substrate 1 has been increased by plasma treatment in a preceding step.

Plasma treatment takes place in a plasma chamber which can be exposed to plasma and a vacuum and/or a defined gas atmosphere and which can be provided in its own module of a corresponding apparatus. To be exposed to a vacuum and/or a defined gas atmosphere means that pressures below 1 mbar can be set and controlled. In the exemplary embodiment described here the

gas is N_2 at a pressure of 0.3 mbar.

It is especially advantageous according to the alternative embodiment to subject the second substrate 2 or the second contact area 4 to plasma treatment in addition, especially simultaneously with the plasma treatment of the first substrate 1.

A reservoir 5 in an oxide layer 6 consisting of the selected TCO has been formed as claimed in the invention by the plasma treatment. Under the oxide layer 6 a semiconductor 7 directly adjoins and can be used among others optionally also as a reaction layer which contains a second educt or a second group of educts. Plasma treatment with N_2 ions with the aforementioned ion energy yields an average thickness R of the reservoir 5 of roughly 15 nm, the plasma ions forming channels or pores in the oxide layer 6. The reservoir is filled with a first educt which reacts with the second educt.

The semiconductor 7 is temporarily supported by a carrier 8 in the illustrated embodiment.

The second substrate 2 on the second contact area 4 consists of a fourth oxide layer 9, directly followed by a third oxide layer 10 (precursor layer), the latter in turn directly followed by a second oxide layer 11.

The oxide layer 10 (precursor layer) consists especially of a TCO which contains incompletely oxidized components so that the layer has an oxygen volume S_1 which is smaller than the maximum oxygen volume S_{max} which would be contained in the layer if the entire volume were completely oxidized. In particular the oxygen volume S_1 is a maximum 70% of S_{max}. Advantageously this percentage is 55%, more advantageously 40% and most advantageously 25%.

The second oxide layer 11 is joined tightly to a semiconductor 12 of the second substrate 2 which in turn is temporarily fixed on a carrier 13.

The semiconductor 12 is used especially as a reaction layer which contains a second educt or a second group of educts.

A growth layer is formed by the reaction of the first educt with the second educt between the oxide layers 6, 9, 10, 11 and optionally the reaction layers (semiconductor 7, 12).

In one preferred embodiment the first educt which has been intercalated in the reservoir 5 formed in the oxide layer 6 reacts with the precursor layer 10. This reaction results in an increase in volume since the reaction product of the first educt and the precursor layer has a higher molar volume.

By increasing the molar volume and diffusion of the H_2O molecules, especially on the interface between the oxide layers 9 and 10, a volume in the form of a growth layer grows, due to the objective of minimizing the free Gibb's enthalpy intensified growth taking place in regions in which gaps are present between the contact areas 3, 4. The gaps are closed by the increase in the volume of the growth layers.

The oxide layers 6, 9, 10, and 11 after bonding jointly form an interconnection layer 14.

This interconnection layer in one preferred embodiment after the reaction advantageously consists of a homogenous material which corresponds essentially to the same TCO comprising the originally deposited oxide layers 9, 11 and 6.

Reference number list

1	first substrate
2	second substrate
3	first contact area
4	second contact area
5	reservoir
6	first oxide layer
7	first semiconductor
8	first carrier
9	fourth oxide layer
10	third oxide layer
11	second oxide layer
12	second semiconductor
13	second carrier
14	interconnection layer

Claims

1. A method for bonding of a first contact area (3) of a first at least largely transparent substrate (1) to a second contact area (4) of a second at least largely transparent substrate (2), on at least one of the contact areas (3, 4) an oxide being used for bonding, from which an at least largely transparent interconnection layer (14) is formed with:

- an electrical conductivity of at least $10e^1$ S/cm (measurement: four point method, relative to temperature of 300K) and
- an optical transmittance greater than 0.8 for a wavelength range from 400 nm to 1500 nm on the first and second contact area (3, 4),
- application of a first oxide layer (6) with the aforementioned electrical conductivity and the aforementioned optical transmittance to the first substrate (1),
- application of a second oxide layer (11) to the second substrate (2),
- plasma activating at least one of the substrates (1, 2), and
- bonding of the substrates (1, 2) at room temperature.

2. A method for producing a first substrate (1) with a first contact area (3) for bonding to a second contact area (4) of a second substrate (2), wherein an upper surface of the first contact area (3) comprises a first oxide layer (6) with:

- an electrical conductivity of at least $10e^1$ S/cm (measurement: four point method, relative to temperature of 300K) and
- an optical transmittance greater than 0.8for a wavelength range from 400 nm to 1500 nm being applied to the first substrate (1),
- application of a first oxide layer (6) with the aforementioned electrical conductivity and the aforementioned optical transmittance to the first substrate (1),
- application of a second oxide layer (11) to the second substrate (2),
- plasma activating at least one of the substrates (1, 2), and
- bonding of the substrates (1, 2) at room temperature.

3. The method as claimed in one of the preceding claims, wherein the first contact area (3) is plasma-activated, especially prior to contact-making.

4. A method for producing a second substrate (2) with a second contact area (4) for bonding to a first contact area (3) of a first substrate (1), with the following steps, especially the following sequence:

- application of a second oxide layer (11) to the second substrate (2),
- application of a third oxide layer (10) to the second oxide layer (11), the third oxide layer (10) having an oxygen volume S_1 which is smaller than 70% of the maximum oxygen volume S_{max} of the third oxide layer (10) and
- application of a fourth oxide layer (9) to the third oxide layer (10),
- application of a first oxide layer (6) with the electrical conductivity and the optical transmittance of claim 1 to the first substrate (1),
- plasma activating at least one of the substrates (1, 2), and
- bonding of the substrates (1, 2) at room temperature.

5. The method as claimed in one of the preceding claims, wherein the oxide or one or more of the oxide layers (6, 9, 10, 11) contain at least one of the following components, especially as doping:

- indium,
- tin,
- aluminum,
- zinc,
- gallium,
- fluorine or
- antimony.

6. The method as claimed in one of the preceding claims, wherein the oxide or one or more of the oxide layers (6, 9, 10, 11) are applied by one of the following methods:

- metal organic chemical vapor deposition,
- metal organic molecular beam deposition,
- spray pyrolysis,
- pulsed laser deposition or
- sputtering.