

Method for Permanent Bonding of Wafers

Specification

This invention relates to a method for bonding of a first solid substrate which contains a first material, especially semiconductor wafers, to a second solid substrate, especially semiconductor wafers.

The objective in permanent or irreversible bonding of solid substrates is to produce a connection as strong and especially as permanent as possible, therefore a high bond force, between the two contact surfaces of the solid substrates. For this purpose, in the prior art there are various approaches and production methods, especially the welding of the surfaces at higher temperatures.

All types of materials, predominantly however metals and ceramics, are permanently bonded. One of the most important systems of permanent bonding is metal-metal systems. Cu-Cu systems have appeared increasingly in recent years. The development of 3D structures specifically requires mostly the joining of different functional layers. This joining is more and more often done by way of so-called TSVs (Through Silicon Vias). The contact-making of these TSVs with one another very often takes place by copper contact sites. At the instant of bonding very often there are full-value, serviceable structures, for example microchips, on one or more surfaces of the solid substrates. Since different materials with different coefficients of thermal expansion are used in microchips, increasing the temperature during bonding is not desirable. This can lead to thermal expansions and thus thermal stresses which can destroy parts of the microchip or its vicinity.

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 are used at present often use high temperatures, especially $> 400^{\circ}\text{C}$, 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 in part 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, or application of force as low as possible.
- 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, especially when the insulating layers between the metallic conductors are made from so-called "low-k" materials.

The welding of two surfaces works better, the flatter the surfaces, the less contamination on

the surfaces, and the more perfect their surface structure. In reality it has to do with surfaces which are contaminated by water, organic substances, particles or the like which have a not negligible surface roughness and are very often more or less highly oxidized. The particles are removed in industry by various processes, generally in several modules which are independent of one another. The removal of oxides is certainly one of the most difficult challenges, since metal oxides are chemically rather stable. Even if all adhesive substances and chemically produced products are removed from the metal surface, there is still the rough surface as the last barrier to a perfect bond.

Current bonding methods are designed primarily for high pressures and temperatures. Mainly avoiding a high temperature is of essential importance for the welding of future semiconductor applications, since different materials with different coefficients of thermal expansion generate thermal stresses which cannot be ignored during heating and cooling processes. Furthermore, the diffusion of doping elements as the temperature rises is increasingly becoming a problem. The doped elements should not leave the intended three-dimensional region after the doping process. Otherwise the physical properties of the circuits would fundamentally change. In the best case this leads to a deterioration, in the worst and most probable case to unserviceability of the component. Mainly memories are susceptible to high temperatures due to their high transistor density and their high doping density. On the other hand, there are memories in which 3D technology is being increasingly used to raise the capacity and performance.

The problem in the existing prior art is to create a surface as flat as possible after decontamination of the surface. To some extent this is enabled by grinding processes. Grinding processes are however unable to perfectly planarize the surface. Another working step would be polishing. Here tools with special surfaces which further reduce the metal surface roughness are

used. By a combination of grinding and polishing, roughnesses in the nanometer, often even in the subnanometer range, are produced. In most cases so-called CMP methods are used. It is a chemical-mechanical polishing process. Regardless of how long or how precisely grinding is done, a residual roughness which cannot be eliminated always results. This residual roughness upon contact of two surfaces always leads to formation of pores in the nanometer and subnanometer range.

Embodiments of this invention devise a method for careful production of a permanent bond between two solid substrates with a bond force as high as possible at a temperature which is simultaneously as low as possible.

According to an aspect, there is provided a method for bonding of a first solid substrate to a second solid substrate which contains a first material with the following steps, especially the following sequence: formation or application of a function layer which contains a second material to the second solid substrate, making contact of the first solid substrate with the second solid substrate on the function layer, pressing together the solid substrates for forming a permanent bond between the first and second solid substrate, at least partially reinforced by solid diffusion and/or phase transformation of the first material with the second material, an increase of volume on the function layer being caused, wherein the function layer is formed or applied on a surface of the second solid substrate in an average thickness between 0.1 nm and 25 nm, and wherein gaps present due to unevenness of the surface are closed by expansion of the volume of a contact surface formed by the function layer.

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 which lie within the indicated boundaries will also be considered disclosed as boundary values and will be claimed in any combination.

The basic idea of embodiments of this invention is to apply or create at least on one of the solid substrates a function layer with a first material which reacts with a second material of the other solid substrate especially after contact-making or production of a prebond between the solid substrates, and thus forms an irreversible or permanent bond between the solid substrates. The two solid substrates need not necessarily form a prebond with one another. Simple contact-making without formation of a prebond is also possible. As per embodiments of the invention the "reaction" is solid diffusion and/or a phase transformation. Before and/or after formation/application of the function layer on the first and/or second substrate, cleaning of the solid substrates or of the solid substrates generally takes place, especially by a rinsing step. This cleaning should generally ensure that there are no particles on the

surfaces which would result in unbonded sites.

The function layer and the material contained in the function layer create the technical possibility of inducing a reaction (first material with the second material) which increases the bond rate and which strengthens the permanent bond directly on the contact surfaces between the solid substrates after producing the temporary or reversible bond in a controlled manner, especially by deformation of at least one of the contact surfaces (preferably the contact surface formed by the function layer) by the reaction, gaps present due to unevenness of the surfaces/contact surfaces being closed, especially in conjunction with pressing together by applying pressure to the solid substrates against one another. Deformation is an expansion of the volume in general, a phase transformation or plasticization which leads to a change in the shape of the crystallites and/or amorphous regions of the surface.

Solid substrates as per embodiments of the invention are those solid substrates whose material is able to react or mix as material with another supplied material to form a mixed material with a higher molar volume, as a result of which growth on the function layer is caused, especially on valleys of the surfaces of the solid substrates which form on gaps. The following combinations of materials are especially advantageous, either due to the possibility of forming mixed crystals, of plastically deforming well, of passing through phase transformations which lead to an increase of volume, or due to any other direct or indirect methods named in the specification for closing the gaps in the bond interface:

- Cu-Fe, Cu-Ge, Cu-In, Cu-Li, Cu-Mg, Cu-Mn, Cu-Nb, Cu-Nd, Cu-Ni, Cu-Si, Cu-Sn, Cu-Zn, Cu-Zr, Cu-Ti, Cu-W, Cu-Ta, Cu-Au, Cu-Al, Cu-Cu,
- W-Fe, W-Ge, W-In, W-Li, W-Mg, W-Mn, W-Nb, W-Nd, W-Ni, W-Si, W-Sn, W-Zn, W-

- Zr, W-Ti, W-Ti, W-Ta, W-Au, W-Al,
- Ti-Fe, Ti-Ge, Ti-In, Ti-Li, Ti-Mg, Ti-Mn, Ti-Nb, Ti-Nd, Ti-Ni, Ti-Si, Ti-Sn, Ti-Zn, Ti-Zr, Ti-Ta, Ti-Au, Ti-Al,
 - Ta-Fe, Ta-Ge, Ta-In, Ta-Li, Ta-Mg, Ta-Mn, Ta-Nb, Ta-Nd, Ta-Ni, Ta-Si, Ta-Sn, Ta-Zn, Ta-Zr, Ta-Ti, Ta-W, Ta-Ti, Ta-Ta, Ta-Au, Ta-Al,
 - Au-Fe, Au-Ge, Au-In, Au-Li, Au-Mg, Au-Mn, Au-Nb, Au-Nd, Au-Ni, Au-Si, Au-Sn, Au-Zn, Au-Zr, Au-Ti, Au-W, Au-Ti, Au-Ta, Au-Au, Au-Au, Au-Al,
 - Al-Fe, Al-Ge, Al-In, Al-Li, Al-Mg, Al-Mn, Al-Nb, Al-Nd, Al-Ni, Al-Si, Al-Sn, Al-Zn, Al-Zr, Al-Ti, Al-W, Al-Ti, Al-Al, Al-Al, Al-Al,

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

- III-V: GaP, GaAs, InP, InSb, InAs, GaSb, GaN, AlN, InN, $\text{Al}_x\text{Ga}_{1-x}\text{As}$, $\text{In}_x\text{Ga}_{1-x}\text{N}$
- 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: $\text{In}_{2-x}\text{Sn}_x\text{O}_{3-y}$

Although the aforementioned binary, tertiary and quaternary phase systems generally have extremely low edge solubilities, due to their covalent bonding affinity they behave in a rather brittle manner, occur mostly as single crystals and only very rarely as polycrystals, the properties claimed for metals as per embodiments of the invention can also occur in semiconductor systems. It should be noted that the surface roughnesses of current semiconductor wafers can be reduced to such a degree that the gaps which are to be closed as per embodiments of the invention can only have a volume in the angstrom

range. It is a fact that even for poor edge solubility of a multicomponent system components can dissolve in the main component even if only in the ppm range. Therefore the ideas as per embodiments of the invention will and should be considered as disclosed even for nonmetallic systems.

It is especially advantageous as per embodiments of the invention if contact-making of the solid substrates after application of the function layer takes place as near as possible in time, especially within 2 hours, preferably within 30 minutes, even more preferably within 10 minutes, ideally within 5 minutes. This measure minimizes possible unwanted reactions such as oxidation of the function layer or of the surfaces of the solid substrates.

As per embodiments of the invention there can be means for inhibiting these reactions of the function layer and/or of the surfaces of the solid substrates before the contact surfaces make contact, especially by passivation of the reaction layer of the solid substrates, 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. Systems with an inert atmosphere or vacuum atmosphere can preferably be implemented as systems in which the transfer of the solid substrates from one process chamber to the next process chamber takes place by means of a solid substrate handling system which can carry out the transfer of the solid substrates completely in a controlled, adjustable atmosphere, especially a vacuum atmosphere. These systems are known to one skilled in the art.

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 per embodiments of the invention is suitable for allowing the function layer to grow by 0.1 to 10 nm, especially 0.1 to 1 nm, preferably by 0.1 to 0.3 nm, for a conventional wafer surface of a circular wafer with a diameter of up to 450 mm, especially locally on gaps between the contact surfaces of the solid substrates.

The (additionally applied) function layer is applied by one or more of the following methods:

- PECVD,
- LPCVD,
- vapor deposition
- epitaxy
- MOCVD
- sputtering

Embodiments of the invention thus solve the problem of better welding of the surfaces of solid substrates which have been brought into contact with one another by on at least one of the surfaces a solid reaction with another material which is located in the function layer being produced which leads to a volume expansion of the corresponding region near the surface and thus closes the gaps or pores which are present due to surface roughness in the interface (boundary surface between the solid substrates which have been brought into contact). It should be mentioned here that the two solid substrates which are to be welded to one another are already for the most part in contact with one another. At the contact sites a volume expansion onto the solid substrates is of course normally not possible since the material in this direction is subject to obstruction of expansion. Still all methods

as per embodiments of the invention which increase the energy state so dramatically that the material spreads into the pores are explicitly mentioned. Either the material expands by the methods as per embodiments of the invention directly into the pores (by way of example but not restrictively here let the volumetric expansion by mixed crystal formation or a phase transformation be mentioned) or the material cannot expand in one direction due to the methods as per embodiments of the invention since it is subject to obstruction of expansion, but fills the nearby pores, since based on the increased energy state it deforms plastically. For the sake of completeness it should be mentioned that plastic deformation can take place by dislocations, twinning or diffusion and in a strict physical sense is not accompanied by a volume expansion. There is no longer any explicit differentiation between plasticization and (residual elastic) volume expansion hereinafter. The term volume expansion will stand for a residual enlargement and/or deformation of a surface part.

The second material can be applied either as a layer to at least one of the two substrates (Figure 2), can penetrate by grain boundary diffusion between the grains of a first especially polycrystalline material into the volume (Figure 3), can alternate in a layer structure with layers of the first material (Figure 4) or can be applied to the second solid substrate by mechanical alloying of microparticles and/or nanoparticles (Figure 5).

This results in higher bond strengths at lower temperatures.

According to one advantageous embodiment of the invention it is provided that formation and/or reinforcement of the permanent bond by diffusion of the second material into the first material takes place especially with formation of a mixed material C.

According to another advantageous embodiment of the invention, it is provided that the formation of the permanent bond takes place at a temperature between room temperature and

200°C, especially between room temperature and 150°C, preferably between room temperature and 100°C, even more preferably between room temperature and 50°C, especially during a maximum 12 days, preferably a maximum 1 day, even more preferably a maximum 1 hour, at best a maximum 15 minutes.

Here it is especially advantageous if the irreversible bond has a bond strength of greater than 1.5 J/m², especially greater than 2 J/m², preferably greater than 2.5 J/m².

The bond strength can be increased especially advantageously in that during solid diffusion and/or phase transformation a mixed material C with a greater molar volume than the molar volume of the second material and of first material is formed. In this way growth on the second solid substrate or on the function layer is effected, as a result of which gaps between the contact surfaces can be closed by the chemical reaction as 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 prior to application/formation of the function layer plasma activation of the surfaces of the solid substrates takes place especially with an activation frequency between 10 and 600 kHz and/or a power density between 0.075 and 0.2 watt/cm² and/or with application of a pressure between 0.1 and 0.6 mbar, additional effects such as smoothing of the contact surface are effected. Here application of pressure is defined as the pressure of the working atmosphere during plasma activation.

In another advantageous embodiment of the invention it is advantageously provided that the solid diffusion and/or phase transformation is limited to one surface layer (3o) of the first solid substrate (1) with a maximum initial density D less than 1 µm, especially less than 100 nm, preferably less than 10 nm, even more preferably less than 1 nm.

To the extent the solid substrates are pressed together at a pressure between 0.1 MPa and 10 MPa, optimum results can be achieved. Preferably the pressure is between 0.1 and 10 MPa, still more preferably between 0.1 and 1 MPa, most preferably between 0.1 and 0.3 MPa. The pressure must be chosen to be greater, the greater the irregularities and the thinner the layers.

Advantageously according to one embodiment of the invention it is provided that the formation/application of the function layer is carried out in a vacuum. Thus the contamination of the function layer with unwanted materials or compounds can be avoided.

It is especially effective for the method sequence if the function layer is made preferably in an average 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.

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 and a second solid substrate as claimed in the invention at the instant of the method as claimed in the invention immediately after contact of the first solid substrate is made with the second solid substrate,

Figure 1b shows permanently joined solid substrates after carrying out the method as claimed in the invention,

Figure 2a shows one step of the method as claimed in the invention for formation/application of one function layer,

Figures 2b to 2d show enlargements of the boundary surface between the second solid substrate and the function layer according to Figure 2a,

Figure 3 shows one alternative step of the method as claimed in the invention for

formation/application of one function layer,

Figures 3b to 3d show enlargements of the boundary surface between the second solid substrate and the function layer according to Figure 3a,

Figure 4 shows one alternative step of the method as claimed in the invention for formation/application of one function layer,

Figures 4b to 4d show enlargements of the boundary surface between the second solid substrate and the function layer according to Figure 4a,

Figure 5 shows one alternative step of the method as claimed in the invention for formation/application of one function layer,

Figures 5b to 5d show enlargements of the boundary surface between the second solid substrate and the function layer according to Figure 5a.

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

The invention describes a method for a volume expansion of regions near the surface (proceeding from an effective contact surface 6 between the solid substrates 1, 2 which are to be bonded), specifically of a first surface layer 3 of the first solid substrate 1 and/or a second surface layer 4 of the second solid substrate 2 and/or a function layer 5 which is provided on a surface layer 3, 4.

The volume expansion takes place by a solid reaction between the first material A and a second material B such that gaps 10 are closed between the contacted solid substrates 1, 2 along the effective contact surface 6 (interface 11) during an additional application of pressure in a bond process. The gaps 10 immediately after the solid substrates 1, 2 that have made contact according to

Figure 1a are still comparatively large due to their unevenness. In this way the effective contact surface 6 is accordingly small. In Figure 1b a volume expansion (growth) has been caused by the solid reaction so that the gaps 10 have been distinctly reduced in size, in particular in the volume at least by a factor of 2, preferably at least by a factor of 5, even more preferably at least by a factor of 10. Accordingly the effective contact surface 6 has become larger.

The solid state reaction takes place here between the first material A which is preferably present in the function layer 5 (> 50% by volume) and the second material of one of the solid substrates 1 and/or 2, preferably at least of the first, especially upper solid substrate 1.

The function layer 5 can be produced using various methods which are described below, as a result of which an altered second surface side 4' (since it additionally has the function layer 4) with a new surface 4o' is formed.

As claimed in the invention it is also conceivable for the two solid substrates 1, 2 to consist of two different materials A_1 and A_2 . If the material B is chosen such that a volume expansion in a reaction/mixture with the two materials A_1 and A_2 takes place, this description can be applied thereto and is covered by the invention. In one preferred case the materials A_1 , A_2 and B are chosen to be single-phase, single-component systems. Alternatively A_1 and A_2 are identical, especially materials A and B being chosen from the group of metals.

The surface layers 3 and/or 4 are those volumetric regions under the surfaces 3o, 4o of the substrates 1, 2 in which the solid reaction as claimed in the invention at least largely proceeds. The surface layers 3, 4 have especially an average thickness D smaller than 1 μm , preferably smaller than 100 nm, even more preferably smaller than 10 nm, most preferably smaller than 1 nm. If the material B is made as polycrystalline material, the average thickness D of the surface layers 3, 4 is

especially a maximum 50 times as large as the average grain diameter of the material B (especially of the single crystals of material B), more preferably a maximum 20 times as large, even more preferably a maximum 10 times as large, most preferably a maximum 5 times as large, most preferably of all a maximum twice as large. Figures 1a and 1b are thus shown highly enlarged.

Figure 1a shows the state of contact-making of the surfaces 3o, 4o before the solid reaction between the two materials A and B, while Figure 1b shows the surface layers 3, 4 after completed volume expansion and the successful bonding process. The figures show the change of the volume and the gap closure which occurs with it along the interface 11 or along the effective contact surface 6 which becomes larger due to the gap closure. By enlarging the effective contact surface 6 and by distinctly reducing the average distance between the surfaces 3o, 4o, the bond force is greatly increased. Even more ideally the holes are completely closed so that at least later the bond interface can no longer be recognized.

The material B of the function layer is at least partially consumed by the solid reaction in the surface layer 3 and/or 4. The average thickness R of the function layer 5 is dependent on the most varied parameters (temperature, choice of materials A and B, bond pressure, time progression, diffusion rates). The materials A and B can be metals, plastics, ceramics or semiconductors, metals being preferred. The solid substrates 1, 2 can be made especially as wafers.

The different embodiments of the invention according to the invention are now detailed. Here the materials A and B are selected as single-phase, single-component materials. The material A and or the material B each consist preferably of a single or uniform material. In the illustrated embodiments the material B is applied only to the second solid substrate 2.

One embodiment as claimed in the invention consists in expanding the volume by

dissolving the component B in A. By way of example, for this embodiment as claimed in the invention the copper-tin system has been named. The substance for material A is the metal copper and material B is the metal tin.

The expansion of the copper which contributes to closing of the gaps 10 in the interface 11 takes place by the formation of a copper mixed crystal C.

A mixed crystal C is a crystalline phase which consists of at least two different materials, here the materials A and B which are completely miscible with one another within a concentration range. According to Cu-Sn phase diagrams, copper at room temperature has a solubility for tin. The solubility increases as temperature rises and has a peak at roughly 850K. Conversely tin has a negligibly low solubility for copper up to the melting point. Based on the relationship between the volume and the concentration of each mixed crystal (Vegard's rule), in the simplest embodiment tin as material B is deposited on the surface layer 4 of the second solid substrate 2 (at least surface layer 4 of copper as first material A) (Figure 2a). The method parameters are chosen such that the second material B (tin) at this instant does not join the first material (copper). The amount of tin is such that in a diffusion of the tin into the copper which takes place later (Figure 2c) an intermetallic phase preferably never forms. In other words: The surface layer 4 is not saturated with tin at any point such that intermetallic phases can form. For the binary phase system Cu-Sn according to the phase diagram at room temperature a molar concentration for Sn in Cu of roughly 0.01 (corresponds to roughly 14% by weight Sn) may not be exceeded. Thus the formation of the Cu_3Sn phase is suppressed since the solubility limit of copper for the Sn has not yet been exceeded. For rising temperature the solubility of Sn in Cu becomes accordingly greater.

The volume of the copper mixed crystal very probably changes however by the absorption

of the second material B (tin) into the first material A (copper). Since tin has a larger atomic radius than copper, the volume of the copper mixed crystal C rises with increasing tin content (Figure 2d). The start of the diffusion process of tin into copper is controlled preferably based on process parameters, especially by a temperature increase since the diffusion constants depend explicitly on the temperature.

In the embodiment presented here the permanent bonding takes place below 200°C. The temperature at which a noticeable diffusion of the tin into the copper begins, with the other process parameters which have been chosen as claimed in the invention, is between room temperature (RT) and 200°C, more preferably between RT and 150°C, even more preferably between RT and 100°C, most preferably between RT and 50°C. For one skilled in this art it is clear that any parameter which can control the desired diffusion can be used to achieve the desired effect.

Copper accepts tin by the controlled use of diffusion, thus increases its volume and can thus close the gaps 10 in the interface 11. For metals the high plasticity additionally promotes the process of closing of the gaps 10.

As claimed in the invention the intention is moreover to prevent the solubility boundary of the first material (copper) for the second material (tin) from being exceeded so that the separation of intermetallic phases is prevented as extensively as possible, preferably completely. To the extent materials A and B are chosen which are completely miscible in the solid state, the solubility boundary as claimed in the invention can remain ignored.

The deposition of the second material B (tin) on the first material A (copper) is carried out as claimed in the invention such that the solubility boundary of the copper for tin at the corresponding temperature is exceeded at as few sites as possible, more preferably at no site in the

surface layer 4 (see Figure 2b). The components (single crystals or multicrystals) of material A are shown schematically.

According to Figure 2c the second material B (tin) diffuses into the first material A only on the boundary surface between the function layer 5 and the surface 4o before application of the function layer 4; this is the preferred embodiment especially for single crystals as the first material A. The growth of the first material A in the form of the mixed material C is shown schematically in Figure 2d. Intermediate spaces 7 (if present) between components of the first material A become smaller, so that the components try to expand in the direction of the contact surface 6. In doing so the mixed material C expands primarily in the region of the gaps 10 due to the pressure of the opposing solid substrate 1, which pressure is prevailing on the active contact surface 6.

In order to largely prevent the formation of intermetallic phases, according to another version it is provided that the second material (tin) as a function layer 5 is deposited not only on the surface 4o of the first material (copper) (Figure 2), before the actual dissolution process starts, but to be introduced into the surface layer 4 within the layer thickness d (Figure 3) without allowing the tin to pass into solution with the copper [sic].

For this purpose the second material B (tin) will travel especially via grain boundary diffusion processes to greater depths of the polycrystalline first material A (copper), preferably will not yet pass into the volume of the grains, at most penetrate on the outer edge of the grains slightly into the depth and only in a decisive bonding process actually penetrate into the volume in order to cause the increase of the volume (Figure 3). The polycrystalline microstructure of the first material A is polycrystalline, therefore consists of individual grains which are separated from one another by intermediate spaces 7 (here: grain boundaries). The intermediate spaces 7 for a polycrystalline

microstructure are two-dimensional lattice structural defects into which atoms of different species can penetrate. Preferably the microstructure of at least one of the solid substrates 1, 2 which are to be bonded is produced such that the second material (tin) is located not only on the surface 4o, but also in the surface layer 4 without dissolving in the copper. Thus the function layer 5 in this embodiment is at least partially identical to the surface layer 4.

One version as claimed in the invention therefore consists in using the difference between grain boundary diffusion and volumetric diffusion to convey the tin into the volumetric depth of the copper layer without obtaining concentration elevations in the copper grains (see especially Figure 3). The process parameters here are chosen such that the grain boundary diffusion takes place before a volumetric diffusion since for the diffusing species - in the exemplary embodiment tin - it is much easier to advance into the extensive grain boundaries than through the narrow lattice of the bulk (of the copper grains). Here the consideration of the diffusion coefficient is decisive. The diffusion coefficient for the grain boundary diffusion for an intended temperature is larger than the diffusion coefficient for the corresponding volumetric diffusion. The grain boundary surface to grain volume ratio must also be considered here since at a higher ratio per unit of volume there are accordingly more grain boundaries. Especially preferably the aggregate state of the phase which is moving along the grain boundaries is liquid. Therefore as claimed in the invention materials are recommended which have a very low melting point. The diffusion rate of the liquid phase along the grain boundary is accordingly high.

Thus the second material B here diffuses into the first material A not only on the boundary surface between the function layer 5 and the surface 4o before application of the function layer 4, due to the penetration of the surface layer 4 from more or less all sides of each component (copper

grain) of the first material.

Another version consists in depositing a layer structure (Figure 4). The components copper and tin are deposited in layers, preferably in alternation material A and B by conventional deposition methods. In this way there is an "intermediate solution" to the pure "surface solution" according to Figure 2 and the "mixed solution" according to Figure 3 in which there are several boundary surfaces for diffusion of the second material B into the first material A.

According to another embodiment of the invention it is provided that the first material A (copper) and the second material B (tin) as microparticles and/or nanoparticles 8, 9 will be deposited from a solution on the surface 4o, therefore a mechanical alloy will be applied to the second solid substrate 2 (Figure 5). For spherical particles at the known density of the copper and of the tin and the known average spherical radii of the copper and tin particles the required mixing ratio for the copper-tin mixed crystal can be exactly computed. Formulas which have been adapted accordingly can be used for particles with a different shape.

In the bonding process in this embodiment preferably sinter bridges arise which weld the microparticles and/or nanoparticles 9 to one another into a sinter matrix 10. At the same time diffusion of the second component B into the sinter matrix 10 takes place. Since the microparticles and/or nanoparticles 8 of the second material B are present statistically uniformly distributed through the mechanical alloy in the sinter matrix 10 of the first material A, an optimum uniform distribution of the second material B over a volumetric region which can be sharply delineated is possible. The materials A and B are chosen as claimed in the invention such that the volume of the newly formed mixed crystal C (via the sinter process) is larger than the volume of the mechanical alloy prior to the bonding process.

It must be considered here that mechanical alloys due to the microparticles and/or nanoparticles 8, 9 have a generally lower density than bulk materials since between the microparticles and/or nanoparticles 8, 9 there is a large amount of empty space which is closed only after by the sinter process. In the most optimum case the empty space is completely broken down. Preferably the structure after the bonding process is again a polycrystalline structure with a mixed crystal.

As claimed in the invention there is also a preferred version in which copper and tin are directly deposited with the intended concentration onto the second solid substrate by PVD and/or CVD processes. In this way the mixed material C (mixed crystal) is directly produced. An overly large tin concentration would lead to intermetallic phases.

In another embodiment the increase of the volume is accomplished by the formation of a completely new phase, therefore a phase transformation instead of diffusion (also conceivable in combination as claimed in the invention). The reaction of the second material B with the first material A leads to any compound A_xB_y whose molar volume is greater than the sum of the two molar volumes of the components A and B. The phase transformation will proceed in a controlled manner by the choice of corresponding process parameters. Therefore the deposited component B should only then preferably react only with component A if this is desirable, therefore during the bond process. The increase of the volume is therefore caused by a phase transformation.

In one specific embodiment of the phase transformation the increase of volume is produced by a martensitic transformation. A martensitic transformation is a diffusion-less phase transformation which takes place by a shear mechanism process of the lattice. The shear mechanism process takes place only by a very rapid temperature drop. Another advantage of a martensite

consists in the often extremely high dislocation densities which are caused by the shear processes of martensite formation. In the bond process the pores would be closed by means of the volume expansion during the martensitic transformation, but at the same time the structure would be extremely consolidated, i.e. its dislocation density would rise. The dislocation density can possibly be used in some martensites as an aid for a later recrystallization process.

In another embodiment the increase of the volume during the bond process in the regions near the surface is caused by the spinodal decomposition of an alloy. A spinodal decomposition is a spontaneous separation of a homogeneous structure into at least two phases by a critical parameter being exceeded, preferably the critical temperature. The homogeneous structure was produced by a cooling process of a multicomponent system whose concentration is within the spinodals. It is known to one skilled in the art which alloys can decompose spinodally, and how these alloys have to be produced and heat-treated. In particular alloys with spinodal decomposition whose decomposition process leads to an expansion of volume are chosen.

Reference number list

1	first solid substrate
2	second solid substrate
3	first surface layer
3o	surface
4, 4'	second surface layer
4o, 4o'	surface
5, 5'	function layer
6	effective contact surface
7	intermediate spaces
8	microparticles and/or nanoparticles
9	microparticles and/or nanoparticles
10	sinter matrix
11	interface
A	first material
B	second material
C	mixed material
R	average thickness
D	average thickness

Claims

1. A method for bonding of a first solid substrate (1) to a second solid substrate (2) which contains a first material with the following steps, especially the following sequence:

- formation or application of a function layer (5) which contains a second material to the second solid substrate (2),
- making contact of the first solid substrate (1) with the second solid substrate (2) on the function layer (5),
- pressing together the solid substrates (1, 2) for forming a permanent bond between the first and second solid substrate (1, 2), at least partially reinforced by solid diffusion and/or phase transformation of the first material with the second material, an increase of volume on the function layer being caused,

wherein the function layer (5) is formed or applied on a surface (4o) of the second solid substrate (2) in an average thickness (R) between 0.1 nm and 25 nm, and

wherein gaps present due to unevenness of the surface (4o) are closed by expansion of the volume of a contact surface formed by the function layer.

2. The method as claimed in Claim 1, wherein formation and/or reinforcement of the permanent bond by diffusion of the second material into the first material takes place, especially with formation of a mixed material.

3. The method as claimed in one of the preceding claims, wherein the formation of the permanent bond takes place at a temperature between room temperature and 500°C, especially between room temperature and 200°C, preferably between room temperature and 150°C, even more preferably between room temperature and 100°C, most preferably between room temperature and 50°C, especially during a maximum 12 days, preferably a maximum 1 day, even more preferably a maximum 1 hour, at best a maximum 15 minutes.

4. The method as claimed in one of the preceding claims, wherein the step of pressing together the solid substrates (1, 2) comprises pressing together the solid substrates (1, 2) to form a permanent bond having 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 .

5. The method as claimed in one of the preceding claims, wherein during solid diffusion and/or phase transformation a mixed material (C) with a greater molar volume than the molar volume of the second material and of first material is formed.

6. The method as claimed in one of the preceding claims, wherein prior to and/or after application/formation of the function layer plasma activation of the surfaces of the solid substrates takes place.

7. The method as claimed in one of the preceding claims, wherein the step of pressing together the solid substrates (1,2) comprises pressing together the solid substrates (1, 2) to form a permanent bond between the first and second solid substrate (1, 2), at least partially reinforced by solid diffusion and/or phase transformation of the first material with the second material which forms a first surface layer (3) of the first solid substrate (1) having a maximum initial thickness D smaller than 1 μm , especially smaller than 100 nm, preferably smaller than 10 nm, even more preferably smaller than 1 nm.

8. The method as claimed in one of the preceding claims, wherein the pressing together takes place at a pressure between 0.1 and 10 MPa.

9. The method as claimed in Claim 8, wherein the function layer (5) before formation of the permanent bond has an average thickness R between 1 angstrom and 10 nm.

10. The method as claimed in one of the preceding claims, wherein the solubility boundary of the first material for the second material during formation of the permanent bond is exceeded at least only slightly, especially at no site of solid diffusion and/or phase transformation.

11. The method as claimed in one of the preceding claims, wherein the solid diffusion take place at least predominantly as grain boundary diffusion.

Method for Permanent Bonding of Wafers

Abstract

This invention relates to a method for bonding of a first solid substrate (1) to a second solid substrate (2) which contains a first material with the following steps, especially the following sequence:

- formation or application of a function layer (5) which contains a second material to the second solid substrate (2),
- making contact of the first solid substrate (1) with the second solid substrate (2) on the function layer (5),
- pressing together the solid substrates (1, 2) for forming a permanent bond between the first and second solid substrate (1, 2), at least partially reinforced by solid diffusion and/or phase transformation of the first material with the second material, an increase of volume on the function layer being caused.

Figure 1a