Method for Applying a Bonding Layer

Specification

The invention relates to a method as disclosed herein as well as a substrate as disclosed herein.

In the state of the art, countless methods to connect various materials to one another exist. In the semiconductor industry, in recent years, primarily the bonding technology to connect two substrates temporarily or permanently to one another has gained acceptance. Very often, the bonding process takes place between semiconductor(s) and/or metal structures on the substrate. The best-known metal bonding technology of recent times is copper bonding. Substrates are the carriers for functional assemblies such as microchips, memory chips, or MEMS assemblies. In recent years, increasingly attempts were made to produce a connection between assemblies arranged on various substrates in order to avoid a wire-bonding process between the assemblies that is labor-intensive, costly, and susceptible to flaws. In addition, the direct bonding variant has the enormous advantage of elevated assembly density. The assemblies must no longer be positioned beside one another and connected via wires, but rather are stacked on one another and connected vertically to one another by various technologies. In most cases, the vertical connections are produced by contact points. The contact points of different substrates must be identical to one another and are oriented to one another before the actual bonding process.

components in turn frequently requires bonding processes, so that the need for a reliable aluminum bonding process increases. Outside of the semiconductor industry, aluminum is also a structural material that is in demand, since it is light, inexpensive, and primarily hardenable. In the semiconductor industry, based on the above-mentioned reasons, it has been attempted for some time to develop processes that make aluminum usable as structural material and in particular material for bonding connections.

The greatest problem when using oxygen-affine materials such as copper and aluminum is the avoidance of oxidation on bonding surfaces and/or the complete removal of oxide from bonding surfaces before a bonding process. Extremely oxygen-affine materials such as aluminum produce, moreover, oxides that are strong and difficult to reduce. Plants for oxide removal are expensive, labor-intensive and under certain circumstances dangerous (toxic substances).

The object of this disclosure is therefore to indicate a method as well as a substrate provided with a bonding layer, with which an oxidizable material (such as in particular aluminum) can be used for bonding.

This object is achieved with the features as disclosed herein. Advantageous further developments of the disclosure are indicated. All combinations of at least two of the features indicated in the specification also fall within the scope of the disclosure. In the indicated ranges of values, values that lie within the above-mentioned limits are also to be disclosed as boundary values and can be claimed in any combination.

It is an essential idea of this disclosure to provide a bonding layer, consisting of a basic layer and a protective layer, in particular as a diffusion pair, on the substrate,

whereby a basic material of the basic layer can be oxidized, while a protective material of the protective layer can be oxidized at least less easily.

The disclosure therefore in particular is a matter of a process in which the oxidation of oxygen-affine materials such as in particular aluminum (preferred) or copper is prevented from the start. The protection of oxygen-affine basic material is achieved according to the disclosure in particular by the deposition of a protective material, which covers the basic material at least partially, in particular primarily, and preferably completely.

The objective breakdown of the elements relative to their oxygen affinity can be most simply defined by the electrochemical voltage sequence. Oxygen-affine elements such as lithium are extremely base materials, are easily oxidized, and therefore act as reducing agents, easily release electrons, and therefore have an extremely negative standard electrode potential. However, elements with a low oxygen affinity are referred to as noble, since the latter can be easily reduced and therefore act as oxidizing agents, accommodate electrons, and have an extremely positive standard electrode potential. As basic material, in particular a material with a standard electrode potential is used that is less than 2.00 V, preferably less than 1.00 V, more preferably less than 0.0 V, most preferably less than -1.0 V, with utmost preference less than -2.0 V, and even more preferably less than -3.0 V. Copper has a standard electrode potential of approximately 0.16 V, aluminum of approximately -1.66 V. The noblest metal is gold with a standard electrode potential of approximately 1.69 V (for the first oxidation stage).

In an especially preferred variant, the basic material and the protective material are located as targets, separated from one another, in a coating chamber and are applied in

succession under vacuum, so that no contact of the basic material with an oxygen-containing atmosphere is produced.

The disclosure consists in leaving the protective material on the basic material during the bonding process and, because of its chemical-physical properties, in at least partially, in particular predominantly, and preferably completely dissolving the protective material in the basic material during the bonding process. The selection of the basic material-protective material combination is carried out in such a way that the latter allows a solid dissolution process. The protective material is preferably more readily soluble in the basic material than vice versa.

The protective material is dissolved in particular under specific process conditions in the basic material. The basic material therefore has a boundary solubility for the protective material and/or the basic material can be mixed at least partially, in particular predominantly, and preferably completely with the basic material. In the case of an existing boundary solubility of the protective material in the basic material, the boundary solubility at room temperature is in particular great enough to keep a specific amount of the protective material dissolved. In this way, the protective material according to the disclosure can be applied as an extremely thin layer in order to avoid local concentration peaks during the diffusion process of the protective material into the basic material that can lead to an (undesired) precipitate.

This disclosure is advantageous in preventing a contact of the oxygen-affine basic material with an oxygen-containing or oxygen-rich atmosphere, in particular by at least predominant covering of the surfaces of the basic layer, not covered by the substrate, with the protective layer.

The protective material itself is preferably a solid, in particular at least at room temperature. The latter is therefore not liquid and allows the transport of the protected basic material through an oxygen-containing atmosphere.

In an advantageous example of the disclosure, the protective material is selected in such a way that the latter is less oxygen-affine than the basic material, or any oxide that is formed on the protective material can be removed with simpler means than would be the case in an oxide formed on the basic material. Oxide-forming material for the protective layer is advantageously selected in such a way that in addition to the simple removal of the oxide, new oxide is only slowly formed again after the oxide removal. In particular, less than 0.3 nm of oxide, preferably less than 0.1 nm of oxide, is formed on time lapses of at least 2 minutes, preferably at least 5 minutes, more preferably at least 10 minutes, and most preferably at least 15 minutes.

An incorporation of any oxide, formed on the protective layer, in the basic material is in particular at least predominantly prevented according to the disclosure. To this end, the oxide of the protective material is removed in particular immediately before a bonding process. In the case of a smaller amount of formed oxide, a breaking of the oxide during the later desired bonding process and a direct incorporation into the boundary layer are also conceivable. Protective materials with one or more of the properties cited below are preferably used:

- A low oxygen affinity, in particular defined by a standard electrode potential of more than 0 V, preferably more than 1.00 V, more preferably more than 2.00 V, preferably less than the oxygen affinity of the basic material,

- A high solubility in the basic material, in particular more than 10^{-5} mol%, preferably more than 10^{-3} mol%, more preferably more than 1 mol%, most preferably more than 10 mol%, and with utmost preference more than 40 mol%,
- The properties of the basic material are not negatively influenced, and therefore in the case of the desired high conductivity do not impair the conductivity and in the case of the desired high level of strength do not reduce the strength,
- Airtight relative to the atmosphere,
- Economical,
- High level of availability,
- Slightly toxic, in particular non-toxic, and/or
- Good bonding properties.

Accordingly, the disclosure relates in particular to a method for covering, in particular coating, a first material tending toward oxidation, the basic material, in particular a metal or a semiconductor, with a second material, the protective material. The protective material is in particular dissolved at least partially, in particular predominantly, and preferably completely in another process step by a dissolution process of the basic material and/or forms precipitates partially, in particular predominantly, and preferably completely, in a quite special, expanded example. The example that is preferred according to the disclosure comprises a complete dissolution of the protective material into the basic material, whereby in this case, no precipitates are produced. The object of the protective layer formed from the protective material consists in particular in the prevention of the oxidation of the basic material. The protective

material can itself oxidize upon contact with an oxygen-containing atmosphere and is optionally removed from oxide, before the dissolution process according to the invention begins in the basic material. In a quite special example, the removal of this oxide on the protective layer is performed in a unit in which a renewed oxidation of the protective layer is prevented for design reasons on the way to the bonder. For example, the use of an oxide removal module and a bonding chamber in a corresponding vacuum cluster, which separates the module from the surrounding, oxygen-containing atmosphere, would be conceivable. Such cluster systems are well known to one skilled in the art.

The preferred target of the process according to the disclosure primarily consists in protecting oxygen-affine basic materials, in particular aluminum but also copper, which are to be bonded in an additional process step, up to the actual bonding step before an oxidation. The removal of any oxides of the protective material, which preferably has a much lower oxygen affinity than the basic material to be protected, is considerably simpler, faster, and primarily more reliable, so that the process can be accelerated.

According to a preferred example, the protective material, in particular after a removal of oxides of the protective material, is then bonded with another substrate that is formed in particular according to the invention. Preferably, the protective material is at least partially, in particular predominantly, and preferably completely dissolved during the bonding process in the basic material, so that in the ideal case, no contact occurs between the basic material and the oxygen-rich atmosphere until the bonding takes place.

The method according to the disclosure is therefore primarily suitable for temporarily protecting with the protective material oxygen-affine basic materials, in particular aluminum or copper, directly after the coating on a substrate.

To the extent the basic material is not full-surface but rather is applied on the substrate in particular in a structured manner and/or only in partial areas (for example copper contacts or aluminum boundaries, which are to be part of a hermetically-sealed space of a MEMS component), the protective material is applied in the form of a film that is as uniformly thick as possible, and in particular is sealed. According to the disclosure, primarily the ratio of the (in particular middle) layer thickness of the basic material to the layer thickness of the protective material is important. In addition, the chemical, physical and/or metallurgical behavior of the basic material with the protective material according to the disclosure plays a role.

The basic material is preferably a solid solvent. In particular, the basic material can be a multi-phase-multi-component system. In the case of a multi-phase material, all considerations for the dissolution process are valid at least for a phase, in the ideal case for all phases. As basic material, an individual chemical element is preferably selected, in particular a metal, a semi-metal, or a non-metal, in particular silicon, gallium, aluminum, nickel, titanium or copper. These metals are the materials that are most often used in the semiconductor industry for the production of conductive compounds, contact or structural building blocks (for example MEMS assemblies).

In order to disclose the process according to the disclosure as simply as possible, the process according to the disclosure is described by way of example, but not in a limiting manner, with regard to the basic material aluminum. Aluminum is especially

suitable according to the disclosure, since it is a highly-available, economical structural material.

The protective material can in particular also be a multi-phase-multi-component system, but it is preferably a simple chemical element that preferably occurs only in one phase. In this case, it is preferably a metal, a semi-metal, an alkali metal or an alkaline–earth metal. The use of non-metallic elements such as carbon would also be conceivable according to the disclosure as long as the chemical-physical properties correspond between the non-metal with basic material in terms of the process according to the disclosure.

The following materials are considered according to the disclosure in principle as basic material and/or protective material. In this case, the processes according to the disclosure require that the protective material be at least partially, in particular predominantly, and preferably completely, dissolvable in the basic material.

- Metals, in particular
    - Cu, Ag, Au, Al, Fe, Ni, Co, Pt, W, Cr, Pb, Ti, Te, Sn, Zn, Ga
- Alkali metals, in particular
    - Li, Na, K, Rb, Cs
- Alkaline-earth metals, in particular
    - Mg, Ca, Sr, Ba
- Alloys
- Semiconductors, provided in particular with corresponding doping
    - Element semiconductors, in particular
        - Si, Ge, Se, Te, B, Sn

- Sol-gel method

The systems of basic layer and protective layer according to the disclosure are designed as layer systems and in particular represent a system that is not located in thermodynamic equilibrium. As a result, at a temperature that is elevated relative to room temperature, an interdiffusion, preferably at least predominantly and in particular exclusively, brings about a diffusion of the protective material into the basic material between basic material and protective material.

The systems according to the disclosure are designed in particular as a diffusion pair. The described phase diagram as well as any phase diagram of the above-mentioned material combinations represent equilibrium states of several phases at various temperatures and concentrations. The conclusions that can be drawn from equilibrium diagrams such as phase diagrams regarding kinetic processes such as diffusion are very limited. In principle, equilibrium diagrams do not allow any assessment on kinetic processes. The phase diagrams are therefore used exclusively to make an assessment as to whether the protective material in general could dissolve at a specific temperature in the basic material. To the extent that local concentration build-ups occur during the diffusion process of the protective material into the basic material, which exceed the solubility of the protective material in the basic material and thus lead to a possible separation, phase formation or the like, this is ignored in the description below. Hereinafter, in principle, the assumption is that the diffusion of the protective material into the basic material is carried out quickly, so that at a given temperature, at no time anywhere in the basic material is the maximum solubility of protective material exceeded.

This is achieved in particular according to the disclosure in that the greater the solubility of the protective material in the basic material at a given temperature, the faster the protective material diffuses into the basic material and/or the smaller the transfer of protective material into the basic material in the protective-material-basic material interface.

The depicted and described phase diagrams were determined by metallurgy. Many components have a very low solubility in the second components in each case, so that the solubility limit is hardly recognizable based on the depiction.

In order to be able to better describe the ideas according to the disclosure, the idea according to the disclosure of several systems that are as simple as possible is described. As basic material, the technically very important and to date material that is very difficult to bond, aluminum, is used. Therefore, basic material after the deposition on the bonding side of the substrate is a one-component one-phase system.

As protective materials for the protective layer, four important materials are presented below by way of example, and said materials have the necessary properties according to the invention, namely germanium, gallium, zinc and magnesium. Therefore, this protective material after the deposition is also a one-component-one-phase system. The above-mentioned material combinations are preferred according to the disclosure, whereby reference is made to the examples described below with the above-mentioned advantages relative to the individual material combination.

The basic material-protective material system of the bonding layer is accordingly a layer system, which is converted preferably during the bonding process by a dissolution process into a two-component-one-phase system. In this case, a mixed crystal that

consists of basic material and protective material is preferably produced. The bonding process itself takes place either in an inert gas atmosphere, but more preferably in a vacuum.

In an advantageous example of this disclosure, precipitates are desired, in particular by at least one heat treatment being carried out after the (successful) bonding process, in order to produce a two-component-two-phase system by at least partial, in particular predominant, and preferably complete, precipitation of the protective material out of the basic material.

Below, based on more advantageous examples, the disclosure is explained, whereby the examples in each case can be considered independent disclosure aspects per se, which aspects are to be disclosed as separate disclosures and are to be claimable, in particular in combination with the above general disclosure.

In one aspect, the present disclosure provides a method for bonding a first substrate with a second substrate, said method comprising: forming a plurality of structures of oxidizable basic material on a bonding side of the first substrate; removing oxide layers respectively formed on the oxidizable basic material by one or more of chemical oxide removal, grinding, and polishing; at least partially covering each of the oxidizable basic material structures with a layer of protective material having a thickness of less than 100 nm; and bonding the first and second substrates, wherein the protective material is dissolved completely in the oxidizable basic material during the bonding.

In another aspect, the present disclosure provides a method for bonding a first substrate with a second substrate, said method comprising: forming a plurality of areas of oxidizable basic material on a bonding side of the first substrate; removing oxide layers respectively formed on the oxidizable basic material by chemical-mechanical polishing; at least partially covering each of the oxidizable basic material areas with a layer of protective material having a thickness of less than 100 nm; and bonding the first and second substrates, wherein the protective material is dissolved completely in the oxidizable basic material during the bonding.

First Embodiment

A first system, to which the idea according to the invention can be applied, is the aluminum-germanium system, Al-Ge for short. The binary Al-Ge system is a purely eutectic system with a partial boundary solubility for germanium in aluminum and a disappearing low boundary solubility of aluminum in germanium. As basic material, aluminum is therefore selected.

In order to protect the aluminum against oxidation, it is immediately covered with a germanium layer as a protective layer after the successful deposition on the substrate. Germanium is therefore the protective material according to the invention.