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(54) TEMPORARY WAFER BONDING METHOD USING A CYCLOOLEFIN BONDING COMPOSITION

VERFAHREN ZUM TEMPORÄREN WAFERBONDEN UNTER VERWENDUNG EINER CYCLOOLEFIN-VERBINDUNGSZUSAMMENSETZUNG

PROCÉDÉ DE LIAISON DE PLAQUETTES TEMPORAIRE EN UTILISANT UNE COMPOSITION DE LIASON CYCLOOLÉFINE

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- **SHIN J Y ET AL: "Chemical structure and physical properties of cyclic olefin copolymers", PURE & APPLIED CHEMISTRY, PERGAMON PRESS, OXFORD, GB, vol. 77, no. 5, 1 January 2005 (2005-01-01), pages 801-814, XP003019503, ISSN: 0033-4545, DOI: 10.1351/PAC200577050801**
- **"The New Penguine Dictionary of Science, Copolymer", 1 January 1998 (1998-01-01), THE NEW PENGUINE DICTIONARY OF SCIENCE, PENGUINE BOOKS, LONDON, GB, PAGE(S) 150, XP002695434, ISBN: 978-0-14-051271-7 * page 150, 10th paragraph ***

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Description

Background of The Invention

Field of the Invention

[0001] The present invention is broadly concerned with methods of using compositions to form bonding compositions that can support active wafers on a carrier wafer or substrate during wafer thinning and other processing.

Description of the Prior Art

[0002] Wafer (substrate) thinning has been used to dissipate heat and aid in the electrical operation of integrated circuits (IC). Thick substrates cause an increase in capacitance, requiring thicker transmission lines, and, in turn, a larger IC footprint. Substrate thinning increases impedance while capacitance decreases impedance, causing a reduction in transmission line thickness, and, in turn, a reduction in IC size. Thus, substrate thinning facilitates IC miniaturization.

[0003] Geometrical limitations are an additional incentive for substrate thinning. Via holes are etched on the backside of a substrate to facilitate frontside contacts. In order to construct a via using common dry-etch techniques, geometric restrictions apply. For substrate thicknesses of less than 100 μm, a via having a diameter of 30-70 μm is constructed using dry-etch methods that produce minimal post-etch residue within an acceptable time. For thick substrates, vias with larger diameters are needed. This requires longer dry-etch times and produces larger quantities of post-etch residue, thus significantly reducing throughput. Larger vias also require larger quantities of metallization, which is more costly. Therefore, for backside processing, thin substrates can be processed more quickly and at lower cost.

[0004] Thin substrates are also more easily cut and scribed into ICs. Thinner substrates have a smaller amount of material to penetrate and cut and therefore require less effort. No matter what method (sawing, scribe and break, or laser ablation) is used, ICs are easier to cut from thinner substrates. Most semiconductor wafers are thinned after frontside operations. For ease of handling, wafers are processed (i.e., frontside devices) at their normal full-size thicknesses, e.g., 600-700 μm. Once completed, they are thinned to thicknesses of 100-150 μm. In some cases (e.g., when hybrid substrates such as gallium arsenide (GaAs) are used for high-power devices) thicknesses may be taken down to 25 μm.

[0005] Mechanical substrate thinning is performed by bringing the wafer surface into contact with a hard and flat rotating horizontal platter that contains a liquid slurry. The slurry may contain abrasive media along with chemical etchants such as ammonia, fluoride, or combinations thereof. The abrasive provides "gross" substrate removal, i.e., thinning, while the etchant chemistry facilitates "polishing" at the submicron level. The wafer is maintained in contact with the media until an amount of substrate has been removed to achieve a targeted thickness.

[0006] For a wafer thickness of 300 μm or greater, the wafer is held in place with tooling that utilizes a vacuum chuck or some means of mechanical attachment. When wafer thickness is reduced to less than 300 μm, it becomes difficult or impossible to maintain control with regard to attachment and handling of the wafer during further thinning and processing. In some cases, mechanical devices may be made to attach and hold onto thinned wafers, however, they are subject to many problems, especially when processes may vary. For this reason, the wafers ("active" wafers) are mounted onto a separate rigid (carrier) substrate or wafer. This substrate becomes the holding platform for further thinning and post-thinning processing. Carrier substrates are composed of materials such as sapphire, quartz, certain glasses, and silicon, and usually exhibit a thickness of 1000 μm. Substrate choice will depend on how closely matched the coefficient of thermal expansion (CTE) is between each material. However, most of the currently available adhesion methods do not have adequate thermal or mechanical stability to withstand the high temperatures encountered in backside processing steps, such as metallization or dielectric deposition and annealing. Many current methods also have poor planarity (which contributes excessive total thickness variation across the wafer dimensions), and poor chemical resistance.

[0007] One method that has been used to mount an active wafer to a carrier substrate is via a thermal release adhesive tape. This process has two major shortcomings. First, the tapes have limited thickness uniformity across the active wafer/carrier substrate interface, and this limited uniformity is often inadequate for ultra-thin wafer handling. Second, the thermal release adhesive softens at such low temperatures that the bonded wafer/carrier substrate stack cannot withstand many typical wafer processing steps that are carried out at higher temperatures.

[0008] Thermally stable adhesives, on the other hand, often require excessively high bonding pressures or bonding temperatures to achieve sufficient melt flow for good bond formation to occur. Likewise, too much mechanical force may be needed to separate the active wafer and carrier wafer because the adhesive viscosity remains too high at practical debonding temperatures. Thermally stable adhesives can also be difficult to remove without leaving residues.

[0009] US2008/0200011 A1 discloses a temporary wafer bonding method using bonding compositions which have thermal stability at 200°C.

[0010] There is a need for new compositions and methods of adhering an active wafer to a carrier substrate that can endure high processing temperatures and that allow for ready separation of the wafer and substrate at the appropriate stage of the process.

Summary of the Invention

[0011] The present invention provides a temporary wafer bonding method as defined in claim 1. Preferred embodiments are defined in the dependent claims.

[0012] The present invention overcomes the problems of the prior art by broadly providing a wafer bonding method, which includes providing a stack comprising first and second substrates bonded together via a bonding layer, and separating the first and second substrates. The bonding layer is formed from a composition comprising a cycloolefin copolymer (COC) dissolved or dispersed in a solvent system.

Brief Description of the Drawings

[0013]

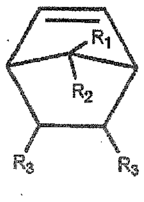
Figure (Fig.) 1 illustrates a method of thinning and debonding two wafers according to an embodiment of the present invention;
Fig. 2 is a flow diagram showing the typical process steps followed in the examples;
Fig. 3 is a graph depicting the rheological analysis results of bonding compositions debonded at 150°C;
Fig. 4 is a graph depicting the rheological analysis results for bonding compositions debonded at 200°C; and
Fig. 5 is a graph depicting the rheological analysis results for bonding compositions debonded at 250°C.

Detailed Description of the Preferred Embodiments

[0014] In more detail, the inventive method employs bonding compositions which comprise a cycloolefin copolymer (COC) dispersed or dissolved in a solvent system. The copolymer is preferably present in the composition at levels of from about 5% to about 85% by weight, more preferably from about 5% to about 60% by weight, and most preferably from about 10% to about 40% by weight, based upon the total weight of the composition taken as 100% by weight.

[0015] The copolymers are thermoplastic and have a weight average molecular weight (M_w) of from about 2,000 Daltons to about 200,000 Daltons, and more preferably from about 5,000 Daltons to about 100,000 Daltons. Preferred copolymers preferably have a softening temperature (melt viscosity at 3,000 Pa·S) of at least about 100°C, more preferably at least about 140°C, and even more preferably from about 160°C to about 220°C. Suitable copolymers also preferably have a glass transition temperature (T_g) of at least about 60°C, more preferably from about 60°C to about 200°C, and most preferably from about 75°C to about 160°C.

[0016] The cycloolefin copolymers are comprised of recurring monomers of cyclic olefins and acyclic olefins. Cyclic olefins for use in the present invention are selected from the group consisting of norbornene-based olefins, tetracyclododecene-based olefins, dicyclopentadiene-based olefins, and derivatives thereof. Derivatives include alkyl (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls), alkylidene (preferably C_1-C_{20} alkylidenes, more preferably C_1-C_{10} alkylidenes), aralkyl (preferably C_6-C_{30} aralkyls, more preferably C_6-C_{18} aralkyls), cycloalkyl (preferably C_3-C_{30} cycloalkyls, more preferably C_3-C_{18} cycloalkyls), ether, acetyl, aromatic, ester, hydroxy, alkoxy, cyano, amide, imide, and silyl-substituted derivatives. Cyclic olefins for use in the present invention are those selected from the group consisting of



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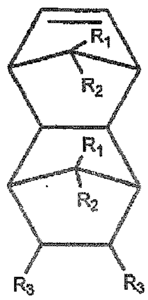

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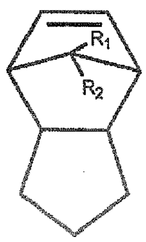

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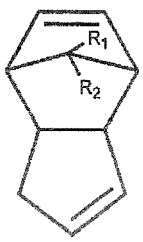

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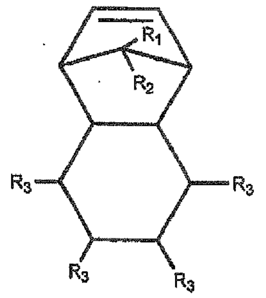

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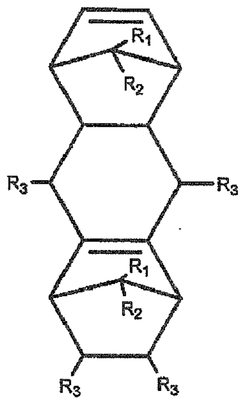

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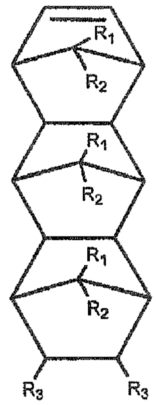

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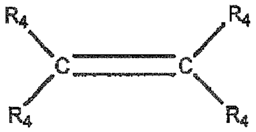
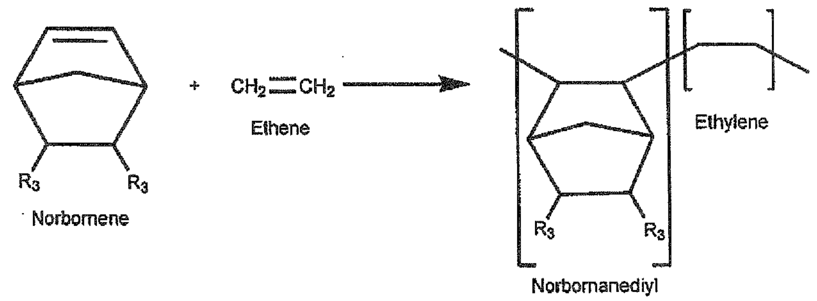
and combinations of the foregoing, where each R_1 and R_2 is individually selected from the group consisting of-H, and alkyl groups (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls), and each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups (preferably C_6-C_{18} aryls), alkyl groups (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls), cycloalkyl groups (preferably C_3-C_{30} cycloalkyl groups, more preferably C_3-C_{18} cycloalkyl groups), aralkyl groups (preferably C_6-C_{30} aralkyls, more preferably C_6-C_{18} aralkyl groups such as benzyl, phenethyl, and phenylpropyl, etc.), ester groups, ether groups, acetyl groups, alcohols (preferably C_1-C_{10} alcohols), aldehyde groups, ketones, nitriles, and combinations thereof.

[0017] Acyclic olefins are selected from the group consisting of branched and unbranched C_2-C_{20} alkenes (preferably C_2-C_{10} alkenes). More preferably, suitable acyclic olefins for use in the present invention have the structure



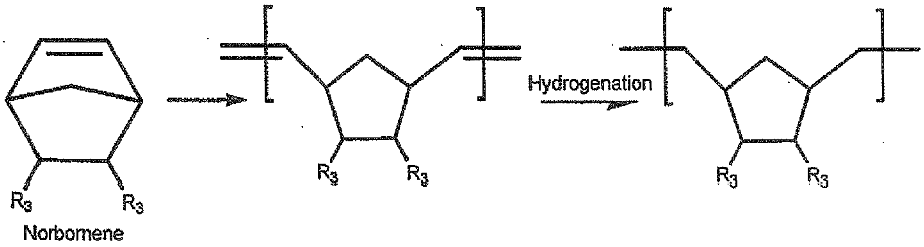
where each R_4 is individually selected from the group consisting of-H and alkyl groups (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls). Particularly preferred acyclic olefins for use in the present invention include those selected from the group consisting of ethene, propene, and butene, with ethene being the most preferred.

[0018] Methods of producing cycloolefin copolymers are known in the art. For example, cycloolefin copolymers can be produced by chain polymerization of a cyclic monomer with an acyclic monomer (such as norbornene with ethene as shown below).

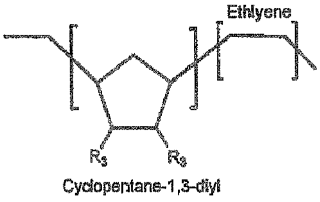


The reaction shown above results in an ethene-norbornene copolymer containing alternating norbornanediyl and ethylene units. Examples of copolymers produced by this method include TOPAS®, produced by Goodfellow Corporation and TOPAS Advanced Polymers, and APEL®, produced by Mitsui Chemicals. A suitable method for making these copolymers is disclosed in U.S. Patent No. 6,008,298, incorporated by reference herein.

[0019] Cycloolefin homopolymers, which are not used as bonding compositions in the present invention, can be produced by ring-opening metathesis polymerization of various cyclic monomers followed by hydrogenation as illustrated below.



The polymers resulting from this type of polymerization can be thought of conceptually as a copolymer of ethene and a cyclic olefin monomer (such as alternating units of ethylene and cyclopentane-1,3-diyl as shown below).



Examples of polymers produced by this method include ZEONOR® from Zeon Chemicals, and ARTON® from JSR Corporation. A suitable method of making these polymers is disclosed in U.S. Patent No. 5,191 ,026.

[0020] The bonding compositions may be formed by simply mixing the cycloolefin copolymer and any other ingredients with the solvent system, preferably at room temperature to about 150°C, for time periods of from about 1-72 hours.

[0021] The composition preferably comprises at least about 15% by weight solvent system, preferably from about 30% to about 95% by weight solvent system, more preferably from about 40% to about 90% by weight solvent system, and even more preferably from about 60% to about 90% by weight solvent system, based upon the total weight of the composition taken as 100% by weight. The solvent system preferably has a boiling point of from about 50-280°C, and preferably from about 120-250°C. Suitable solvents include, but are not limited to, methyl ethyl ketone (MEK) and cyclopentanone, as well as hydrocarbon solvents selected from the group consisting of limonene, mesitylene, dipentene, pinene, bicyclohexyl, cyclododecene, 1-tert-butyl-3,5-dimethylbenzene, butylcyclohexane, cyclooctane, cycloheptane, cyclohexane, methylcyclohexane, and mixtures thereof.

[0022] The total solids level in the composition are preferably at least about 5% by weight, preferably from about 5% to about 85% by weight, more preferably from about 5% to about 60% by weight, and even more preferably from about 10% to about 40% by weight, based upon the total weight of the composition taken as 100% by weight.

[0023] The bonding composition can include additional ingredients, including low molecular weight cycloolefin copolymer (COC) resins and/or tackifier resins or rosins. The composition can also include a number of optional ingredients selected from the group consisting of plasticizers, antioxidants, and mixtures thereof.

[0024] When a low molecular weight COC resin is used in the composition, it is preferably present in the composition at a level of from about 2% to about 80% by weight, more preferably from about 5% to about 50% by weight, and even more preferably from about 15% to about 35% by weight, based upon the total weight of the composition taken as 100% by weight. The term "low molecular weight cycloolefin copolymer" is intended to refer to COCs having a weight average molecular weight (M_w) of less than about 50,000 Daltons, preferably less than about 20,000 Daltons, and more preferably from about 500 to about 10,000 Daltons. Such copolymers also preferably have a T_g of from about 50°C to about 120°C, more preferably from about 60°C to about 90°C, and most preferably from about 60°C to about 70°C. Exemplary low molecular weight COC resins for use in the present compositions are those sold under the name TOPAS® Toner TM (M_w 8,000), available from Topas Advanced Polymers.

[0025] When a tackifier or rosin is utilized, it is preferably present in the composition at a level of from about 2% to about 80% by weight, more preferably from about 5% to about 50% by weight, and even more preferably from about 15% to about 35% by weight, based upon the total weight of the composition taken as 100% by weight. The tackifiers are chosen from those having compatible chemistry with the cycloolefin copolymers so that no phase separation occurs in the compositions. Examples of suitable tackifiers include, but are not limited to, polyterpene resins (sold under the name SYLVARES™ TR resin; Arizona Chemical), beta-polyterpene resins (sold under the name SYLVARES™ TR-B resin; Arizona Chemical), styrenated terpene resins (sold under the name ZONATAC NG resin; Arizona Chemical), polymerized rosin resins (sold under the name SYLVAROS® PR resin; Arizona Chemical), rosin ester resins (sold under the name EASTOTAC™ resin; Eastman Chemical), cyclo-aliphatic hydrocarbon resins (sold under the name PLASTOLYN™ resin; Eastman Chemical, or under the name ARKON™ resin; Arakawa Chemical), C5 aliphatic hydrocarbon resins (sold under the name PICCOTAC™ resin; Eastman Chemical), hydrogenated hydrocarbon resins (sold under the name REGALITE™ resin; Eastman Chemical), and mixtures thereof.

[0026] When an antioxidant is utilized, it is preferably present in the composition at a level of from about 0.1% to about 2% by weight, and more preferably from about 0.5% to about 1.5% by weight, based upon the total weight of the composition taken as 100% by weight. Examples of suitable antioxidants include those selected from the group consisting of phenolic antioxidants (such as pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate sold under the name IRGANOX® 1010 by Ciba), phosphite antioxidants (such as tris(2,4-ditert-butylphenyl)phosphite sold under the name IRGAFOS® 168 by Ciba), phosphonite antioxidants (such as tetrakis(2,4-di-tert-butylphenyl)[1,1-biphenyl]-4,4'-diylbisphosphonite sold under the name IRGAFOX® P-EPQ by Ciba), and mixtures thereof.

[0027] In alternative embodiments, it is preferred that the compositions are essentially free (less than about 0.1% and preferably about 0% by weight) of adhesion promoting agents, such as bis(trimethoxysilylethyl)benzene, aminopropyl tri(alkoxy silanes) (e.g., aminopropyl tri(methoxy silane), aminopropyl tri(ethoxy silanes), -phenyl aminopropyl tri(ethoxy silane)), and other silane coupling agents, or mixtures thereof. In some embodiments, the final composition is also thermoplastic (i.e., noncrosslinkable). Thus, in these alternative embodiments, the composition will be essentially free (less than about 0.1% by weight and preferably about 0% by weight) of crosslinking agents, such as POWDERLINK® by Cytec, and EPI-CURE™ 3200 by Hexion Specialty Chemicals.

[0028] According to one aspect, the melt viscosity (complex coefficient of viscosity) of the final composition will preferably be less than about 100 Pa·S, more preferably less than about 50 Pa·S, and even more preferably from about 1 Pa·S to about 35 Pa·S. For purposes of these measurements, the melt viscosity is determined via rheological dynamic analysis (TA Instruments, AR-2000, two parallel-plate configuration where the plates have a diameter of 25 mm). Furthermore, the melt viscosity is preferably determined at the preferred debonding temperature of the composition in question. As used herein, the term "preferred debonding temperature" of the composition is defined as the temperature at which the melt viscosity of the composition is below 100 Pa·S, and is determined by dynamic measurement at 1 Hz oscillation frequency in temperature ramp. The compositions also preferably have a storage modulus (G') of less than about 100 Pa, preferably less than about 50 Pa, and even more preferably from about 1 Pa to about 26 Pa, when measured at the preferred debonding temperature of the composition. The storage modulus is determined by dynamic measurement at 1 Hz oscillation frequency in temperature ramp.

[0029] The compositions are thermally stable up to about 350°C. There is also preferably less than about 5% by weight, and more preferably less than about 1.5% by weight, loss of the composition after one hour at the preferred debonding temperature plus 50°C (preferably at a temperature of from about 200°C to about 300°C), depending upon the composition. In other words, very little to no thermal decomposition occurs in the composition at this temperature, as determined by thermogravimetric analysis (TGA), described herein.

[0030] Although the composition could be applied to either the carrier substrate or active wafer first, it is preferred that it be applied to the active wafer first. These compositions can be coated to obtain void-free thick films required for bump wafer applications and to achieve the required uniformity across the wafer. A preferred application method involves spin-coating the composition at spin speeds of from about 500-5000 rpm (more preferably from about 1000-3500 rpm), at accelerations of from about 3000-10,000 rpm/second, and for spin times of from about 30-180 seconds. It will be appreciated that the application steps can be varied to achieve a particular thickness.

[0031] After coating, the substrate can be baked (e.g., on a hot plate) to evaporate the solvents. Typical baking would be at temperatures of from about 70-250°C, and preferably from about 80-240°C for a time period of from about 1-60 minutes, and more preferably from about 2-10 minutes. The film thickness (on top of the topography) after bake will typically be at least about 1 μm, and more preferably from about 10-200μm.

[0032] After baking, the desired carrier wafer is contacted with, and pressed against, the layer of inventive composition. The carrier wafer is bonded to this inventive composition by heating at a temperature of from about 100-300°C, and preferably from about 120-180°C. This heating is preferably carried out under vacuum and for a time period of from about 1-10 minutes, under a bond force of from about 0.1 to about 25 kiloNewtons. The bonded wafer can be subjected to backgrinding, metallization, patterning, passivation, via forming, and/or other processing steps involved in wafer thinning, as explained in more detail below.

[0033] Fig. 1(a) illustrates an exemplary stack 10 comprising active wafer 12 and carrier wafer or substrate 14. It will be appreciated that stack 10 is not shown to scale and has been exaggerated for the purposes of this illustration. Active wafer 12 has an active surface 18. As shown in Fig. 1(a), active surface 18 can comprise various topographical features 20a-20d. Typical active wafers 12 can include any microelectronic substrate. Examples of some possible active wafers 12 include those selected from the group consisting of microelectromechanical system (MEMS) devices, display devices, flexible substrates (e.g., cured epoxy substrates, roll-up substrates that can be used to form maps), compound semiconductors, low k dielectric layers, dielectric layers (e.g., silicon oxide, silicon nitride), ion implant layers, and substrates comprising silicon, aluminum, tungsten, tungsten silicide, gallium arsenide, germanium, tantalum, tantalum nitrite, SiGe, and mixtures of the foregoing.

[0034] Carrier substrate 14 has a bonding surface 22. Typical carrier substrates 14 comprise a material selected from the group consisting of sapphire, ceramic, glass, quartz, aluminum, silver, silicon, glass-ceramic composites (such as products sold under the name Zerodur®, available from Schott AG), and combinations thereof.

[0035] Wafer 12 and carrier substrate 14 are bonded together via bonding composition layer 24. Bonding layer 24 is formed of the cycloolefin copolymer compositions described above, and has been applied and dried as also described above. As shown in the Fig. 1(a), bonding layer 24 is bonded to active surface 18 of wafer 12 as well as to bonding surface 22 of substrate 14. Unlike prior art tapes, bonding layer 24 is a uniform (chemically the same) material across its thickness. In other words, the entire bonding layer 24 is formed of the same composition.

[0036] It will be appreciated that, because bonding layer 24 can be applied to active surface 18 by spin-coating or spray-coating, the bonding composition flows into and over the various topographical features. Furthermore, the bonding layer 24 forms a uniform layer over the topography of active surface 18. To illustrate this point, Fig. 1 shows a plane designated by dashed line 26, at end portion 21 and substantially parallel to back surface 16. The distance from this plane to bonding surface 22 is represented by the thickness "T." The thickness "T" will vary by less than about 20%, preferably by less than about 10%, more preferably by less than about 5%, even more preferably by less than about 2%, and most preferably less than about 1% across the length of plane 26 and substrate 14.

[0037] The wafer package can then be subjected to subsequent thinning (or other processing) of the substrate as shown in Fig. 1(b), where 12' presents the wafer 12 after thinning. It will be appreciated that the substrates can be thinned to thicknesses of less than about 100 μm, preferably less than about 50 μm, and more preferably less than about 25 μm. After thinning, typical backside processing, including backgrinding, patterning (e.g., photolithography, via etching), passivation, and metallization, and combinations thereof, may be performed.

[0038] Advantageously, the dried layers of the inventive compositions possess a number of highly desirable properties. For example, the layers will exhibit low outgassing for vacuum etch processes. That is, if a 15-μm thick film of the composition is baked at 80-250°C for 2-60 minutes (more preferably 2-4 minutes), the solvents will be driven from the composition so that subsequent baking at 140-300°C for 2-4 minutes results in a film thickness change of less than about 5%, preferably less than about 2%, and even more preferably less than about 1.0% or even 0% (referred to as the "Film Shrinkage Test"). Thus, the dried layers can be heated to temperatures of up to about 350°C, preferably up to about 320°C, more preferably up to about 300°C, without chemical reactions occurring in the layer. In some embodiments, the layers can also be exposed to polar solvents (e.g., *N*-methyl-2-pyrrolidone) at a temperature of 80°C for 15 minutes without reacting.

[0039] The bond integrity of the dried layers can be maintained even upon exposure to an acid or base. That is, a dried layer of the composition having a thickness of about 15 μm can be submerged in an acidic media (e.g., concentrated sulfuric acid) or base (e.g., 30 wt. % KOH) at 85°C for about 45 minutes while maintaining bond integrity. Bond integrity can be evaluated by using a glass carrier substrate and visually observing the bonding composition layer through the glass carrier substrate to check for bubbles, voids, etc. Also, bond integrity is maintained if the active wafer and carrier substrate cannot be separated by hand.

[0040] After the desired processing has occurred, the active wafer or substrate can be separated from the carrier substrate. In one embodiment, the active wafer and substrate are separated by heating to a temperature sufficient to soften the bonding layer. More specifically, the stack is heated to temperatures of at least about 100°C, preferably at least about 120°C, and more preferably from about 150°C to about 300°C. These temperature ranges represent the preferred debonding temperatures of the bonding composition layer. This heating will cause the bonding composition layer to soften and form softened bonding composition layer 24' as shown in Fig. 1(c), at which point the two substrates can be separated, for example, by sliding apart. Fig. 1(c) shows an axis 28, which passes through both of wafer 12 and substrate 14, and the sliding forces would be applied in a direction generally transverse to axis 28. Instead of sliding, wafer 12 or substrate 14 can be separated by lifting upward (i.e., in a direction that is generally away from the other of wafer 12 or substrate 14) to separate the wafer 12 from the substrate 14.

[0041] Alternatively, instead of heating to soften the layer, the bonding composition can be dissolved using a solvent. Once the layer is dissolved, the active wafer and substrate can be thereafter separated. Suitable solvents for use in dissolving the bonding layer can be any solvent that was part of the composition prior to drying, such as those selected from the group consisting of MEK and cyclopentanone, as well as hydrocarbon solvents selected from the group consisting of limonene, mesitylene, dipentene, pinene, bicyclohexyl, cyclododecene, 1-tert-butyl-3,5-dimethylbenzene, butylcyclohexane, cyclooctane, cycloheptane, cyclohexane, methylcyclohexane, and mixtures thereof.

[0042] Whether the bonding composition is softened or dissolved, it will be appreciated that separation can be accomplished by simply applying force to slide and/or lift one of wafer 12 or substrate 14 while maintaining the other in a substantially stationary position so as to resist the sliding or lifting force (e.g., by applying simultaneous opposing sliding or lifting forces to wafer 12 and substrate 14). This can all be accomplished via conventional equipment.

[0043] Any bonding composition remaining in the device areas can be easily removed by rinsing with a suitable solvent followed by spin-drying. Suitable solvents include the original solvent that was part of the composition prior to drying as well as those solvents listed above suitable for dissolving the composition during debonding. Any composition remaining behind will be completely dissolved (at least about 98%, preferably at least about 99%, and more preferably about 100%) after 5-15 minutes of exposure to the solvent. It is also acceptable to remove any remaining bonding composition using a plasma etch, either alone or in combination with a solvent removal process. After this step, a clean, bonding composition-free wafer 12' and carrier substrate 14 (not shown in their clean state) will remain.

EXAMPLES

[0044] The following examples set forth preferred methods in accordance with embodiments of the invention. It is to be understood, however, that these examples are provided by way of illustration and nothing therein should be taken as a limitation upon the overall scope of the invention.

EXAMPLE 1

Cycloolefin Copolymer Resin and Low Molecular Weight COC Resin Blends

[0045] In this Example, formulations containing cycloolefin copolymers and a low molecular weight COC resin were made. Antioxidants were added to some of the formulations.

1. *Sample 1.1*

[0046] In this procedure, 1.2 grams of an ethene-norbornene copolymer (TOPAS® 5010, T_g 110°C; obtained from TOPAS Advanced Polymers, Florence, KY) were dissolved in 6 grams of D-limonene (Florida Chemical Co.), along with 2.8 grams of a low molecular weight cycloolefin copolymer (TOPAS® Toner TM, M_w 8,000, M_w/M_n 2.0). The solution was allowed to stir at room temperature until the ingredients were in solution. The solution had about 40% solids.

2. *Sample 1.2*

[0047] In this procedure, 0.75 grams of an ethene-norbornene copolymer (TOPAS® 8007, T_g 78°C) and 3.25 grams of low molecular weight COC (TOPAS® Toner TM) were dissolved in 6 grams of D-limonene. The solution was allowed to stir at room temperature until the ingredients were in solution. The solution had about 40% solids.

3. *Sample 1.3*

[0048] For this procedure, 1.519 grams of an ethene-norbornene copolymer (TOPAS® 5013, T_g 134°C) were dissolved in 5.92 grams of D-limonene along with 2.481 grams of a low molecular weight cycloolefin copolymer (TOPAS® Toner TM), 0.04 grams of a phenolic antioxidant (IRGANOX® 1010), and 0.04 grams of a phosphonite antioxidant (IRGAFOX® P-EPQ). The solution was allowed to stir at room temperature until the ingredients were in solution. The solution had about 40% solids.

4. *Sample 1.4*

[0049] In this procedure, 1.2 grams of an ethene-norbornene copolymer (TOPAS® 8007) were dissolved in 5.92 grams of D-limonene along with 2.8 grams of a low molecular weight cycloolefin copolymer (TOPAS® Toner TM), 0.04 grams of a phenolic antioxidant (IRGANOX® 1010), and 0.04 grams of a phosphonite antioxidant (IRGAFOX® P-EPQ). The solution was allowed to stir at room temperature until the ingredients were in solution. The solution had about 40% solids.

5. *Sample 1.5*

[0050] For this procedure, 2.365 grams of an ethene-norbornene copolymer (TOPAS® 5013) were dissolved in 5.92 grams ofD-limonene along with 1.635 grams of a low molecular weight cycloolefin copolymer (TOPAS® Toner TM), 0.04 grams of a phenolic antioxidant (IRGANOX® 1010), and 0.04 grams of a phosphonite antioxidant (IRGAFOX® P-EPQ). The solution was allowed to stir at room temperature until the ingredients were in solution. The solution had about 40% solids.

6. *Sample 1.6*

[0051] In this procedure, 2.2 grams of a hydrogenated norbornene-based copolymer prepared by ring-opening polymerization (ZEONOR® 1060, T_g 100°C; obtained from Zeon Chemicals, Louisville, KY) and 1.8 grams of a low molecular weight cycloolefin copolymer (TOPAS® Toner TM) were dissolved in 5.92 grams of cyclooctane (Aldrich, Milwaukee, WI). The solution was allowed to stir at room temperature until the ingredients were in solution. The solution had about

40% solids.

EXAMPLE 2

Cycloolefin Copolymer Resins and Tackifier Blends

[0052] In this Example, formulations were made containing cycloolefin copolymers blended with various tackifiers. As in Example 1, antioxidants were added to some of the formulations.

1. *Sample 2.1*

[0053] In this procedure, 0.83 grams of an ethene-norbornene copolymer (TOPAS® 8007) were dissolved in 5.92 grams of D-limonene, along with 3.17 grams of a hydrogenated hydrocarbon resin (REGALITE® R1125; obtained from Eastman Chemical Co., Kingsport TN), 0.04 grams of a phenolic antioxidant (IRGANOX® 1010), and 0.04 grams of a phosphonite antioxidant (IRGAFOX® P-EPQ). The solution was allowed to stir at room temperature until the ingredients were in solution. The solution had about 40% solids.

2. *Sample 2.2*

[0054] For this procedure, 0.7 grams of an ethene-norbornene copolymer (TOPAS® 8007) and 3.3 grams of a styrenated terpene resin (ZONATAC® NG98; obtained from Arizona Chemical, Jacksonville, FL) were dissolved in 5.92 grams of D-limonene, along with 0.04 grams of a phenolic antioxidant (IRGANOX® 1010), and 0.04 grams of a phosphonite antioxidant (IRGAFOX® P-EPQ). The solution was allowed to stir at room temperature until the ingredients were in solution. The solution had about 40% solids.

3. *Sample 2.3*

[0055] In this formulation, 1.9 grams of an ethene-norbornene copolymer (TOPAS® 5013) were dissolved in 5.92 grams of D-limonene, along with 2.1 grams of a cyclo-aliphatic hydrocarbon resin (ARKON® P-140; obtained from Arakawa Chemical USA Inc., Chicago, IL), 0.04 grams of a phenolic antioxidant (IRGANOX® 1010), and 0.04 grams of a phosphonite antioxidant (IRGAFOX® P-EPQ). The solution was allowed to stir at room temperature until the ingredients were in solution.

4. *Sample 2.4*

[0056] For this procedure, 2.42 grams of an ethene-norbornene copolymer (TOPAS® 5013) were dissolved in 5.92 grams of D-limonene, along with 1.58 grams of a cyclo-aliphatic hydrocarbon resin (PLASTOLYN® R-1140; obtained from Arakawa Chemical USA Inc., Chicago, IL), 0.04 grams of a phenolic antioxidant (IRGANOX® 1010), and 0.04 grams of a phosphonite antioxidant (IRGAFOX® P-EPQ). The solution was allowed to stir at room temperature until the ingredients were in solution. The solution had about 40% solids.

EXAMPLE 3

Application, Bonding and Debonding, and Analysis

[0057] The formulations prepared in Examples 1 and 2 above were spin-coated onto various substrate wafers. After baking to evaporate the solvent and allowing the bonding composition to reflow, a second wafer was bonded to each coated wafer by applying pressure. A typical procedure for temporary wafer bonding using the bonding compositions is illustrated in Fig. 2. The bonded wafers were tested for mechanical strength, thermal stability, and chemical resistance. The wafers were tested for debonding by manually sliding them apart at acceptable temperatures. After debonding, the bonding composition residue was cleaned using a solvent rinse and spinning.

[0058] The rheological properties of each formulation from Examples 1 and 2 were tested. All of these materials were successfully tested for debonding. It was determined that the preferred debonding temperature for samples 1.1, 1.2, 2.1, and 2.2 was 150°C. The preferred debonding temperature for samples 1.3, 1.4, and 2.3 was 200°C, and the preferred debonding temperature for samples 1.5, 1.6, and 2.4 was 250°C. The storage modulus (G') and melt viscosity (η^*, complex coefficient of viscosity) for each sample at their preferred debonding temperatures are reported below. The rheological data is also illustrated in Figs. 3-5 for each debonding temperature.

Table 1

Sample number	Storage Modulus, G' (Pa)	Viscosity, η^* (Pa•s)	Debonding Temperature (°C)
1.1	25.5	35.0	150
1.2	9.6	16.7	150
1.3	8.0	13.9	200
1.4	3.5	5.1	200
1.5	16.3	20.1	250
1.6	8.1	15.1	250
2.1	24.9	14.5	150
2.2	1.3	2.4	150
2.3	21.7	28.7	200
2.4	5.5	14.1	250

[0059] Further studies on thermal stability and chemical resistance were also carried out on these compositions. Thermogravimetric analysis (TGA) was carried out on a TA Instruments thermogravimetric analyzer. The TGA samples were obtained by scraping off the spin-coated and baked bonding composition samples from Examples 1 and 2. For the isothermal TGA measurement, the samples were heated in nitrogen at a rate of 10°C/min., up to their preferred debonding temperature plus 50°C, and kept constant at that temperature for 1 hour to determine the thermal stability of the particular bonding composition. The isothermal measurements for each sample formulation are reported below in Table 2. For the scanning TGA measurement, the samples were heated in nitrogen at a rate of 10°C/min. from room temperature to 650°C.

Table 2 - Isothermal thermogravimetric results - thermal stability (in N_2)

Sample	Weight Loss (%) (Isothermal for 1 hour)	Isothermal temperature (°C)
1.1	0.123	200
1.2	0.847	200
1.3	1.268	250
1.4	0.764	250
1.5	0.752	300
1.6	0.596	300
2.1	5.496	200
2.2	4.650	200
2.3	5.737	250
2.4	5.191	300

[0060] As can be seen from the Table above, all of the COC-low molecular weight COC resin blends (Example 1) possessed the required thermal stability at least up to 300°C and exhibited minimal weight loss (< 1.5-wt%). The COC-tackifier blends (Example 2) had an average weight loss of about 5-wt% when maintained at the testing temperature. However, as shown in Table 3, below, the 1-wt% weight loss temperatures were higher than their respective bonding/debonding temperatures, suggesting sufficient thermal resistance for wafer-bonding applications.

Table 3 - Scanning thermogravimetric results

Sample	Temperature at 1.0% weight loss (°C)	Debonding Temperature (°C)
2.1	214	150
2.2	223	150

(continued)

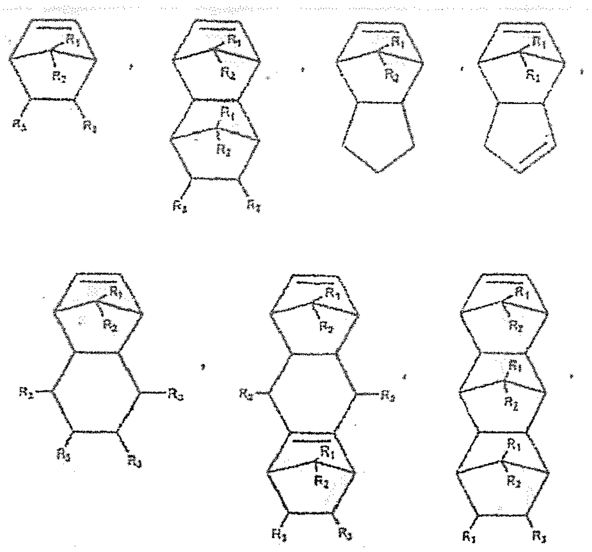
Sample	Temperature at 1.0% weight loss (°C)	Debonding Temperature (°C)
2.3	228	200
2.4	252	250

[0061] To determine chemical resistance, two silicon wafers were bonded using the particular bonding composition to be tested. The bonded wafers were put into chemical baths of *N*-Methyl-2-Pyrrolidone (NMP) or 30% by weight KOH at 85°C, and concentrated sulfuric acid at room temperature to determine chemical resistance. The bond integrity was visually observed after 45 minutes, and the stability of the bonding composition against the respective chemical was determined. All bonding compositions retained the bond integrity.

Claims

1. A temporary wafer bonding method comprising:

- Applying a bonding composition comprising a cycloolefin copolymer dissolved or dispersed in a solvent system to either a first substrate or a second substrate by spin-coating to form a bonding layer, said layer being a uniform material formed of the same composition across its thickness,
wherein the cycloolefin copolymer has a weight average molecular weight (Mw) of from 2,000 Daltons to 200,000 Daltons and is comprised of recurring monomers of cyclic olefins and acyclic olefins, said cyclic olefins being selected from the group consisting of norbornene-based olefins, tetracyclododecene-based olefins, and dicyclopentadiene-based olefins, said acyclic olefins being selected from the group consisting of branched and unbranched C_2-C_{20} alkenes, and wherein the cyclic olefins are selected from the group consisting of



and combinations of the foregoing, where each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups, and each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof, and
wherein spin-coating is applied at spin speeds of from 500-5000 rpm, at accelerations of from 3000-10,000 rpm/second, and for spin times of from 30-180 seconds,

- Temporarily bonding the first and second substrates together via the bonding layer, and
- Separating the first and second substrates after temporarily bonding.

2. The method of claim 1, wherein the first substrate is an active wafer with an active surface comprising topographical features, on which the layer is applied.

3. The method of claim 2, wherein the bonding composition flows into and over the topographical features.

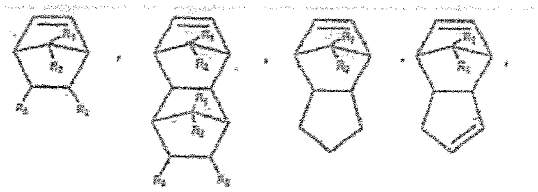
4. The method of claim 2, wherein the bonding layer forms a uniform layer over the topography of the active surface.

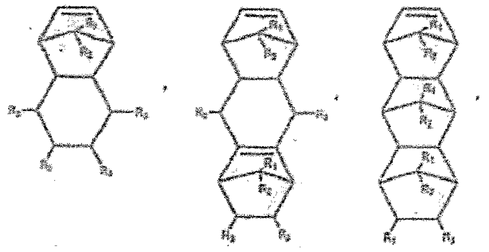
5. The method of claim 1, wherein the bonding layer is applied in that the thickness T of the bonding layer after said step of bonding varies by less than about 20%, preferably less than about 10%, more preferably by less than about 5%, even more preferably by less than about 2%, and most preferably less than about 1 % across the length of the second substrate.

Patentansprüche

1. Verfahren zum temporären Waferbondieren, umfassend:

   - Auftragen einer Bondierzusammensetzung umfassend ein Cycloolefincopolymer, das in einem Lösungsmittelsystem gelöst oder dispergiert ist, auf entweder ein erstes Substrat oder ein zweites Substrat durch Schleuderauftragen, um eine Bondierschicht zu bilden, wobei die Schicht ein gleichförmiges Material ist, das aus derselben Zusammensetzung über ihre Dicke gebildet ist,
   wobei das Cycloolefincopolymer ein gewichtsdurchschnittliches Molekulargewicht (Mw) von 2.000 Dalton bis 200.000 Dalton aufweist und aus sich wiederholenden Monomeren cyclischer Olefine und acyclischer Olefine besteht, wobei die cyclischen Olefine aus der Gruppe ausgewählt sind bestehend aus Olefinen auf Norbornenbasis, Olefinen auf Tetracyclodecenbasis und Olefinen auf Dicyclopentadienbasis, wobei die acyclischen Olefine aus der Gruppe ausgewählt sind bestehend aus verzweigten oder unverzweigten C_2-C_{20}-Alkenen und wobei die cyclischen Olefine aus der Gruppe ausgewählt sind bestehend aus





   und Kombinationen der obigen, wobei R_1 und R_2 einzeln aus der Gruppe ausgewählt sind bestehend aus -H und Alkylgruppen und jedes R_3 einzeln aus der Gruppe ausgewählt ist bestehend aus -H, substituierten und unsubstituierten Arylgruppen, Alkylgruppen, Cycloalkylgruppen, Aralkylgruppen, Estergruppen, Ethergruppen, Acetylgruppen, Alkoholen, Aldehydgruppen, Ketonen, Nitrilen und Kombinationen davon und wobei das Schleuderbeschichten bei Schleudergeschwindigkeiten von etwa 500-5000 UpM, bei Beschleunigungen von 3000-10.000 UpM/Sekunde und für Schleuderzeiten von 30-180 Sekunden angewendet wird,

   - temporäres Zusammenbondieren der ersten und zweiten Substrate über die Bondierschicht und
   - Trennen der ersten und zweiten Substrate nach dem temporären Bondieren.

2. Verfahren nach Anspruch 1, wobei das erste Substrat ein aktiver Wafer mit einer aktiven Oberfläche ist, die topographische Merkmale umfasst, auf die die Schicht aufgebracht wird.

3. Verfahren nach Anspruch 2, wobei die Bondierzusammensetzung in und über die topographischen Merkmale fließt.

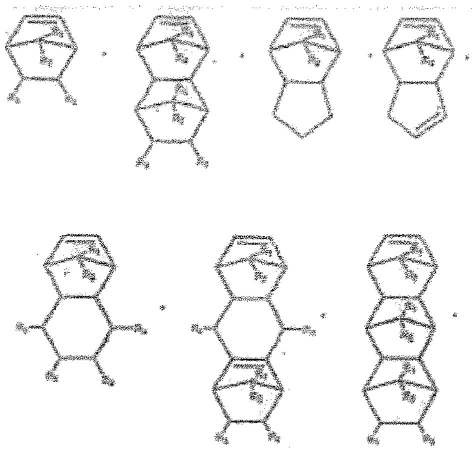
4. Verfahren nach Anspruch 2, wobei die Bondierschicht eine gleichförmige Schicht über die Topographie der aktiven Oberfläche bildet.

5. Verfahren nach Anspruch 1, wobei die Bondierschicht so aufgebracht wird, dass die Dicke T der Bondierschicht nach dem Schritt des Bondierens um weniger als etwa 20 %, bevorzugt um weniger als etwa 10 %, noch bevorzugter um weniger als etwa 5 %, sogar noch bevorzugter um weniger als etwa 2 % und am bevorzugtesten um weniger als etwa 1 % über die Länge des zweiten Substrats variiert.

Revendications

1. Procédé de liaison temporaire de tranches comprenant :

   - l'application d'une composition de liaison comprenant un copolymère de cyclooléfine dissous ou dispersé dans un système de solvant soit à un premier substrat soit à un second substrat par revêtement par centrifugation afin de former une couche de liaison, ladite couche étant un matériau uniforme formé de la même composition dans le sens de l'épaisseur,
   dans lequel le copolymère de cyclooléfine a un poids moléculaire moyen en poids (Mw) allant de 2000 Dalton à 200 000 Dalton et est constitué de monomères récurrents d'oléfines cycliques et d'oléfines acycliques, lesdites oléfines cycliques étant choisies dans le groupe constitué d'oléfines à base de norbornène, d'oléfines à base de tétracyclododécène et d'oléfines à base de dicyclopentadiène, lesdites oléfines acycliques étant choisies dans le groupe constitué d'alkènes en C_{2-20} ramifiés et non ramifiés, et dans lequel les oléfines cycliques sont choisies dans le groupe constitué de



   et des combinaisons de ce qui précède, où chaque R_1 et R_2 est individuellement choisi dans le groupe constitué de -H et des groupes alkyle, et chaque R_3 est individuellement choisi dans le groupe constitué de -H, de groupes aryle substitués et non substitués, de groupes alkyle, de groupes cycloalkyle, de groupes aralkyle, de groupes ester, de groupes éther, de groupes acétyle, d'alcools, de groupes aldéhyde, de cétones, de nitriles et de combinaisons de ceux-ci, et
   dans lequel le revêtement par centrifugation est appliqué à des vitesses de centrifugation comprises entre 500 et 5000 tours par minute, à des accélérations allant de 3000 à 10 000 tr/min/seconde et pendant des temps de centrifugation allant de 30 à 180 secondes,

   - la liaison temporaire des premier et second substrats conjointement par l'intermédiaire de la couche de liaison, et
   - la séparation des premier et second substrats après la liaison temporaire.

2. Procédé selon la revendication 1, dans lequel le premier substrat est une tranche active comportant une surface active comprenant des accidents topographiques, sur lesquels la couche est appliquée.

3. Procédé selon la revendication 2, dans lequel la composition de liaison s'écoule dans et sur les accidents topographiques.

4. Procédé selon la revendication 2, dans lequel la couche de liaison forme une couche uniforme sur la topographie de la surface active.

5. Procédé selon la revendication 1, dans lequel la couche de liaison est appliquée en ce que l'épaisseur T de la couche de liaison après ladite étape de liaison varie de moins d'environ 20 %, de préférence de moins d'environ 10 %, plus préférablement de moins d'environ 5 %, encore plus préférablement de moins d'environ 2 % et le plus préférablement de moins d'environ 1 % sur la longueur du second substrat.

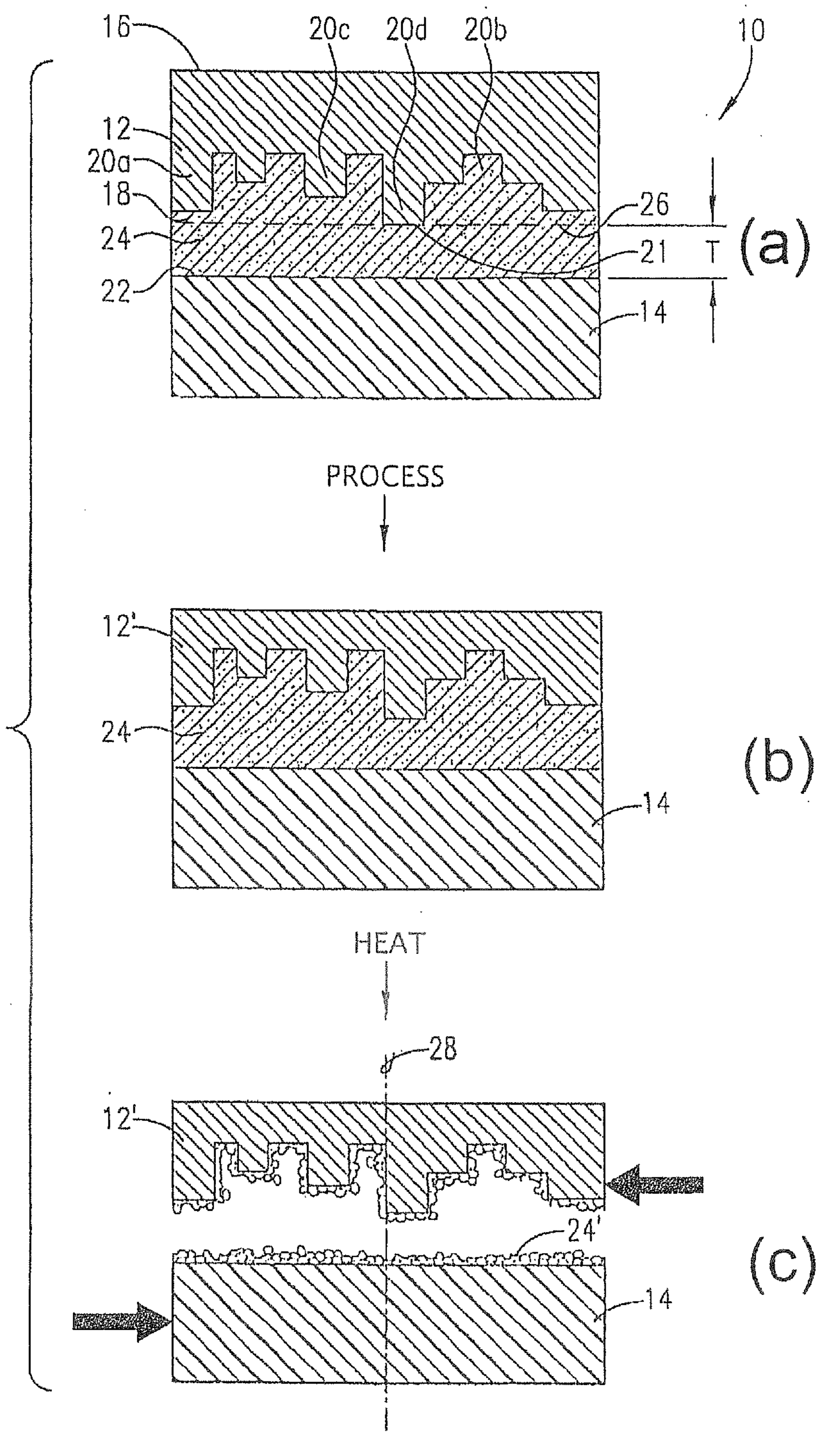

16
20c
20d
20b
10
12
20a
18
24
22
26
21
T
14
(a)
PROCESS
12'
24
14
(b)
HEAT
28
12'
24'
14
(c)

Fig. 1

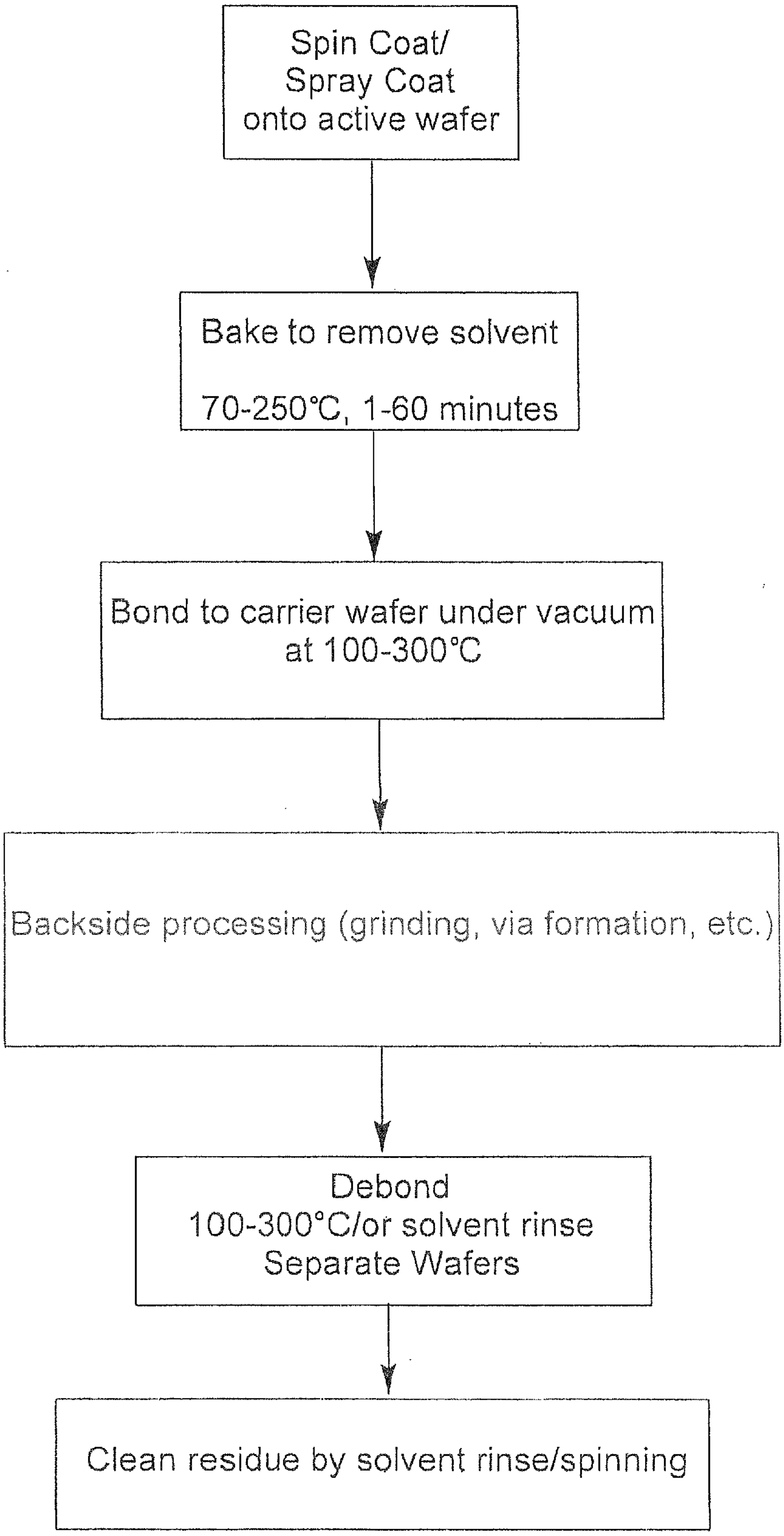

Spin Coat/
Spray Coat
onto active wafer
Bake to remove solvent
70-250°C, 1-60 minutes
Bond to carrier wafer under vacuum
at 100-300°C
Backside processing (grinding, via formation, etc.)
Debond
100-300°C/or solvent rinse
Separate Wafers
Clean residue by solvent rinse/spinning

Fig. 2

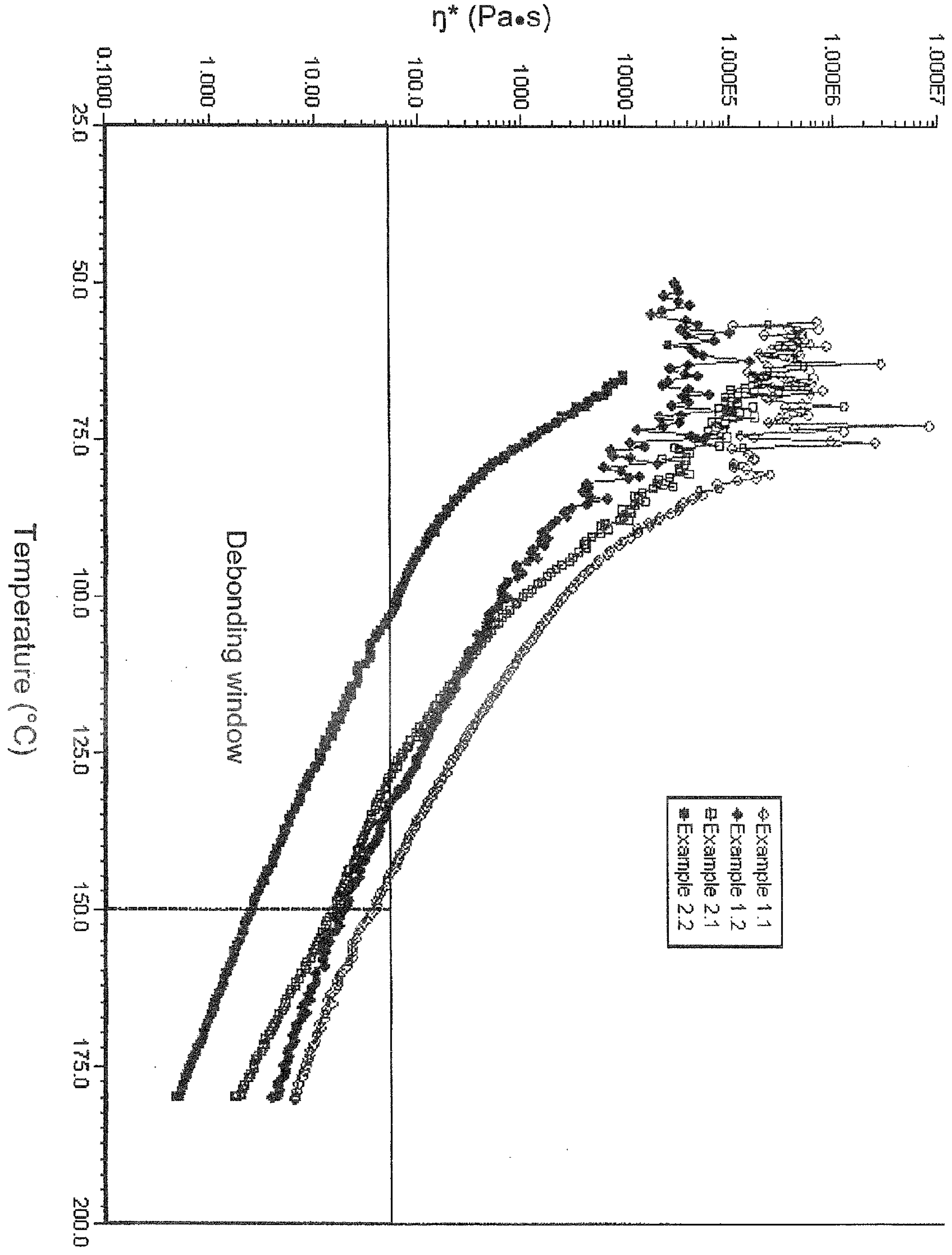

η* (Pa•s)
0.1000
1.000
10.00
100.0
1000
10000
1.000E5
1.000E6
1.000E7
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
Temperature (°C)
Debonding window
Example 1.1
Example 1.2
Example 2.1
Example 2.2

Fig. 3

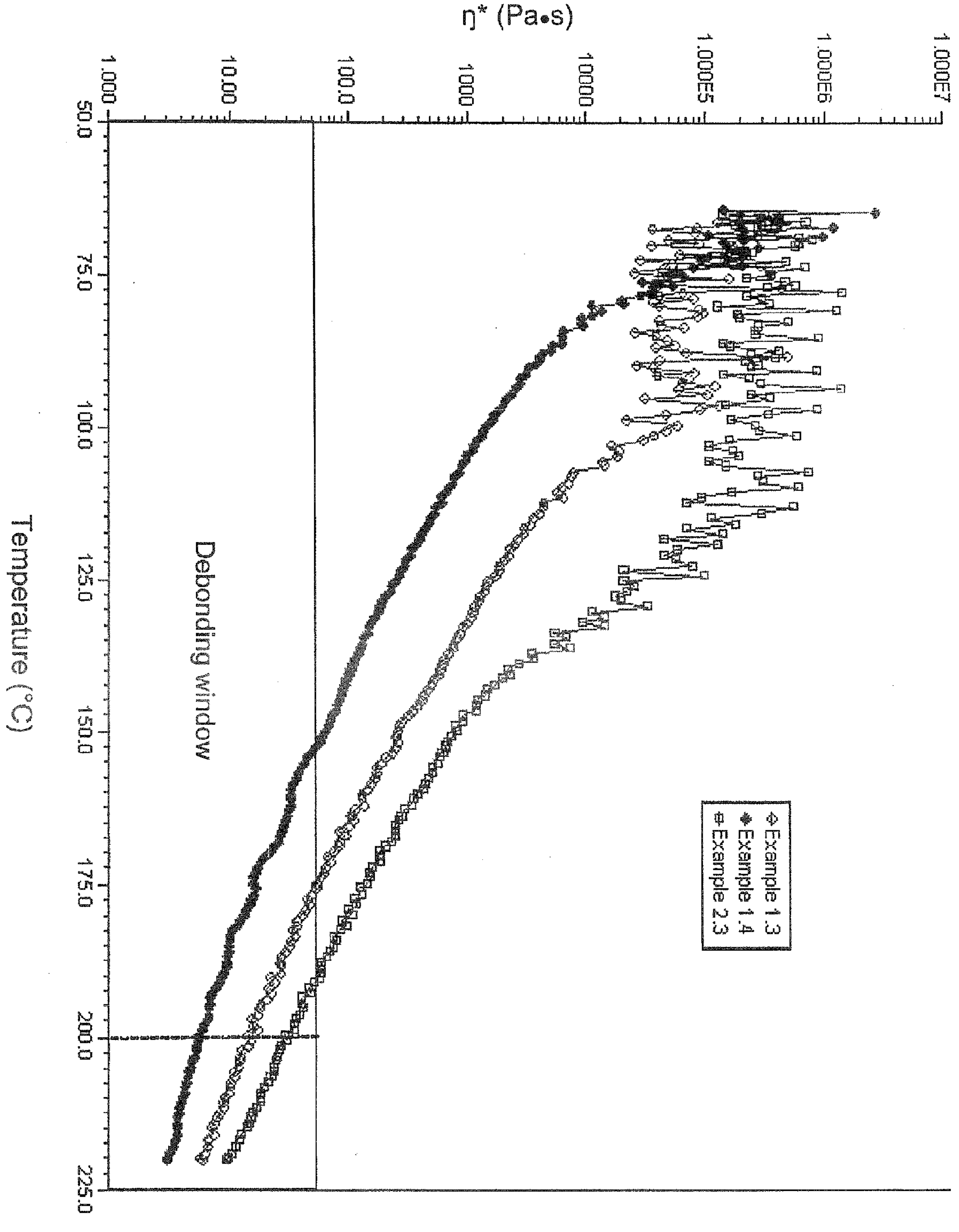

η* (Pa•s)
1.000
10.00
100.0
1000
10000
1.000E5
1.000E6
1.000E7
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
Temperature (°C)
Debonding window
◇ Example 1.3
◆ Example 1.4
□ Example 2.3

Fig. 4

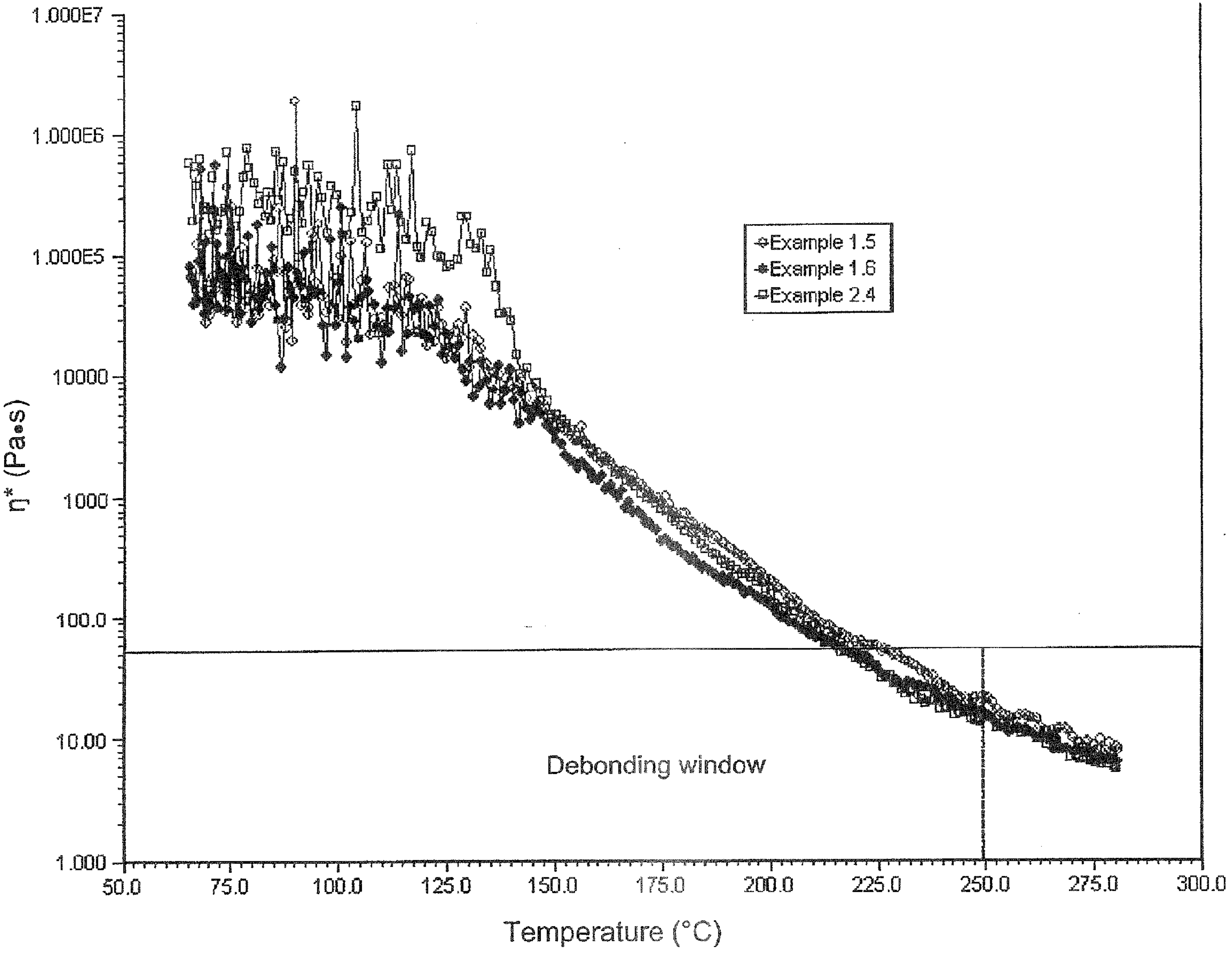

η* (Pa•s)
1.000E7
1.000E6
1.000E5
10000
1000
100.0
10.00
1.000
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
Temperature (°C)
Example 1.5
Example 1.6
Example 2.4
Debonding window

Fig. 5

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

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- US 6008298 A **[0018]**
- US 5191026 A **[0019]**