

air-stored *J. J. J. J.*
A method for manufacturing parts, use thereof, work piece, and vacuum-processing chamber

The present invention relates to a method for manufacturing parts according to the characterising clause of claim 1, use of this method according to claims 15 to 18, a work piece stored in air according to claim 19, and a vacuum-processing chamber according to claim 20.

Definitions:

The term "intimate connecting method" is understood to include bonding (welding, soldering), gluing, moulding, and coating, especially in a vacuum-coating process, whether PVD or CDV or methods derived therefrom, as well as the so-called "direct bonding", during which carefully cleaned surfaces are connected to one another directly by interatomic forces, as used, for example, in direct wafer bonding of Si on Si, Si on SiO₂, and, furthermore, in the joining of metal surfaces with one another or of metal surfaces with silicon surfaces, for example, Cu - Si or Au - Si. At least one of the surfaces to be intimately joined is always the surface of a solid body.

The following are addressed, in particular, within the scope of the present invention:

- Metal surfaces, especially those made of Cu, Ni, Ag, Au, Pd, Pb, Sn, In or of alloys with at least one of these metals,
- Semi-metal surfaces, especially those made of Si, Ge, B, C, GaAs, GaN, SiC, ZnO, or of a material with at least one of these semi-metals,
- Ceramic surfaces, especially those made of quartz, aluminium oxide, aluminium nitride, zirconium oxide, boron nitride, diamond, and silicon nitride,
- Plastic surfaces on an epoxy or ester basis polyimides, polyvinyl chlorides, polyethylene, polystyrene, polyolymethacrylate, polyamide, polyurethane, phenolic plastics, phenolic resins, siloxanes, Teflon,
- in particular, materials like those typically used in packaging processes for semiconductors, namely hardened epoxy resins, SCSS (semiconductor system substrates) materials made of epoxy (epoxy base laminate substrates), solder resist, photo-resist, etc.

It is essential that those surfaces, which undergo the intimate connecting method, can consist of different portions made of the mentioned various materials. The energy supply for the intimate connecting is, in most cases, of a thermal nature, and is supplied to the surfaces to be joined, for example, by heated tools, Joule effect, UV radiation, or preferably by ultrasound, or by reaction energy during the gluing process and possibly also during moulding.

The present invention is used especially advantageously in packaging of integrated circuits. In this sense, its primary domain of application lies in the field of the semiconductor industry. However, the present invention can also be used in other areas of technology, basically in all those in which, within the scope of the manufacturing method according to the invention, organic or organic/oxidic contaminating compounds must be removed from at least one surface of a solid body before the creation of an intimate bonding.

Although surface materials have been defined above, for which the present invention is known to be suitable, it should be noted that other surface materials, for example, oxides, nitrides, carbides, oxynitrides, oxycarbides, carbonitrides, oxycarbonitrides of at least one of the metals Ti, Ta, Zr, and Hf can be processed according to the invention, especially taking into consideration the intimate connection by coating.

As mentioned above, the procedure according to the invention is also especially suitable for the surfaces of solid bodies that consist of different materials, and especially for those areas consisting of various materials. As far as intimate connection is concerned, such multi-material surfaces pose especially difficult problems.

In the so-called packing of integrated circuits, as a preferred area of application of the present invention, a distinction is made between several work steps that include an intimate connection of surfaces in the above sense:

1. Individual integrated circuits are cut from a silicon wafer, mounted on a semiconductor system substrate (SCSS) and joined with them (the so-called "die-bonding"). The SCSS surface to be joined is usually made of copper or nickel, silver or gold and/or of a material on an epoxy basis, generally of a plastic as mentioned above. Examples of such SCSS are stamped or etched metal lead frames, ceramic substrates, or BGA (Ball Grid Arrays) - substrate carriers made of plastic or also printed circuit boards. The bonding methods used include hard soldering, soft soldering, and gluing. In flip-chip soldering processes, the integrated circuit is mounted on an SCSS by geometrically arranged solder balls, which are simultaneously used as I/O contacts.
2. Joining the integrated circuits with contact supporting points on an SCSS, for example, on a "lead frame": The surfaces involved are metallic, made for example of Al, Au, Cu, Ni, Pd, Ag, Pb, Sn, or alloys of these metals. In this case, soldering or welding are primarily used as joining techniques, especially fluxless soldering or ultrasonic welding. This step is known as "wire bonding".
3. Moulding: in this procedural step, the circuits on the SCSS, for example the lead frames - following "wire bonding" - are encapsulated with a moulding compound, with the aforementioned surfaces of the SCSS and the integrated circuits being involved with the moulding compound.

A cleaning procedure is known from EP-0 371 693 within the scope of a manufacturing process, in which the surfaces later to be bonded in the manner described above exclusively by applying energy are first exposed to a microwave plasma discharge in a vacuum atmosphere containing hydrogen. Then, without breaking the vacuum, the solder layer provided for connecting the surfaces is melted by a plasma discharge. Thus, the formation of a contaminating surface coating that would seriously interfere with subsequent connecting processes is prevented simply by avoiding contact with air.

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J. Gaudin

It is also known from US 5 409 543 that activated hydrogen may be used to prepare a soldering process. As a result, an oxide layer is removed to allow a direct access of the soldering process to the metal surface.

Furthermore, it is known from EP-A-0 427 0 20 that passivated and oxide layers can be pickled, i.e., removed from the surfaces to be joined with a high-frequency plasma pre-treatment with a process gas. The process gases that can be used include, among others, the following gases and mixture of gases: O_2 , H_2 , Cl_2 , N_2O , N_2 , CF_4 , etc. If the aforementioned pickling does not take place immediately before the soldering process as in US-A-5 409 543, the parts to be joined must be kept in an intermediate protective storage, for which purpose suitable containers under protective gas are provided to prevent contamination.

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Within the scope of the three packing steps mentioned above, two plasma processing have been introduced in the meanwhile. They are intended primarily for substrate carrier materials made of plastic (plastic ball grid arrays – PBGA). The plasma treatment before the “wire bonding” (Step 2) serves to clean the surfaces of the metal contact pads usually made of aluminium, on the die (chip) and the contact pads that are made of gold on the system substrate (SCSS), so that electrical contact with the connecting wire, usually gold wire, is ensured. The most important source of contamination of these contact pads is a preceding treatment process (curing) that is used for curing an epoxy adhesive used in Step 1.

A second plasma treatment mostly occurs only after the “wire bonding” (Step 2), prior to the moulding process step (Step 3). This is intended to achieve an improved adhesion of the moulding material.

Both plasma treatment steps mentioned above were usually performed in a vacuum under plasma gas excitation. A high-frequency, microwave, or ECR plasma is mostly employed. The plasma – surface interaction and the cleaning process associated with it, or the surface modification occur by sputtering and/or a chemical reaction with plasma excited gases. For sputtering in a non-reactive atmosphere, usually only argon is used in combination with the self-bias potential of the floating substrate to be cleaned to accelerate argon ions toward the latter and to achieve the desired cleaning effect consisting in removing (surface) material. In plasma-chemical material removal, reactive gases, for example oxygen, are excited, dissociated, or ionised and then enter into a reaction with surface impurities, for example carbon, and carry away the gaseous reaction products such as CO_2 through a pumping system.

It has been known from WO97/39472 of the same patent applicant as of the present invention that there exists a highly advantageous treatment procedure for similar use as the aforementioned plasma treatment. In this process, hydrogen is excited preferably in a plasma discharge, which then removes carbon from the surfaces (for example as CH_4) and simultaneously reduces oxides on the surfaces involved to produce H_2O gas. Sputtering – which involves the risk of redeposition – is avoided, and the above-mentioned process can be applied, without any restrictions, also to metallic substrate carrier materials or silver contact surfaces, which would strongly oxidise in an atmosphere containing excited oxygen, especially in a plasma containing oxygen. This would lead to an adverse effect on the “wire bondability” or “mouldability” (see above Steps 2 and 3). This is also particularly important considering applications for the modern

copper metallization of chips. One very important property of this process is that the surfaces are passivated by hydrogen plasma for a technologically sufficient period of time and so can be stored in air before entering into an intimate connecting in the above sense.

A disadvantage of the mentioned process is that the process window, i.e., the range of the relevant process parameters still depends to a certain degree on the material of the surfaces to be processed and intimately joined later. Thus, for example, the plasma treatment of the substrate carrier materials (strips) normally occurs in magazines. These magazines comprise slits so that the gases excited in the plasma can penetrate and reach the substrate surfaces to be treated in the magazine, and the volatile reaction products of the cleaning can leave the magazine and be pumped off. The substrate surfaces, especially in the case of PBGA (Plastic Ball Grid Array) strips, always consist of a plurality of different materials. The solder-resist is a long-chain organic compound, the surface of the "die" (chip) consists for example of polyimide or silicon nitride, the metallization part usually consists of aluminium and gold.

It can never be ruled out that additional organic impurities remain on the surface of the solder resist that originate from preceding processes applied to strips, e.g., cleaning steps, or that precipitated during the curing of the epoxy, or result on the solder resist from targeted surface treatments such as a treatment to improve the wettability of the moulding material. Under certain circumstances, highly volatile compounds - that evaporate in particular at the beginning of the above-mentioned plasma treatment - may also be present. In the case of the above-mentioned magazines - generally in confined space - this results in locally arising high pressures. It can happen that the chemical equilibrium is altered by these local pressure shifts to such extent that the reactive hydrogen no longer removes hydrocarbons in the aforementioned process, but rather promotes polymerisation. The result of such re-covering can be extremely diverse. Thus, for example, the wire bondability at the contact pads in relation to the achieved pull strength may be reduced, or much longer processing times are required to again remove the deposited layer at an optimum pressure and possibly at a higher temperature.

Because of the above-mentioned diversity of materials on the surface to be treated, however, a prolonged processing time or a more intense plasma processing can, for example, treat some surfaces such as metal surfaces better, while - at the same time - changing other surfaces such as solder resist or the passivation layer to such extent that the adhesion of the moulding material to be added later is made worse (see the discussion to Tests II).

The task of the present invention is to provide a method for manufacturing parts of the initially mentioned type, in which the process window, especially the pre-treatment process window, and in particular its dependence on various surface materials, and also on process parameters, especially on parameters "pressure" and "temperature", is widened. In other words, the method proposed according to the present invention should provide uniformly satisfactory results over an expanded range of parameters such as pressure and temperature and over the entire variety of materials mentioned, as far as the quality of the intimate connecting to be performed later is concerned.

On the basis of this enlarged process window, an improved homogenisation of the processing effect distribution is also to be ensured on multi-material surfaces.

As mentioned above, the results should also be ensured especially for substrates in magazines or for substrates with narrow geometry (slits and holes). Since the plasma-chemical reactions on the substrate surface also depend on the substrate temperature, and larger temperature gradients are involved, especially with plasma treatment in magazines and on extensive substrates, the above-mentioned enlargement of the process window should also promote uniformity.

Thus, a constant surface treatment, including gap surfaces, hole surfaces, groove surfaces, etc. is to be made possible on the substrates themselves.

In addition, any re-covering of the treated surface by deposition or polymerisation should be prevented, the method must be economical, and no explosive and/or environmentally hazardous gases must be employed. On the other hand, the advantages of the above-mentioned method known from WO97/39472, especially its preservative properties, are to be maintained.

The following ~~additional~~ definitions apply: *J. Gaecke*

- Passivation or passivized: see *Römpps Chemielexikon*, Franksche Verlagshandlung, Stuttgart, 8th Edition, page 3005. These terms refer to a bonded protective coating on the surface of a solid body. The clean solid body surface is protected against atmospheric air influences. This is accomplished, for example, by forming an oxide or nitride layer. Such a layer must first be broken up by energy applied specifically for this purpose for producing an intimate connection of the type described above, for example by application of higher temperatures than required for the actual joining process, or chemically, for example by using a flux.
- A basic distinction exists between the above-mentioned passivation and preservation, which in particular does not require any layer separation by additional energy for joining. This preservation is known in connection with the method in WO97/39472, the disclosure of which is incorporated herein by reference to its full extent.

The solution of the above-mentioned problem is provided by the procedure of initially mentioned type and is implemented according to the characterising clause of claim 1. The pre-treatment is performed using plasma-activated gas that contains nitrogen.

Furthermore, in one of the preferred design versions of the manufacturing procedure according to this invention, the plasma-activated gas contains also hydrogen.

Although it is quite possible to use any one of the many known plasma discharge types for plasma activation of the above-mentioned gases, in a generally preferred design version the plasma discharge is produced as a low-voltage discharge, preferably with a thermionic cathode.

In addition, the plasma-activated gas preferably contains a working gas, preferably an inert gas, especially argon.

Even if the above-mentioned plasma-activated gas contains – in addition to nitrogen – other gas components, especially hydrogen and/or a working gas, it can contain, in a preferred manner, primarily nitrogen, and can even consist of nitrogen apart from any working gas.

The solid body surfaces to be intimately joined are materials that are metallic and/or semi-metallic and/or ceramic and/or of plastic, especially according to the materials mentioned on the outset, deemed currently preferred. Preferentially, the above-mentioned solid body surfaces are surfaces with areas composed of different materials, especially of the materials mentioned.

The intimate connection is formed by the manufacturing procedure according to this invention preferably by gluing, soldering, welding, moulding, or coating, especially vacuum coating, which is performed by the so-called "direct bonding".

The above-mentioned preferably used low-voltage discharge is further preferentially operated with a discharge voltage of 30 V or more, preferably with a discharge current between 10 A and 300 A including both limits, especially at 40 A to 70 A.

In an especially preferred design version of the procedure according to the invention, at least one solid body surface to be later intimately connected, following the above-mentioned pre-treatment and prior to its intimate connection, is exposed to air for periods ranging from days to weeks. Thus, it is no longer necessary to further process the above-mentioned surface immediately after its pre-treatment and at the same location. The result is a high degree of flexibility regarding the rhythm and processing location for the implementation of the procedure according to the invention without requiring additional costly cleanliness precautions such as storage under protective gas to be provided.

In an especially preferred design version of the procedure according to the invention, at least one solid body phase is stored in a holding device during the pre-treatment. The holding device defines narrower access areas to the mentioned surface in relation to the plasma discharge chamber. In the overwhelming majority of cases, at least one solid body phase is formed by a disk-shaped or plate-shaped substrate, and the holding device is provided with at least one access slit.

Preferably, the holding device has several of the above-mentioned access slits and forms an actual magazine.

One preferred use of the procedure according to the invention consists in joining integrated circuits with SCSS (Semiconductor System Substrate) or in the electrical connection of integrated circuits by "wire bonding", or for sheathing electrical circuits connected with SCSS and connected by "wire bonding" with a moulding material.

Another preferred use of the procedure is for integrated circuits for flip chip connection and positioning. Firstly, the soldering points can be cleaned of oxide and passivated at the same time and secondly, following plasma treatment, a better wetting of the so-called "underfill" (a moulding material that fills the gap between the chip and the chip carrier and which serves to absorb mechanical stresses) is achieved.

In addition, the procedure according to the invention is also used preferably for workpieces of the type specified in claim 17. The procedure according to the invention is also especially suitable for chips with Cu strip conductors according to claim 18.

A workpiece treated with plasma according to the invention and stored in air is characterised by the fact that the above-mentioned surface of the workpiece that has been exposed to air has an increased nitrogen concentration in comparison with a directly produced surface of the workpiece, which however was not stored in air. This can be demonstrated, for example, by Fourier transform infrared spectroscopy with attenuated total reflection (FTIS-ATR) and/or with nuclear reaction analysis (NRA) or with time-of flight secondary ion mass spectroscopy (TOF-SIMS). As a result of the elevated nitrogen concentration, which indicates the pre-treatment according to the invention, the workpiece according to the invention can be stored in air and then immediately used for intimate connection without any additional pre-treatment in the above sense. In yet another preferred design version of the procedure according to the invention, the intimate connection can be performed by the influence of heat in air, preferably at the solid body's temperature of 150° C.

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J. Gaecke

A vacuum treatment chamber according to the invention is also characterised by the wording of claim 20, with a preferred design version according to claims 21 and 22.

To summarise, we can say that the effect of nitrogen recognised and utilised according to the invention is surprising, especially taking into account the current school of thought (see J.L. Vossen et al., Thin Film Processes, ACADEMIC PRESS, INC. 1978), according to which N₂ plasmas do not remove polymer surfaces.

The invention is explained in further text using figures and examples. The figures show:

- Fig. 1 is a schematic diagram of the design of a system according to the invention as used for the experiments described below,
- Fig. 2 shows the Auger spectrum of copper surfaces (lead frames) for producing a soft-soldered connection,
- Fig. 3 shows a schematic definition of the tensile stress or pull strength F_p of wire-bond connection points,
- Fig. 4 is a graph showing the results of tensile stress (pull strength) capacity tests performed, as indicated in Figure 3, with (a) hydrogen-argon plasma treatment, (b) argon plasma treatment, (c) treatment in an Ar/N₂/H₂ plasma, and (d) treatment in an Ar/N₂ plasma,
- Fig. 5 is a diagram, on the basis of a time / pull strength, showing the long-term effect of the plasma treatment used according to the invention and the pull strength of the intimate connections formed on workpieces according to the invention,

Fig. 6 is analogous to Figure 4 and shows the results of additional pull strength tests,

Fig. 7 is a schematic cross-sectional view of substrates that are also suitable for using the procedure according to the invention.

As mentioned, the plasma discharge for exciting the gas is preferably designed as a low-voltage arc discharge. Systems of the preferred type are known, for example, from:

- DE-OS 43 10 941, corresponding with US-5 384 018
- DE-40 29 270, corresponding with EP-478 909 or DE-40 29 268, corresponding with US-5 336 326
- EP-510 340, corresponding with US-5 308 950

These documents, provided only as an example, show all of the treatment chambers for workpieces using low-voltage arc discharges. As far as the design of such treatment chambers is concerned, the disclosure of these documents is incorporated by reference herein.

Figure 1 shows a preferred system for use according to the invention. A thermionic cathode 3 is mounted and insulated in a cathode chamber 1. Parts 17 of cathode chamber 1 surround a diaphragm aperture 9. Cathode chamber 1 is mounted, by insulating supports 22, on the wall of treatment chamber 11, and comprises a shield 20, which is operated with floating potential relative to both cathode chamber 1 and treatment chamber 11, the portions 17 at dark space distance d up to immediately into the area of diaphragm aperture 9. The thermionic cathode is operated by a source 24 with heating current I_H and is conducted by a voltage source 26 and, generally speaking, a unit 28, at least to a part of the cathode chamber wall, preferably to the cathode chamber wall itself. Unit 28 acts as a current limiter and causes a voltage drop u as a function of the current i flowing through it. As indicated by the dashed lines, it can be achieved in the form of a current-controlled voltage source but preferably in the form of a passive circuit element, especially a resistance element 10.

The positive pole of voltage source 26 can be set to a reference potential, either ground or another specified potential, or can be operated in a potential-free manner as shown, purely schematically, by option switch 32. Similarly, since it is electrically insulated from cathode chamber 1, treatment chamber 11, as schematically shown with switch 34, can be operated at ground potential, a reference potential, or possibly even at a floating potential. The treatment chamber's inner wall 36, or at least parts thereof, can be connected as the anode relative to the thermionic cathode 3; preferably, however, a separate anode 38 as indicated by the dashed lines, can be connected by a voltage source 40 relative to the thermionic cathode 3 as an anode, i.e., positively. Anode 38 is then used preferably as the workpiece carrier for the workpieces W shown schematically. A working gas, as an example and preferably argon, is supplied through gas supply line 41 to the cathode chamber. Through another gas supply line 40 shown schematically, as indicated schematically by switch 35, depending on the potential connection, chamber 11 can be connected to the potential, gas G (X , Y , N_2) containing preferably nitrogen is supplied by a gas tank arrangement 50. Gas G is admitted by a valve 52 as schematically shown.

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Especially in the industrial application of the procedure according to the invention, a magazine 51 is used as the workpiece carrier 51 with the treatment chamber according to the invention. A plurality of substrates to be treated is stacked therein and connected only by insertion slits on the front and/or rear for the substrates, as well as access slits 51a additionally provided in the magazine wall. The geometric ratio H relative to the remaining communication apertures (access slits) between the substrate surfaces and treatment chamber P can then be substantially smaller than the dark space distance of the plasma discharge maintained in the chamber. The surface treatment used according to the invention is performed by the gas containing nitrogen that is excited by the discharge and enters the magazine through the above-mentioned apertures and slits.

It is readily apparent that the treatment procedure used according to the invention is suitable for cleaning surface areas on workpieces and/or substrates that are difficult to access, for example edges, holes, blind holes, grooves, etc., and are intended to be subsequently intimately bonded. Such surface areas are schematically shown in Figure 7.

A pumping system 42 is provided to pump down chamber 11 and possibly cathode chamber 1 as shown, with pumping system 42a possibly being provided as well in order to separately pump down the cathode chamber. The diaphragm arrangement with diaphragm aperture 9 acts as a pressure stage between the pressure in cathode chamber 1 and the pressure in treatment chamber 11.

The wall of cathode chamber 1 forms the ignition electrode: to ignite the low-voltage discharge, the thermionic cathode 3 is heated to electron emission with heating current I_H and argon is admitted to the cathode chamber. Based on the distance ratio between the wall of cathode chamber 1 and cathode 3, as a result of the application of the potential of the latter, the discharge is ignited, whereupon a current i flows through unit 28, especially resistance 30. This reduces the potential Φ_2 , previously at the ignition value, of the cathode chamber wall 17, with the wall of chamber 1 acting as an anode during operation only to a negligible degree and the primary discharge being drawn by the diaphragm arrangement with aperture 9 to anode 38 on the treatment chamber side.

The surfaces of workpieces to be connected were treated by a chamber like the one shown in Figure 1. These can be, for example:

- metal lead frames for soft soldering, for example made of copper, nickel-plated copper, and silver-plated copper.
- Organic SCSS (semiconductor system substrate) materials, such as BGA (Ball Grid Array) and MCM (Multi-chip Modules), for example on an epoxy or ester basis, as well as PCBs (Printed Circuit Boards),
- metallic QFPs (quad flat packs), for example made of copper, silver-plated copper, or palladium-plated copper,

- metallization of strip conductors for organic SCSS materials and QFP, for example made of silver-plated copper, gold-plated copper, or gold,
- semiconductor substrate carriers designed as flip chip with soldering points made, for example, of AgSn, PbSn, PbSnAg, PbInAg,
- semiconductor system substrate materials on a ceramic basis, for example aluminium oxide,
- surface protecting layer of chips, for example made of silicon nitride, silicon oxynitride, and polyimide,
- directly bonded Si-Si wafers

Description of treatment:

Treatment chamber according to Figure 1, which was used for the tests to be described, had a volume of

$$V = 150 \text{ litres}$$

The workpieces of the type described above were placed in the chamber and the operation was as follows:

1. Pumping down to a basic pressure of about 10^{-5} mbar;
2. Activation of cathode 3 with I_H approximately 190A;

2.1 Argon/hydrogen plasma (reference test)

Discharge current:	- Tests I:	50A
	- Tests II:	60A
Argon flow:	20 sccm	
Treatment time:	- Tests I:	10 minutes
	- Tests II:	10 and 20 minutes

2.2 Pre-treatment in argon plasma (second reference test)

Discharge current:	- Tests I:	50A
	- Tests II:	60A
Argon flow:	20 sccm	

Treatment time: - Tests I: 10 minutes
 - Tests II: 10 and 20 minutes

2.3 Pre-treatment according to the invention (combination of $N_2 + H_2$)

Discharge current: - Tests I: 50A
 - Tests II: 60A

Argon flow: 20 sccm

Nitrogen and hydrogen flows: total 20 sccm, 4 volume % hydrogen

Treatment time: - Tests I: 10 minutes
 - Tests II: 10 and 20 minutes

2.4 Pre-treatment according to the invention (only N_2)

Arc current: - Tests I: 50A
 - Tests II: 60A

Argon flow: 20 sccm

Nitrogen flows (pure): 20 sccm

Treatment time: - Tests I: 10 minutes
 - Tests II: 10 and 20 minutes

In all tests, following a heating time of the thermionic cathode of about 30 seconds, with a heating current of approximately 190A, an ignition voltage between cathode 3 and ignition electrode 17 (see Figure 1) was applied. Resistance 30 was set to approximately 28 ohms and connected to ground. Following the ignition of the discharge (ignition voltage approximately 20 to 30 V) a discharge voltage develops between cathode 3 and anode 38 of approximately 25 V with 50 A discharge current, with preferred use of a welding generator if recipient wall 11, at ground, is used as the anode. 20 *J. Jacobsen*

Ions and excited neutrons are generated, an indication of which is the typical plasma glow. The workpieces to be treated in the magazines were surface-treated in the plasma thus produced. The nitrogen and possibly the hydrogen volatile compounds with impurities were pumped off by pumping system 42.

The working pressure was approximately 5×10^{-3} mbar.

As shown in Figure 1, magazines 51 were used that had access slit widths H (see Figure 1) from 1 mm to 10 mm.

Instead of placing the magazine and hence the workpieces at ground potential, especially the latter can be set to floating potential or to a different reference potential and then exposed to plasma. In view of the fact that the potential of the workpieces relative to the plasma potential in the low-voltage discharge described above is very low, (≤ 20 V), both the problem of re-deposition of material on the workpiece as it occurs in the so-called free sputtering, and also and especially – the danger of the destruction of integrated circuits that are critical with respect to electrical potential differences can be ruled out. Cleaning and preservation occur solely by chemical processes, which are effected either by electrons, with workpieces suitably connected to potential, or by low-energy ions and electrons in workpieces that are operated in a floating manner.

The large number of electrons present in the plasma ensures a high reactivity of the plasma, and hence short treatment times, which is critical for the economy of the proposed procedure. Another advantage is that the plasma penetrates small hollow spaces especially in the magazine shown. Thus for example workpieces can be treated without being removed from the cassette or magazine shown here, which is especially economical.

PBGA-SCSS as well as lead frames with copper surfaces were treated as workpieces for a subsequent production of a soft-soldered connection.

Results:

Figure 4 shows the tensile strength results. The tensile strength and pulling force F_p of the intimate connections were measured on PBGA SCSS (semiconductor system substrates) treated according to the invention, the connections being produced by gold wire bonding. This procedure is schematically shown in Figure 3. 53 indicates the connecting point with the surface of a lead frame 57a treated according to the invention.

The surfaces of the treated substrates had previously been treated by the manufacturers in an unknown manner. Following this pre-treatment, the danger of a re-deposition from the gas phase, in other words plasma polymerisation, on the surface was foreseeable.

On the substrates not subjected to any further treatment, obtained from the manufacturers, no wire bonding connections could be made. The resulting tensile strengths for Tests I are shown in Figure 4. The treated substrates were precisely the substrates that are unsuitable for an argon/hydrogen plasma treatment: the feared re-deposition from the gas phase, in other words plasma polymerisation, did in fact occur during the argon/hydrogen plasma treatment, as indicated by the relatively poor tensile strength results (a).

A tensile strength of approximately 3.3 cN was measured.

A treatment in argon plasma produced slightly better results (b) with a tensile strength of approximately 3.6 cN. Evidently the simple heating of the substrate surfaces and the associated desorption alone produced better values than could be achieved in argon/hydrogen plasma because of plasma polymerisation.

Clearly better results were measures as the result of treatment according to the invention, namely in an argon/nitrogen plasma with a tiny hydrogen component, in the present case approximately 4 percent according to (chamber) and in argon/nitrogen plasma according to (d). It should be noted at this point that if hydrogen is added to gas G to be excited, it should in any event result in a smaller amount than ~~if the gas contained nitrogen~~ ^{the amount of nitrogen contained in the gas.}

In the substrates treated according to the invention, the tensile strengths measured were approximately 5 cN (c) or far more than 5 cN (d).

As a principle, specified tensile strength required for the described connection is 5 cN.

Figure 5 shows long-term effects of the cleaning effect for substrates, which – as just described – were treated according to Test 1 (chamber), in other words in argon/nitrogen/hydrogen (4 volume_{N2} %) plasmas.

On the one hand, the future tensile strength F_p is to be considered, on the other hand, it is the storage time of the treated substrates in air up to the creation of the wire bonding that matters.

It turns out that the measured tensile strength values remain unchanged, within the measurement accuracy, for seven days, in other words there was no re-contamination of the surfaces exposed in the plasma treatment procedure.

Figure 6 shows the results of Tests II in analogy with the tests according to Figure 4. The results marked with "*" were obtained with a 10-minute treatment, while those marked "***" were obtained with a 20-minute treatment. The discharge current – as mentioned above – was 60 A. The tests (a) to (d) according to Figure 6 and those according to Figure 4 mutually correspond. Figure 6 does not show the tests on the substrates treated in argon plasma, but they were clearly worse than the tests according to (a), in other words those treated in the argon/hydrogen plasma.

From this it becomes clear that despite a higher discharge current as compared with Tests I, with a 10-minute treatment in argon/hydrogen plasma (a), the required tensile strength of 5 cN were still not reached. For the plasma treatment according to (c) and (d), however, they have – even with the above-mentioned 10-minute treatment at an arc current of 60 A, far above the required value, namely approximately 6.5 cN (c) and 6 cN (d). Thus, similarly good results can be obtained in argon/hydrogen plasma only by extending the treatment time. This involves a higher thermal load on the substrate, and with a longer treatment time undesired effects can occur on substrates with different additional material surfaces. While no problems with subsequent moulding occurred on substrates treated according to (c) and (d) according to the invention, a partial delamination of the moulding material was observed in the substrates treated according to (a) (figure 6). It is precisely this that indicates that even with respect to materials to be used, the treatment procedure employed according to the invention has a wider process window.

It is also important to note that the tensile capacity tests presented in Figure 6 were performed on substrates five days after their plasma treatment according to the invention, while Tests I

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according to Figure 1 resulted during bonding on the same day, on which the plasma treatment was applied.

Finally, Figure 2 shows the Auger spectra of copper surfaces (lead frames) for the production of a soft-soldered connection.

Spectrum (a) was recorded on a lead frame not treated according to the invention.

Spectrum (b) was recorded following a 2-minute pre-treatment according to the invention as shown in Figure 4, Tests I (d), spectrum (c) was recorded following a 4-minute pre-treatment of this kind, while spectrum (d) was recorded following a 6-minute pre-treatment of this kind. It is especially the development of the C peak at 271 eV and the N peak at 379 eV, and the O peak at 503 eV that demonstrate the cleaning action of the procedure according to the invention. The substrates, on which the spectra according to Figure 2 were recorded, were treated in argon/nitrogen/hydrogen (4%) plasma. With treatment in argon/nitrogen plasma according to (d) in Figures 4 to 6, the behaviour relative to C and N remains essentially the same but oxygen is not completely reduced. *1) and the stated treatment times.*

which
can According to the invention, workpieces that have been treated in plasma with nitrogen and then simply stored in air, as mentioned above, can be recognised by their significant surface nitrogen concentration.

Patent claims:

1. A procedure for manufacturing parts with intimate connection of at least two material phases, of which at least one is a solid body phase, and in which procedure, prior to intimate connection, at least the surface of the solid body phase to be connected is pre-treated, characterised in that the pre-treatment is performed by means of a plasma-activated gas that contains nitrogen.
2. Procedure according to claim 1, characterised in that the pre-treatment is performed by means of a plasma-activated gas that contains hydrogen.
3. Procedure according to one of claims 1 or 2, characterised in that the plasma discharge is produced as a low-voltage discharge, preferably from a thermionic electron-emitting cathode.
4. Procedure according to one of claims 1 to 3, characterised in that the pre-treatment is performed by means of a plasma-activated gas that primarily contains nitrogen.
5. Procedure according to one of claims 1 to 4, characterised in that the pre-treatment is performed by means of a plasma-activated gas that contains a working gas, preferably an inert gas, while argon is especially preferred.



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according to Figure 1 resulted during bonding on the same day, on which the plasma treatment was applied.

Finally, Figure 2 shows the Auger spectra of copper surfaces (lead frames) for the production of a soft-soldered connection.

Spectrum (a) was recorded on a lead frame not treated according to the invention.

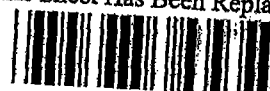
Spectrum (b) was recorded following a 2-minute pre-treatment according to the invention as shown in Figure 4, Tests I (d), spectrum (c) was recorded following a 4-minute pre-treatment of this kind, while spectrum (d) was recorded following a 6-minute pre-treatment of this kind. It is especially the development of the C peak at 271 eV and the N peak at 379 eV, and the O peak at 503 eV that demonstrate the cleaning action of the procedure according to the invention. The substrates, on which the spectra according to Figure 2 were recorded, were treated in argon/nitrogen/hydrogen (4%) plasma. With treatment in argon/nitrogen plasma according to (d) in Figures 4 to 6, the behaviour relative to C and N remains essentially the same but oxygen is not completely reduced. *1) and the stated treatment times.*

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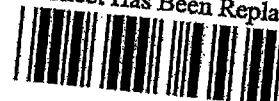
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6. Procedure according to one of claims 1 to 5, characterised in that at least one solid body surface to be intimately connected is metallic and/or semi-metallic and/or ceramic and/or made of plastic.
7. Procedure according to one of claims 1 to 6, characterised in that the intimate connection is performed by gluing, soldering, welding, moulding, or coating, especially vacuum coating, or by direct bonding.
8. Procedure according to claim 3, characterised in that the low-voltage discharge is operated with a discharge voltage ≤ 30 V and preferably with a discharge current between 10 A and 300 A (including both limits).
9. Procedure according to one of claims 1 to 8, characterised in that at least one solid body surface to be connected is exposed to air following the pre-treatment step and prior to the intimate connection step.
10. Procedure according to one of claims 1 to 9, characterised in that the intimate connection is performed by ultrasonic welding.
11. Procedure according to one of claims 1 to 10, characterised in that at least one solid body phase is stored, during the pre-treatment step, in a holding device, which defines – relative to the plasma discharge chamber – narrower access areas on the surface.
12. Procedure according to claim 11, characterised in that at least one solid body phase is formed by a disk-shaped or plate-shaped substrate, and the holding device has at least one access slit therefor.
13. Procedure according to claim 12, characterised in that a magazine (12) with a plurality of access slits is used as the holding device.
14. Procedure according to one of claims 1 to 13, characterised in that the intimate connection is created in air, preferably at a maximum solid body temperature of 150° C.
15. Use of the procedure according to claims 1 to 14 for connecting integrated circuits with a SCSS (semi-conductor system substrate), or for the electrical connection of printed circuits by wire bonding, or for sheathing of electrical circuits joined with SCSS and connected by wire bonding with a moulding compound.
16. Use of the procedure according to one of claims 1 to 11 for integrated circuits that are to be connected to a flip chip and to be positioned and SCSS, by melting the soldering points of the circuit and the SCSS.
17. Use of the procedure according to one of claims 1 to 13 for workpieces with surfaces to be intimately connected with poorly accessible surface areas, especially edges, holes, blind holes, gaps, and grooves.

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18. Use of the procedure according to one of claims 1 to 13 for chips with copper strip conductors.
19. A workpiece stored in air, characterised in that its surface exposed to air has an elevated nitrogen concentration as opposed to a surface produced directly, which is detectable for example by Fourier transform infrared spectroscopy with attenuated total reflection (FTIS-ATR) and/or with nuclear reaction analysis (NRA) or with time-of-flight secondary ion mass spectroscopy (TOF-SIMS).
20. A vacuum-treatment chamber comprising a plasma discharge section, a gas supply to the chamber, connected with a gas tank arrangement and a workpiece holding device, characterised in that the gas tank arrangement comprises a gas with nitrogen, and the holding device comprises at least one access slit open towards the discharge chamber for a disk-shaped or plate-shaped workpiece.
21. A treatment chamber according to claim 20, characterised in that the plasma discharge section is a low-voltage discharge section, preferably with an electron-emitting hot cathode and/or in that the gas in the gas tank arrangement contains hydrogen and/or a working gas, preferably including at least one inert gas, while especially preferred is argon, and primarily nitrogen in a predominant quantity.
22. A chamber according to one of claims 20 or 21, characterised in that the workpiece holding device is a magazine with stacked access slits.

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