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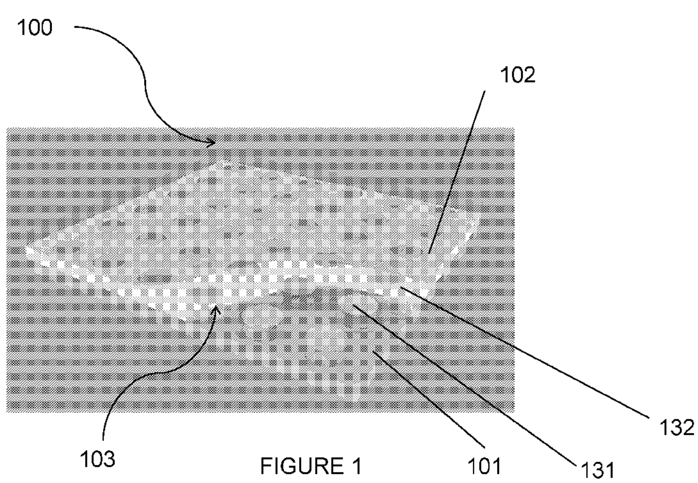

FIGURE 1

(57) Abstract: A hybrid glass including a first layer of glass; a second layer of glass; a first heterogeneous interlayer disposed between the first layer of glass and the second layer of glass; wherein the first heterogeneous interlayer comprises at least a first and a second phase, wherein the first phase has a measured value of a property greater than that of the second phase, wherein the property is selected from a group consisting of Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength; wherein the first and second phases of the first heterogeneous interlayer form areas of contact with the first layer of glass and the second layer of glass; and wherein at least one of the first and second phases of the first heterogeneous interlayer forms an adhesive bond with the first layer of glass and the second layer of glass.

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BIO-INSPIRED TOUGH GLASS HYBRID MATERIALS

RELATED APPLICATION

[0001] This application claims the benefit of priority under 35 U.S.C. §119(e) to United States Appln. Ser. No. 62/168,089, filed May 29, 2015, the contents of which are incorporated by reference.

BACKGROUND

[0002] Transparent structural materials are widely used in both military and commercial applications. In the military, protective armor materials that are transparent to visible light (380-750 nm wavelength range) are needed for many situations, such as soldier eye/face protection (e.g., face shields, goggles), windshields and windows, blast shields, and combat vehicle vision blocks. Transparent armor materials for commercial applications include face shields, security glass, armored cars, and other vehicles. Moreover, light transmitting safety glass is also widely used for windows, windshields, sunroofs, skylights, display cases, picture frames and similar applications. Recently, transparent cover glass with improved scratch and fracture resistance has been widely used for a variety of personal electronic devices, such as tablets and smartphones.

[0003] The most common transparent structural materials are based on glass laminates, which combine multiple layers of glass sandwiched with thin plastic adhesive interlayers such as polyvinyl butyral (PVB). Though there have been some technological advances in producing improved transparent composite materials, the majority of current design and fabrication strategies for protective transparent materials is primarily based on empirical and trial-and-error approaches. Therefore, developing new transparent armor materials is usually time consuming and costly.

[0004] One particular drawback of current glass laminate composites is their low damage tolerance and lack of multi-hit capability. The ability to view through these materials after an initial impact event is dramatically reduced because of the extensive crack propagation through the composite.

SUMMARY OF INVENTION

[0005] In an aspect, a hybrid glass includes a first layer of glass; a second layer of glass; a first heterogeneous interlayer disposed in between the first layer of glass and the second layer of glass; wherein the first heterogeneous interlayer comprises at least a first and a second phase, wherein the first phase has a measured value of a property greater than that of the second phase, wherein the property is selected from a group consisting of Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength; wherein the first and second phases of the first heterogeneous interlayer form a point or area of contact with the first layer of glass and the second layer of glass; and wherein at least one of the first and second phases of the first heterogeneous interlayer forms an adhesive bond with the first layer of glass and the second layer of glass.

[0006] In some embodiments, the measured property of the first phase and the second phase of the first heterogeneous layer are measured using tensile testing, dynamic mechanical analysis, nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, or, microhardness test.

[0007] In some embodiments, one or more of the first glass layer, second glass layer and the first heterogeneous interlayer are transparent. In some embodiments, one or more of the first layer of glass, the second layer of glass and the first heterogeneous interlayer are index-matched.

[0008] In some embodiments, the first phase of the first heterogeneous interlayer comprises a first polymeric adhesive; wherein the first polymeric adhesive forms a discontinuous region in the interlayer. In some embodiments, the second phase of the first heterogeneous interlayer comprises a second polymeric adhesive; wherein the second polymeric adhesive forms a discontinuous region in the interlayer. In some embodiments, the first phase of the first heterogeneous interlayer comprises a first polymeric adhesive; wherein the first polymeric adhesive forms a continuous region in the interlayer. In some embodiments, the second phase of the first heterogeneous interlayer comprises a second polymeric adhesive; wherein the second polymeric adhesive forms a continuous region in the interlayer.

[0009] In some embodiments, the second phase of the first heterogeneous interlayer is air or a liquid.

[0010] In some embodiments, the discontinuous regions of the first phase and the second phase of the first heterogeneous interlayer form an interpenetrating network.

[0011] In some embodiments, the areas of contact of the first phase of the first heterogeneous interlayer with the first layer of glass or the second layer of glass forms a regular array. In some embodiments, the areas of contact of the first phase of the first heterogeneous interlayer with the first layer of glass or the second layer of glass forms an irregular array.

[0012] In some embodiments, the first heterogeneous interlayer is a phase separating polymer that has separated to form at least two phases.

[0013] In some embodiments, the surface of one or more of the first layer of glass and the second layer of glass are treated with an adhesion promoter to improve the adhesion with the first heterogeneous interlayer.

[0014] In some embodiments the hybrid glass further includes, a second heterogeneous interlayer disposed over the first layer of glass or the second layer of glass; and a third layer of glass disposed over, the second heterogeneous interlayer, wherein the second heterogeneous interlayer comprises at least a third and a fourth phase, wherein the third phase has a measured value of a property greater than that of the fourth phase, wherein the property is selected from a group consisting of Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength; wherein the third phase and fourth phase of the second heterogeneous interlayer forms a point or area of contact with the first layer of glass or the second layer of glass, and the third layer of glass; and wherein at least one of the third phase and fourth phase of the second heterogeneous interlayer forms an adhesive bond with the first layer of glass or the second layer of glass, and the third layer of glass.

[0015] In some embodiments, the measured property of the third phase and the fourth phase of the second heterogeneous layer are measured using tensile testing, dynamic mechanical analysis, nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, or, microhardness test.

[0016] In some embodiments, the first heterogeneous interlayer and the second heterogeneous interlayer are made of the same material.

[0017] In some embodiments, the first heterogeneous interlayer and the second heterogeneous interlayer are made of materials with different composition.

[0018] In some embodiments, wherein the fourth phase of the second heterogeneous interlayer is air or a liquid.

[0019] In some embodiments, wherein the discontinuous regions of the third phase and the fourth phase of second heterogeneous interlayer form an interpenetrating network.

[0020] In some embodiments, the areas of contact of the third phase of the second heterogeneous interlayer with the first layer of glass, second layer of glass or third layer of glass forms a regular array. In some embodiments, the areas of contact of the third phase of the second heterogeneous interlayer with the first layer of glass, second layer of glass or third layer of glass forms an irregular array.

[0021] In some embodiments, the second heterogeneous interlayer is a phase separating polymer that has separated to form at least two phases.

[0022] In some embodiments, wherein the surface of one or more of the first layer of glass, the second layer of glass, and the third layer of glass are treated with an adhesion promoter to improve the adhesion with the heterogeneous interlayer.

[0023] In an aspect, a method of manufacturing a hybrid glass includes, providing a first layer of glass; providing a second layer of glass; providing a first heterogeneous interlayer disposed in between the first layer of glass and the second layer of glass; wherein the first heterogeneous interlayer comprises at least a first and a second phase, wherein the first phase has a measured value of a property greater than that of the second phase, wherein the property is selected from a group consisting of Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength; applying the first layer of heterogeneous interlayer material on the first or second layer of glass; wherein the first and second phases of the first heterogeneous interlayer form a point of contact with the first and second layer of glass; and wherein at least one of the first and second phases of the first heterogeneous interlayer forms an adhesive bond with the first and second layer of glass.

[0024] In some embodiments, the measured property of the first phase and the second phase of the first heterogeneous layer are measured using tensile testing, dynamic mechanical analysis, nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, or, microhardness test.

[0025] In some embodiments, one or more of the first glass layer, second glass layer and the first interlayer are transparent. In some embodiments, one or more of the first layer of glass, the second layer of glass and the first heterogeneous interlayer are index-matched.

[0026] In some embodiments, the first phase of the first heterogeneous interlayer comprises a first polymeric adhesive; wherein the first polymeric adhesive forms a discontinuous region in the interlayer. In some embodiments, the second phase of the first heterogeneous interlayer comprises a second polymeric adhesive; wherein the second polymeric adhesive forms a discontinuous region in the interlayer . In some embodiments, the first phase of the first heterogeneous interlayer comprises a first polymeric adhesive; wherein the first polymeric adhesive forms a continuous region in the interlayer. In some embodiments, the second phase of the first heterogeneous interlayer comprises a second polymeric adhesive; wherein the second polymeric adhesive forms a continuous region in the interlayer .

[0027] In some embodiments, the second phase of the first heterogeneous interlayer is air or a liquid.

[0028] In some embodiments, wherein the discontinuous regions of the first phase and the second phase of the transparent interlayer form an interpenetrating network.

[0029] In some embodiments, wherein the areas of contact of the first phase of the first heterogeneous interlayer with the first layer of glass or the second layer of glass forms a regular array. In some embodiments, wherein the areas of contact of the first phase of the first heterogeneous interlayer with the first layer of glass or the second layer of glass forms an irregular array.

[0030] In some embodiments, wherein the first heterogeneous interlayer is a phase separating polymer that has separated to form at least two phases.

[0031] In some embodiments, the surface of the first layer of glass and the second layer of glass is treated with an adhesion promoter to improve the adhesion with the heterogeneous interlayer.

[0032] In some embodiments, the method further includes; providing a second heterogeneous interlayer to be disposed over the first layer of glass or the second layer of glass; and providing a third layer of glass to be disposed over, the second heterogeneous interlayer, wherein the second heterogeneous interlayer comprises at least a third and a fourth phase, wherein the third phase has a measured value of a property greater than that of the fourth phase, wherein the property is selected from a group consisting of Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength; wherein the third and fourth phases of the second heterogeneous interlayer form a point of contact with the first or second, and third layer of glass; and wherein at least one of the third and fourth phases of the second heterogeneous interlayer form an adhesive bond with the first or second, and third layer of glass.

[0033] In some embodiments, the measured property of the third phase and the fourth phase of the second heterogeneous layer are measured using tensile testing, dynamic mechanical analysis, nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, or, microhardness test.

[0034] In some embodiments, wherein the first heterogeneous interlayer layer and the second heterogeneous interlayer are made of the same material.

[0035] In some embodiments, wherein the first heterogeneous interlayer layer and the second heterogeneous interlayer are made of materials with different composition.

[0036] In some embodiments, wherein the fourth phase of the second heterogeneous interlayer is air or a liquid.

[0037] In some embodiments, wherein the discontinuous regions of the third and the fourth phases of second heterogeneous interlayer form an interpenetrating network.

[0038] In some embodiments, wherein the areas of contact of the third phase of the second heterogeneous interlayer with the first, second or third layer of glass forms a regular array. In some embodiments, wherein the areas of contact of the third phase of the second heterogeneous interlayer with the first, second or third layer of glass forms an irregular array.

[0039] In some embodiments, the second heterogeneous interlayer is a phase separating polymer that has separated to form at least two phases.

[0040] In some embodiments, wherein the surface of the first or second, and third glass layer is treated with an adhesion promoter to improve the adhesion with the heterogeneous interlayer.

[0041] In some embodiments, the first heterogeneous layer is deposited using 3-D printing, extrusion, roll-coating, offset-printing, spraying or infiltration. In some embodiments, the second heterogeneous layer is deposited using 3-D printing, extrusion, roll-coating, offset-printing, spraying or infiltration.

[0042] In some embodiments, wherein the first heterogeneous interlayer is directly deposited on the first or second layer of glass. In some embodiments, the second heterogeneous interlayer is directly deposited on the first, second, or third layer of glass.

[0043] In some embodiments, the first heterogeneous interlayer is fabricated separately and then applied to the first or second layer of glass to form an adhesive bond. In some embodiments, the second heterogeneous interlayer is fabricated separately and then applied to the first, second or third layer of glass to form an adhesive bond.

[0044] In some embodiments, the first and second phases of the first heterogeneous interlayer are applied simultaneously. In some other embodiments, the first and second phases of the first heterogeneous interlayer are applied sequentially.

[0045] In some embodiments, the third and fourth phases of the second heterogeneous interlayer are applied simultaneously. In some other embodiments, the third and fourth phases of the second heterogeneous interlayer are applied sequentially.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046] The following figures are provided for the purpose of illustration only and are not intended to be limiting.

[0047] **FIGURE 1** shows a perspective view of the hybrid glass in accordance with one or more embodiments of this disclosure;

[0048] **FIGURE 2** shows a schematic cross section of the hybrid film illustrating the areas of contact of the first phase of the first heterogeneous interlayer and the areas of contact of the second phase of the first heterogeneous interlayer with the first layer of glass or second layer of glass;

[0049] **FIGURE 3** shows a schematic of a structure in cross-section with a second heterogeneous interlayer disposed on the second layer of glass in a structure shown in **FIGURE 1**, and a third layer of glass disposed on top of the second heterogeneous interlayer according to one or more embodiments;

[0050] **FIGURE 4** shows a schematic of patterning with an imprint head according to one or more embodiments;

[0051] **FIGURE 5** shows a schematic of patterning with direct printing according to one or more embodiments;

[0052] **FIGURE 6** shows the cracks formed after impacts in a sample having an area with a heterogeneous interlayer sandwiched between two layers of glass (top half), and a uniform homogeneous interlayer sandwiched between the glass layers (bottom half); and

[0053] **FIGURE 7** shows extreme damage tolerance offered by the hybrid glass according to this disclosure.

DETAILED DESCRIPTION

[0054] A novel glass laminate composite that achieves both damage localization and toughness, enabling multi-hit capability, while maintaining high levels of global optical transparency is described. Methods for producing this novel glass laminate are also described.

These fabrication techniques have ease of implementation, are cost-effective, scalable, and can be integrated with current composite material synthesis processes.

[0055] **FIGURE 1** shows a schematic of the hybrid glass in accordance with this disclosure. The hybrid glass **100** includes a first layer of glass **101**, a second layer of glass **102**, and a first heterogeneous interlayer **103.** The first heterogeneous interlayer **103** includes at least a first phase **131** and a second phase **132**. The first phase **131** has a measured value of a property, such as but not limited to, Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength, greater than that of the second phase **132**.

[0056] In this disclosure the measured value of a property of the first phase **131** and the second phase **132** refer to the values measured in a standard test using samples of free standing films of the materials used for the first phase **131** and the second phase **132.** Suitable standard tests that may be used for evaluation of the properties of the first and second phase **131** and **132** of the heterogeneous interlayer **103** may be selected from, but not limited to, tensile test, dynamic mechanic analysis (DMA), nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, microhardness test, such as, Knoop hardness test. In certain embodiments, when the second phase **132** is air or a liquid, it is assumed that the property of the first phase **131** is greater than that of the second phase **132.** In other embodiments, when the first phase **131** and the second phase **132** result from the phase separation of the material used to form the heterogeneous interlayer **103**, in-situ measurements of the properties of the materials resulting in the formation of the first and second phases **131** and **132** may be carried out after the phase separation has occurred using techniques such as, but not limited to, nanoindentation, dynamic nanoindentation, microhardness testing etc. One of ordinary skill in the art will easily recognize that other techniques of quantifying the properties of the first phase **131** and the second phase **132** may be used as well.

[0057] Additionally, the first phase **131** and second phase **132** of the first heterogeneous interlayer **103** form an area of contact with the first layer of glass **101** and the second layer of glass **102.** Furthermore, at least one of the first phase **131** and second phase **132** of the first heterogeneous interlayer **103** forms an adhesive bond with the first layer of glass **101**and the second layer of glass **102**. In some embodiments, the adhesive bond formed between at least one of the first phase **131** and second phase **132** of the heterogeneous interlayer **103** results in the transmission of the impact energy from the glass layers to the heterogeneous interlayer. Additionally, during crack propagation, the adhesive bond may also assist in arresting the crack propagation. **FIGURE 2** shows a schematic cross section of the hybrid film illustrating the areas of contact **111** of the first phase **131** of the first heterogeneous interlayer **103** and the areas of contact **112** of the second phase **132** of the first heterogeneous interlayer **103** with the first layer of glass **101** or second layer of glass **102**.

[0058] In some embodiments, the hybrid glass further includes a second heterogeneous interlayer **104** disposed over the first layer of glass **101** or second layer of glass **102.** **FIGURE 3** shows a schematic of a hybrid glass **300** where a second heterogeneous interlayer **104** is disposed on the second layer of glass **102** of a structure similar to the ones shown in **FIGURE 1. FIGURE 3** additionally shows a third layer of glass **105** disposed over, the second heterogeneous interlayer **104.** The second heterogeneous interlayer **104** includes at least a third phase **141**and a fourth phase **142.** In some embodiments, the third phase **141** has a measured value of a property, such as but not limited to, Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength greater than that of the fourth phase **142**.

[0059] In this disclosure the measured value of a property of the third phase **141** and the second phase **142** refer to the values measured in a standard test using samples of free standing films of the materials used for the third phase **141** and the fourth phase **142.** Suitable standard tests that may be used for evaluation of the properties of the third and fourth phase **141** and **142** of the heterogeneous interlayer **104** may be selected from, but not limited to, tensile test, DMA, nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, microhardness test, such as, Knoop hardness test. In certain embodiments, when the second phase **142** is air or a liquid, it is assumed that the property of the third phase **141** is greater than that of the fourth phase **142.** In other embodiments, when the third phase **141** and the fourth phase **142** result from the phase separation of the material used to form the heterogeneous interlayer **104**, in-situ measurements of the properties of the materials resulting in the formation of the first and second phases **141** and **142** may be carried out after the phase separation has occurred using techniques such as, but not limited to, nanoindentation, dynamic nanoindentation, microhardness test etc. One of ordinary skill in the art will easily recognize that other techniques of quantifying the properties of the third phase **141** and the fourth phase **142** may be used as well.

[0060] Additionally, the third phase **141** and fourth phase **142** of the second heterogeneous interlayer **104** forms a point of contact with the second layer of glass **102**, and the third layer of glass **105**. Additional layers of glass and heterogeneous layers are contemplated.

[0061] In some embodiments, when the second heterogeneous interlayer is disposed on the first layer of glass **101,** the third phase **141** and a fourth phase **142** of the second heterogeneous interlayer **104** form a point of contact with the first layer of glass **101**, and third layer of glass **105.** Furthermore, at least one of the third phase **141** and fourth phase **142** of the second heterogeneous interlayer **104** forms an adhesive bond with the first layer of glass **101** or the second layer of glass **102**, and the third layer of glass **105**. In some embodiments, the adhesive bond formed between at least one of the third phase **141** and second phase **142** of the second heterogeneous interlayer **104** results in the transmission of the impact energy from the glass layers to the heterogeneous interlayer **104**. Additionally, during crack propagation, the adhesive bond may also assist in arresting the crack propagation.

[0062] In some embodiments, one or more of the first glass layer **101**, second glass layer **102,** the optional third glass layer **105**, the first heterogeneous interlayer **103,** and the optional second heterogeneous interlayer **104** are transparent. In some other embodiments, one or more of t the first glass layer **101**, second glass layer **102,** the optional third glass layer **105**, the first heterogeneous interlayer **103,** and the optional second heterogeneous interlayer **104** are index-matched.

[0063] In some embodiments, the first phase **131** of the first heterogeneous interlayer **103** includes a first polymeric adhesive which forms a discontinuous region in the interlayer. In some other embodiments, the second phase **132** of the first heterogeneous interlayer **103** includes a second polymeric adhesive which forms a discontinuous region in the interlayer. In some embodiments, the first phase **131** of the first heterogeneous interlayer **103** includes a first polymeric adhesive which forms a continuous region in the interlayer. In some other embodiments, the second phase **132** of the first heterogeneous interlayer **103** includes a second polymeric adhesive which forms a continuous region in the interlayer.

[0064] In some embodiments, the second phase **132** of the first heterogeneous interlayer **103** is air or a liquid. In some embodiments, the fourth phase **142** of the second heterogeneous interlayer **104** is air or a liquid.

[0065] In some embodiments, the discontinuous regions of the first phase **131** and the second phase **132** of the first heterogeneous interlayer **103** form an interpenetrating network. In some embodiments, the discontinuous regions of the optional third phase **141** and the optional fourth phase **142** of second heterogeneous interlayer **104** form an interpenetrating network.

[0066] In some embodiments, the areas of contact **111** of the first phase **131** of the first heterogeneous interlayer **103** with the first layer of glass **101** or second layer of glass **102** forms a regular array. In some other embodiments, the areas of contact of the first phase **111** of the first heterogeneous interlayer **103** with the first layer of glass **101** or second layer of glass **102** forms an irregular array. In some embodiments, the areas of contact **113** of the optional third phase **141** of the second heterogeneous interlayer **104** with the first layer of glass **101**, the second layer of glass **102** or third layer of glass **105** forms a regular array. In some other embodiments, the areas of contact **112** of the optional third phase **141** of the second heterogeneous interlayer **104** with the first layer of glass **101**, second layer of glass **102** or third layer of glass **103** forms an irregular array. In some embodiments, the pattern of the contact 112 can be the same pattern for the contact 111. In some other embodiments, the pattern of the contact 112 can adopt a different pattern, in terms of distribution, array pattern and density, in comparison to that of contact 111.

[0067] In some embodiments, one or more of the first phase **131** and second phase **132** of the first heterogeneous interlayer **103** and the optional third phase **141** and fourth phase **142** of the second heterogeneous interlayer **104** is made of thermosetting resin. In some embodiments, one or more of the first phase **131** and second phase **132** of the first heterogeneous interlayer **103** and the optional third phase **141** and fourth phase **142** of the second heterogeneous interlayer **104** is made of thermoplastic resin. Some suitable resins that can be used are acrylics, epoxies, polyurethanes, urea formaldehyde resins, phenolic resins and novolacs. However, as discussed above, while selecting the resins as candidates for the first phase **131** and the second phase **132**, or the option third phase **141** and the optional fourth phase **142,** it must be ensured that the first phase **131** and the optional third phase **141**

have a measured value of a property, such as but not limited to, Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength, greater than that of the second phase **132** and optional fourth phase **142**, respectively**.** Additionally, in some embodiments the second phase **132,** or the optional fourth phase **142,** is air or a liquid**.**

[0068] In some embodiments, one or more of the first heterogeneous interlayer **103** or the optional second heterogeneous interlayer **104** is a phase separating polymer that has separated to form at least two phases. In some embodiments, the phase separating polymer is a blend of homopolymers that eventually phase separate out after application. In some embodiments, the phase separating polymer is a block copolymer. In some other embodiments, the block copolymer can microphase separate to form periodic nanostructures, as found in styrene-butadiene-styrene block copolymer. One skilled in the art would easily recognize other combinations of copolymer blocks can be combined to form the block copolymer. In some embodiments, one of the copolymer block used is a vinylaromatic monomer. In some other embodiments, one of the copolymer blocks used is a diene. Some suitable vinylaromatic monomers that can be used are styrene, alpha-methylstyrene, ring-alkylated styrenes, such as p-methylstyrene, or tert-butylstyrene, or 1,1-diphenylethylene, or a mixture thereof. Some suitable dienes that may be used are butadiene, isoprene, 2,3-dimethylbutadiene, 1,3-pentadiene, 1,3-hexadiene, or piperylene, or a mixture of these.

[0069] In some embodiments, the first glass layer **101,** the second glass layer **102**, or the optional third glass layer **105** is made of silicate glass. Some of the common types of silicate glasses that can be used are, fused quartz, soda-lime-glass, sodium borosilicate glass, lead-oxide glass, aluminosilicate glass and oxide glass. Other types of specialty glass such as sapphire glass, toughened or tempered glass are also envisaged to be within the scope of this disclosure.

[0070] In some embodiments, the first heterogeneous interlayer **103** and the optional second heterogeneous interlayer **104** are made of the same material. In some other embodiments, the first heterogeneous interlayer **102** and the optional second heterogeneous interlayer **104** are made of materials with different composition.

[0071] In some embodiments, the surface of one or more of the first layer of glass **101** and the second layer of glass **102** or the optional third layer of glass **103** is treated with an adhesion promoter to improve the adhesion of the surface of the glass with the first and the second heterogeneous interlayers, **103** and **104,** respectively.

[0072] In an exemplary embodiment, an adhesion promoting treatment for treating the surface of the glass is a coating deposited using a solution of hydrolyzed organofunctional silane. Suitable organofunctional silanes can be selected based on the type of material used in the first and second heterogeneous interlayers, **103** and **104**, respectively. In some other embodiments, organometallic coupling agents can be used to treat the surface of the glass to improve the adhesion of the heterogeneous interlayer with the glass. Some suitable coupling agents are titanates, zirconates, and zircoaluminates. The bonding of the interlayers may be optimized by matching the functionality on the coupling agent selected with the type of material used for in the first and second heterogeneous interlayers, **103** and **104**, respectively.

[0073] In an aspect a method of manufacturing a hybrid glass includes, providing a first layer of glass; providing a second layer of glass; providing a first heterogeneous interlayer disposed in between the first layer of glass and the second layer of glass; wherein the first heterogeneous interlayer comprises at least a first and a second phase, wherein the first phase has a measured value of a property greater than that of the second phase, wherein the property is selected from a group consisting of Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength; applying the first layer of heterogeneous interlayer material on the first or second layer of glass; wherein the first and second phases of the first heterogeneous interlayer form a point of contact with the first and second layer of glass; and wherein at least one of the first phase and the second phase of the first heterogeneous interlayer forms an adhesive bond with the first and second layer of glass.

[0074] In certain embodiments, an imprint head can be used for deposition of the first heterogeneous interlayer. For example, an array of mm-sized cylinders, where the size, height, spacing, and distribution of these cylinders are adjusted depending on specific applications. **FIGURE 4** shows a schematic of patterning with an imprint head **400** with the cylindrical protrusions **401**. First, the imprint head is brought in contact with the uncured resin **402**. Upon release, the uncured resin **402** is adhered to the tips of the cylindrical protrusions **401**, to form the beads **403** attached to the tips of the cylindrical protrusions **401**. Thereafter, the uncured first heterogeneous interlayer material is transferred onto the surface of a first glass sheet 4**04** to form an imprinted glass sheet **405**. After releasing the imprint head, a second glass sheet 4**06** is placed onto the imprinted glass sheet **405**, forming a glass-resin-glass laminate structure 4**07**.

[0075] In some embodiments, the resin coating is a phase separating polymer that segregates into two phases. In such instances it may be necessary to only apply one resin coating and form the first phase and second phase in-situ on the glass during curing. In some other embodiments, after curing the first resin liquid, another resin is allowed to fill at least some of the vacant space of the interlayer. In certain embodiments, the filling of the spaces in the interlayer is facilitated by capillary action. The second resin is cured once the infiltration of the resin is achieved to a desired level. In some embodiments, the infiltration completely fills up all the vacant space left between the two glass layers.

[0076] **FIGURE 5** shows a schematic of patterning with direct printing. In this case, the pattern of the uncured resin **501** is printed on a glass surface **502** with a printing nozzle **503**, which controls the volume, geometry, and position of the droplets in a customizable fashion. In some embodiments, the subsequent steps of fabrication are similar to those discussed above. In certain embodiments, a 3-D printer is used for depositing the heterogeneous interlayer.

[0077] In some embodiments, more than one printing head is used simultaneously to deposit the materials that forms the heterogeneous interlayer. For example, when 3D printing is being used for the deposition of the material for the heterogeneous interlayer including more than one adhesive resin, more than one separate head could be used to deposit the separate adhesive simultaneously in one pass. In another embodiment, sequential passes are used to deposit the adhesives one by one.

[0078] One skilled in the art would appreciate that using such modern additive manufacturing tools, one can deposit extremely intricate geometries with spatial variation in composition of matter to tailor the properties of the heterogeneous interlayer as required. More specifically, to control the location and areas of the point of contact of the resin with the glass layers and alter the mechanical properties of the final heterogeneous interlayer.

[0079] When a crack is initiated from an impact to the glass it propagates. For example, referring to **FIGURE 2,** when a crack is initiated in either of the first or second glass layers

101 or **102**, it continues to propagate in the glass layer. During the propagation of the crack, the leading edge of the crack, e.g., the crack, tip at the interface formed between the first or second glass layers **101** or **102** and the heterogeneous interlayer **103** encounters a change in the region of area of contact **112** to **111.** Upon encountering this change in the area of contact, the crack propagation is arrested. Without being bound by theory, it is believed that the crack propagation is arrested because the stress field at the crack tip is changed when the contact region changes from 112 to 111 due to the change of material properties. The stress intensity factor in the glass layer is greatly reduced as more load is transferred to the stronger phase 131 which forms stronger contact 111 with glass layers. In this case, the relevant material properties for phase 131 and 132 include but are not limited to Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength to the glass layers. This phenomenon can be clearly seen in the samples shown in **FIGURE 6**. The top part of the **FIGURE 6** shows an area having a heterogeneous interlayer sandwiched between two layers of glass, in accordance with this disclosure. In contrast, the bottom part of the same sample has a uniform homogeneous interlayer sandwiched between the glass layers. Upon similar impacts, the bottom portion of the specimen, where homogeneous interlayer is present, shows radial cracks having lengths significantly larger than the cracks formed upon impact in the area where homogeneous interlayer is present.

[0080] Additionally, the specimen also shows ability to take several impacts in a small region. Without being bound to the theory, it is anticipated that due to lack of formation of large cracks, intersection of cracks is avoided. This is expected to significantly improve the endurance to damage for these hybrid glasses. **FIGURE 7** shows the extreme damage tolerance offered by the hybrid glass according to this disclosure. Shown is sample of 50 x 70 mm which has endured around 20 impacts. The zone of crack propagation is limited to the epicenter of the impact and much of the energy of impact is absorbed by the heterogeneous layers and not expended in long radial crack propagation. This phenomenon enables large areas of undamaged glass to remain intact after several impacts.

[0081] The above described properties may be of significant importance in defense related applications. Considering the example of the hybrid glass as a potential replacement material for a visor or windshield, upon impact the hybrid glass can remain functional for longer durations without impairing the field of view entirely. Additionally, the localization of the crack propagation eliminates the possibility of long cracks intersecting upon subsequent impacts. This enhances the durability of the hybrid glasses in these applications. Similar advantages can be expected to be realized in other applications where visibility through the glass and mechanical integrity of the structure may be compromised due to long range crack propagation. Some applications requiring these properties are windows, windshields, sunroofs, skylights, display cases, picture frames, and personal electronic devices, such as tablets and smartphones.

[0082] Upon review of the description and embodiments of the present invention, those skilled in the art will understand that modifications and equivalent substitutions may be performed in carrying out the invention without departing from the essence of the invention. Thus, the invention is not meant to be limiting by the embodiments described explicitly above, and is limited only by the claims which follow.

What is claimed is:

1. A hybrid glass comprising:

a first layer of glass;

a second layer of glass;

a first heterogeneous interlayer disposed in between the first layer of glass and the second layer of glass;

wherein the first heterogeneous interlayer comprises at least a first and a second phase, wherein the first phase has a measured value of a property greater than that of the second phase, wherein the property is selected from a group consisting of Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength;

wherein the first and second phases of the first heterogeneous interlayer form areas of contact with the first layer of glass and the second layer of glass; and

wherein at least one of the first and second phases of the first heterogeneous interlayer forms an adhesive bond with the first layer of glass and the second layer of glass.

2. The hybrid glass of claim 1, wherein the measured property of the first phase and the second phase of the first heterogeneous layer are measured using tensile testing, dynamic mechanical analysis, nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, or, microhardness test.

3. The hybrid glass of claim 1, wherein one or more of the first glass layer, second glass layer and the first heterogeneous interlayer are transparent.

4. The hybrid glass of any of claims 1-3, wherein one or more of the first layer of glass, the second layer of glass and the first heterogeneous interlayer are index-matched.

5. The hybrid glass of any of claims 1-4, wherein the first phase of the first heterogeneous interlayer comprises a first polymeric adhesive; wherein the first polymeric adhesive forms a discontinuous region in the interlayer.

6. The hybrid glass of any of claims 1-4, wherein the second phase of the first heterogeneous interlayer comprises a second polymeric adhesive; wherein the second polymeric adhesive forms a discontinuous region in the interlayer.

7. The hybrid glass of any of claims 1-4, wherein the first phase of the first heterogeneous interlayer comprises a first polymeric adhesive; wherein the first polymeric adhesive forms a continuous region in the interlayer.

8. The hybrid glass of any of claims 1-4, wherein the second phase of the first heterogeneous interlayer comprises a second polymeric adhesive; wherein the second polymeric adhesive forms a continuous region in the interlayer.

9. The hybrid glass of any of claims 1-8, wherein the second phase of the first heterogeneous interlayer is air or a liquid.

10. The hybrid glass of any of claims 5-6, wherein the discontinuous regions of the first phase and the second phase of the first heterogeneous interlayer form an interpenetrating network.

11. The hybrid glass of any of claims 1-10, wherein the areas of contact of the first phase of the first heterogeneous interlayer with the first layer of glass or the second layer of glass forms a regular array.

12. The hybrid glass of any of claims 1-10, wherein the areas of contact of the first phase of the first heterogeneous interlayer with the first layer of glass or the second layer of glass forms an irregular array.

13. The hybrid glass of any of claims 1-4, wherein the first heterogeneous interlayer is a phase separating polymer that has separated to form at least two phases.

14. The hybrid glass of any of claims 1-13, wherein the surface of one or more of the first layer of glass and the second layer of glass are treated with an adhesion promoter to improve the adhesion with the first heterogeneous interlayer.

15. The hybrid glass of any of claims 1-14, further comprising:

a second heterogeneous interlayer disposed over the first layer of glass or the second layer of glass; and

a third layer of glass disposed over, the second heterogeneous interlayer,

wherein the second heterogeneous interlayer comprises at least a third and a fourth phase, wherein the third phase has a measured value of a property greater than that of the fourth phase, wherein the property is selected from a group consisting of Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength;

wherein the third phase and fourth phase of the second heterogeneous interlayer forms areas of contact with the first layer of glass or the second layer of glass, and the third layer of glass; and

wherein at least one of the third phase and fourth phase of the second heterogeneous interlayer forms an adhesive bond with the first layer of glass or the second layer of glass, and the third layer of glass.

16. The hybrid glass of claim 15, wherein the measured property of the third phase and the fourth phase of the second heterogeneous layer are measured using tensile testing, dynamic mechanical analysis, nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, or, microhardness test.

17. The hybrid glass of claim 15, wherein the first heterogeneous interlayer and the second heterogeneous interlayer are made of the same material.

18. The hybrid glass of claim 15, wherein the first heterogeneous interlayer and the second heterogeneous interlayer are made of materials with different composition.

19. The hybrid glass of claim 15, wherein the fourth phase of the second heterogeneous interlayer is air or a liquid.

20. The hybrid glass of claim 15, wherein the discontinuous regions of the third phase and the fourth phase of second heterogeneous interlayer form an interpenetrating network.

21. The hybrid glass of claim 15, wherein the areas of contact of the third phase of the second heterogeneous interlayer with the first layer of glass, second layer of glass or third layer of glass forms a regular array.

22. The hybrid glass of claim 15, wherein the areas of contact of the third phase of the second heterogeneous interlayer with the first layer of glass, second layer of glass or third layer of glass forms an irregular array.

23. The hybrid glass of claim 15, wherein the second heterogeneous interlayer is a phase separating polymer that has separated to form at least two phases.

24. The hybrid glass of claim 15, wherein the surface of one or more of the first layer of glass, the second layer of glass, and the third layer of glass are treated with an adhesion promoter to improve the adhesion with the heterogeneous interlayer.

25. A method of manufacturing a hybrid glass comprising:

providing a first layer of glass;

providing a second layer of glass;

providing a first heterogeneous interlayer disposed in between the first layer of glass and the second layer of glass;

wherein the first heterogeneous interlayer comprises at least a first and a second phase, wherein the first phase has a measured value of a property greater than that of the second phase, wherein the property is selected from a group consisting of Young's modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength;

applying the first layer of heterogeneous interlayer material on the first or second layer of glass;

wherein the first and second phases of the first heterogeneous interlayer form areas of contact with the first and second layer of glass; and

wherein at least one of the first and second phases of the first heterogeneous interlayer forms an adhesive bond with the first and second layer of glass.

26. The method of claim 25, wherein the measured property of the first phase and the second phase of the first heterogeneous layer are measured using tensile testing, dynamic mechanical analysis, nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, or, microhardness test.

27. The method of claim 25, wherein one or more of the first glass layer, second glass layer and the first interlayer are transparent.

28. The method of any of claims 25-27, wherein one or more of the first layer of glass, the second layer of glass and the first heterogeneous interlayer are index-matched.

29. The method of any of claims 25-28, wherein the first phase of the first heterogeneous interlayer comprises a first polymeric adhesive; wherein the first polymeric adhesive forms a discontinuous region in the interlayer.

30. The method of any of claims 25-28, wherein the second phase of the first heterogeneous interlayer comprises a second polymeric adhesive; wherein the second polymeric adhesive forms a discontinuous region in the interlayer .

31. The method of any of claims 25-28, wherein the first phase of the first heterogeneous interlayer comprises a first polymeric adhesive; wherein the first polymeric adhesive forms a continuous region in the interlayer.

32. The method of any of claims 25-28, wherein the second phase of the first heterogeneous interlayer comprises a second polymeric adhesive; wherein the second polymeric adhesive forms a continuous region in the interlayer .

33. The method of any of claims 25-32, wherein the second phase of the first heterogeneous interlayer is air or a liquid.

34. The method of any of claims 29-30, wherein the discontinuous regions of the first phase and the second phase of the transparent interlayer form an interpenetrating network.

35. The method of claim 25, wherein the areas of contact of the first phase of the first heterogeneous interlayer with the first layer of glass or the second layer of glass forms a regular array.

36. The method of claim 35, wherein the areas of contact of the first phase of the first heterogeneous interlayer with the first layer of glass or the second layer of glass forms an irregular array.

37. The method of claim 25, wherein the first heterogeneous interlayer is a phase separating polymer that has separated to form at least two phases.

38. The method of any of claims 25-37, wherein the surface of the first layer of glass and the second layer of glass is treated with an adhesion promoter to improve the adhesion with the heterogeneous interlayer.

39. The method of any of claims 25-38, further comprising:

providing a second heterogeneous interlayer to be disposed over the first layer of glass or the second layer of glass; and

providing a third layer of glass to be disposed over, the second heterogeneous interlayer,

wherein the second heterogeneous interlayer comprises at least a third and a fourth phase, wherein the third phase has a measured value of a property greater than that of the fourth phase, wherein the property is selected from a group consisting of Young’s modulus, fracture strength, fracture toughness, storage modulus, loss modulus, elastic modulus, hardness and interfacial adhesion strength;

wherein the third and fourth phases of the second heterogeneous interlayer form areas of contact with the first or second, and third layer of glass; and wherein at least one of the third and fourth phases of the second heterogeneous interlayer form an adhesive bond with the first or second, and third layer of glass.

40. The method of claim 39, wherein the measured property of the third phase and the fourth phase of the second heterogeneous layer are measured using tensile testing, dynamic mechanical analysis, nanoindentation, dynamic nanoindentation, shore hardness test, Rockwell hardness test, Vickers hardness test, Brinell hardness test, or, microhardness test.

41. The method of claim 39, wherein the first heterogeneous interlayer layer and the second heterogeneous interlayer are made of the same material.

42. The method of claim 39, wherein the first heterogeneous interlayer layer and the second heterogeneous interlayer are made of materials with different composition.

43. The method of claim 39, wherein the fourth phase of the second heterogeneous interlayer is air or a liquid.

44. The method of claim 39, wherein the discontinuous regions of the third and the fourth phases of second heterogeneous interlayer form an interpenetrating network.

45. The method of claim 39, wherein the areas of contact of the third phase of the second heterogeneous interlayer with the first, second or third layer of glass forms a regular array.

46. The method of claim 39, wherein the areas of contact of the third phase of the second heterogeneous interlayer with the first, second or third layer of glass forms an irregular array.

47. The method of claim 39, wherein the second heterogeneous interlayer is a phase separating polymer that has separated to form at least two phases.

48. The method of claim 39, wherein the surface of the first or second, and third glass layer is treated with an adhesion promoter to improve the adhesion with the heterogeneous interlayer.

49. The method of claim 25, wherein the first heterogeneous layer is deposited using 3-D printing, extrusion, roll-coating, offset-printing, spraying or infiltration.

50. The method of claim 39, wherein the second heterogeneous layer is deposited using 3-D printing, extrusion, roll-coating, offset-printing, spraying or infiltration.

51. The method of claim 25, wherein the first heterogeneous interlayer is directly deposited on the first or second layer of glass.

52. The method of claim 39, wherein the second heterogeneous interlayer is directly deposited on the first, second, or third layer of glass.

53. The method of claim 25, wherein the first heterogeneous interlayer is fabricated separately and then applied to the first or second layer of glass to form an adhesive bond.

54. The method of claim 39, wherein the second heterogeneous interlayer is fabricated separately and then applied to the first, second or third layer of glass to form an adhesive bond.

55. The method of claim 25, wherein the first and second phases of the first heterogeneous interlayer are applied simultaneously.

56. The method of claim 25, wherein the first and second phases of the first heterogeneous interlayer are applied sequentially.

57. The method of claim 39, wherein the third and fourth phases of the second heterogeneous interlayer are applied simultaneously.

58. The method of claim 39, wherein the third and fourth phases of the second heterogeneous interlayer are applied sequentially.

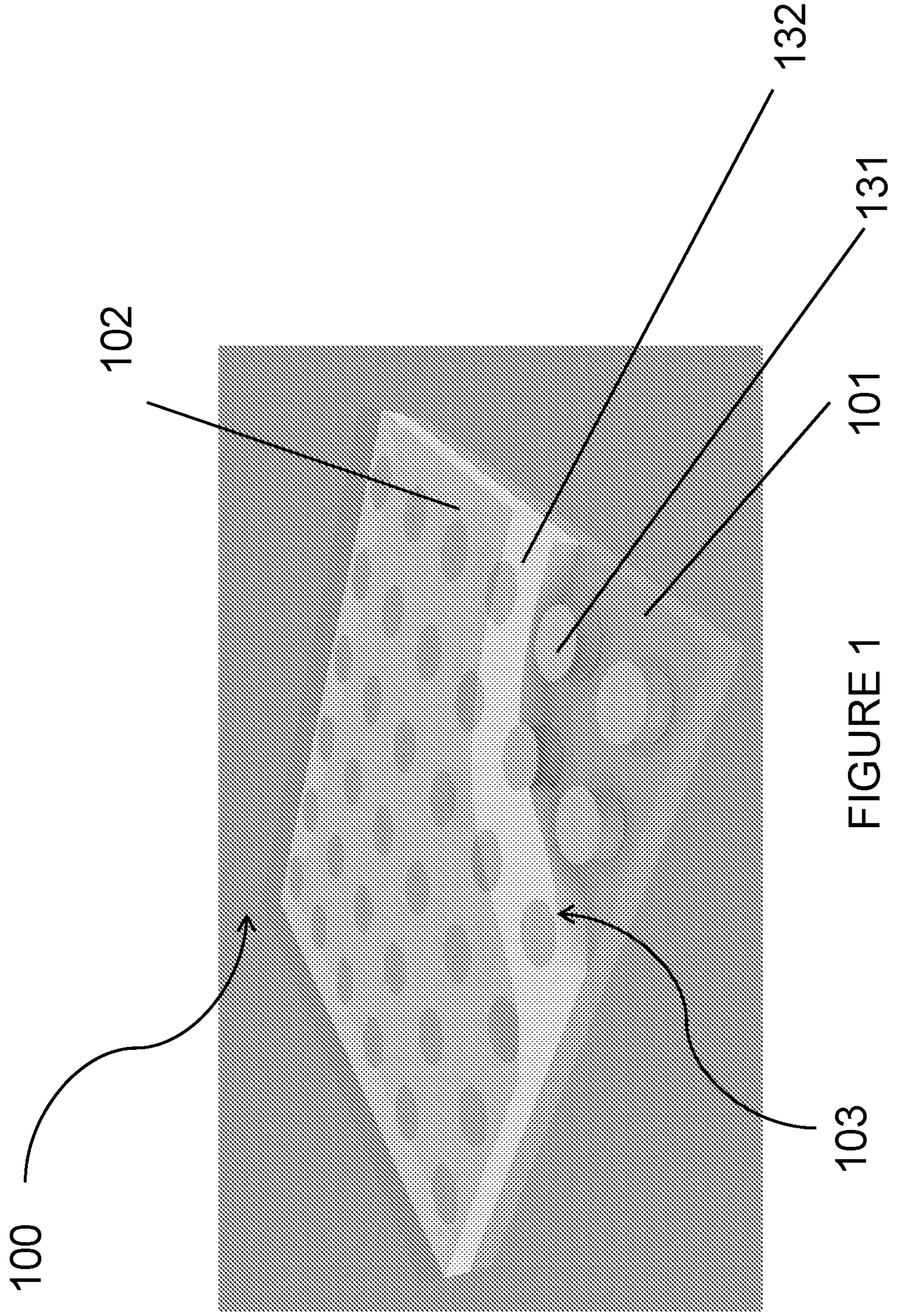

FIGURE 1

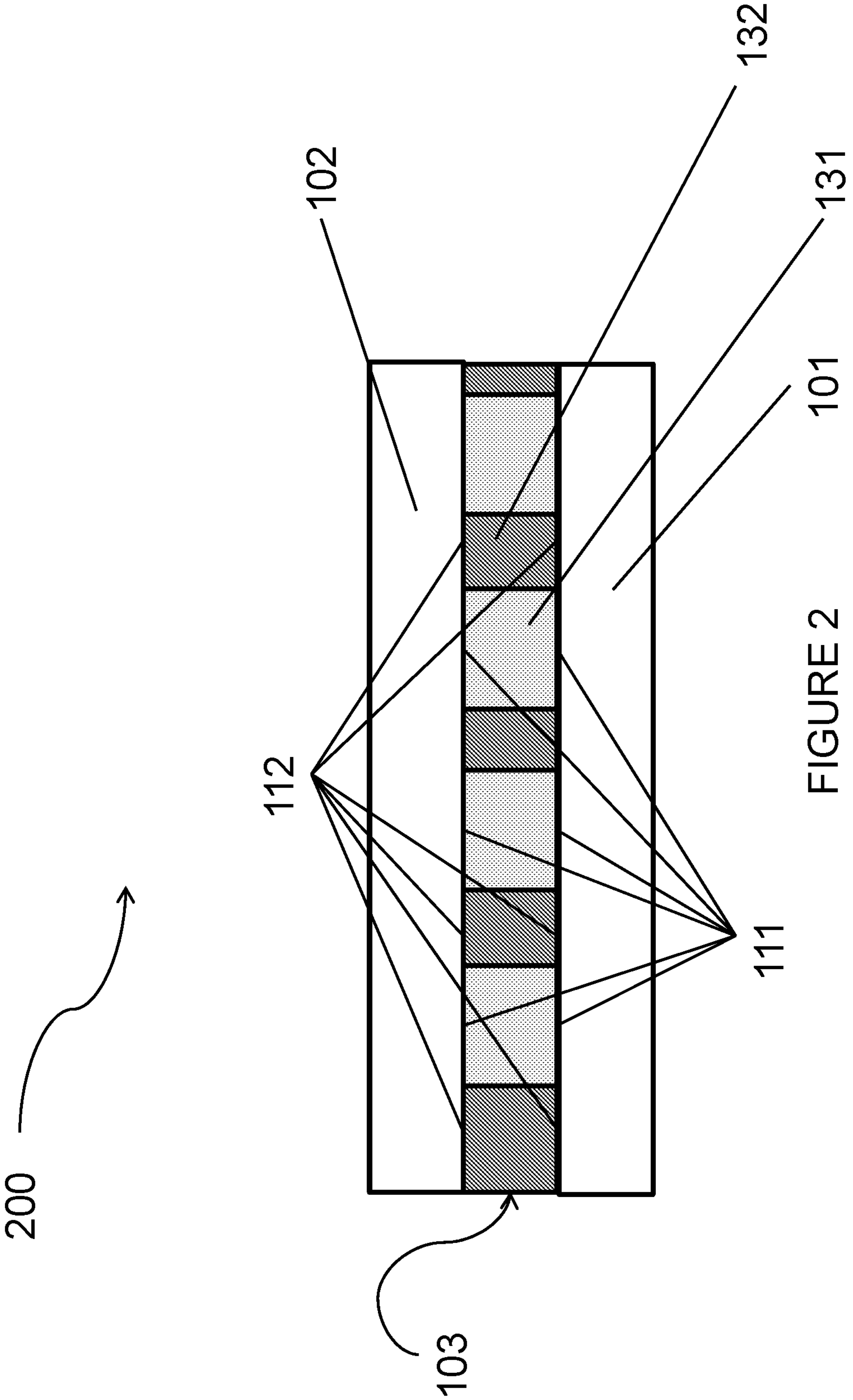

FIGURE 2

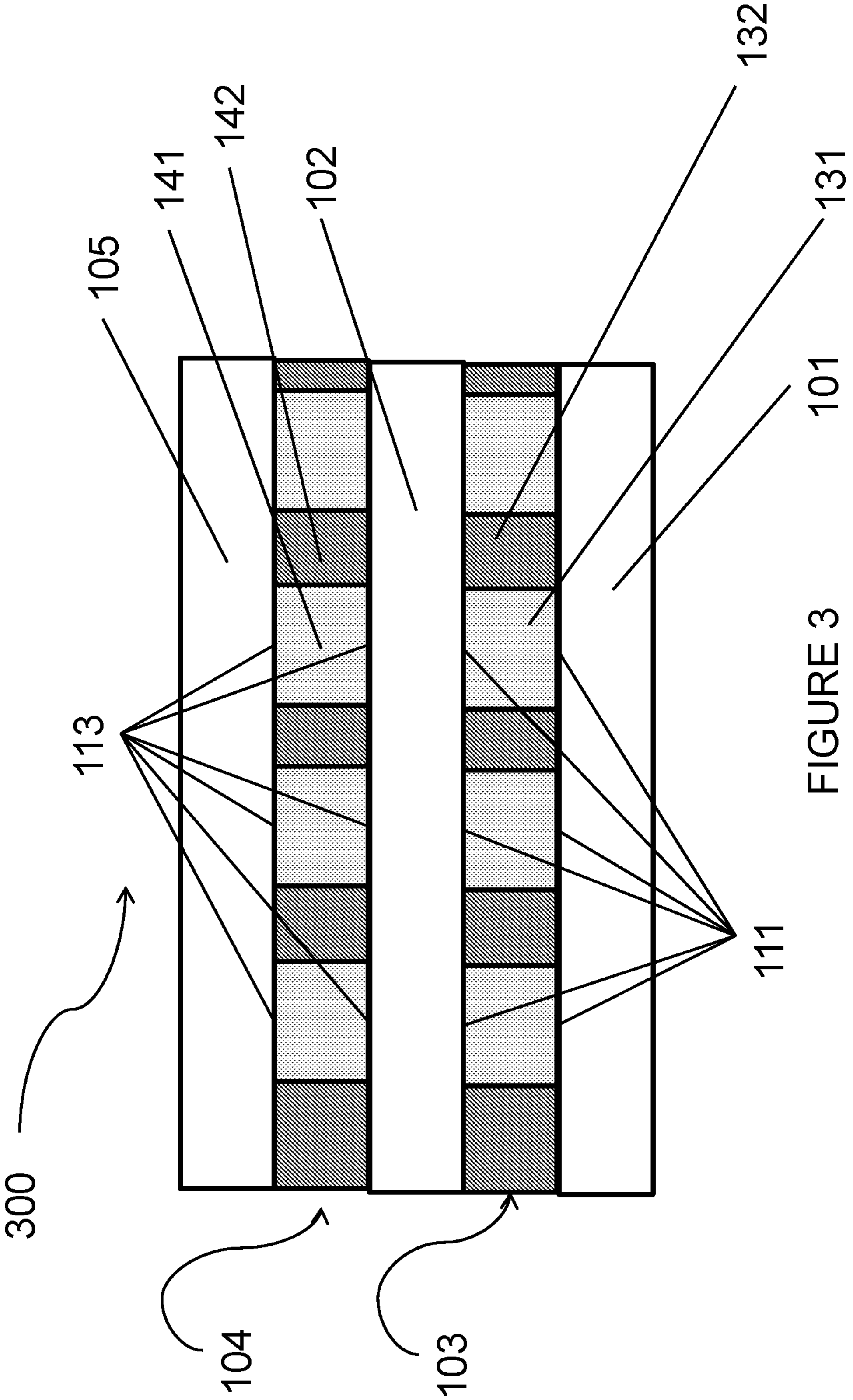

FIGURE 3

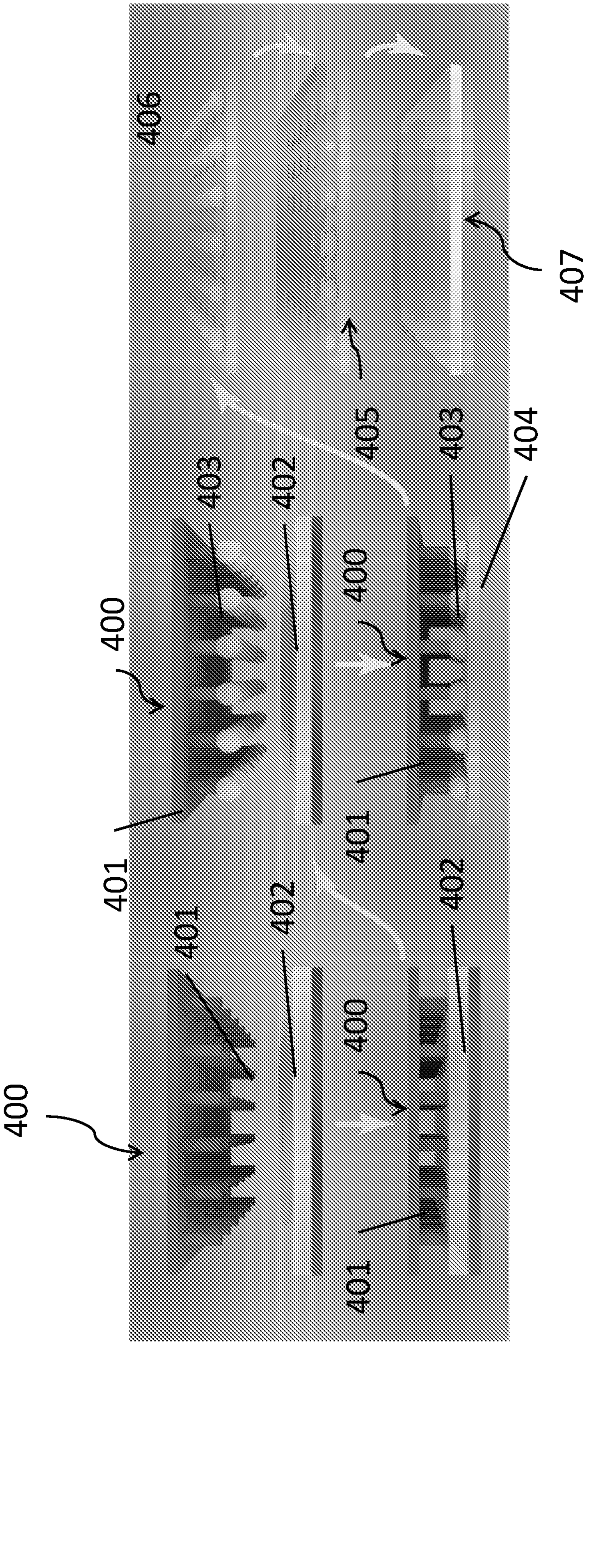
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FIGURE 4

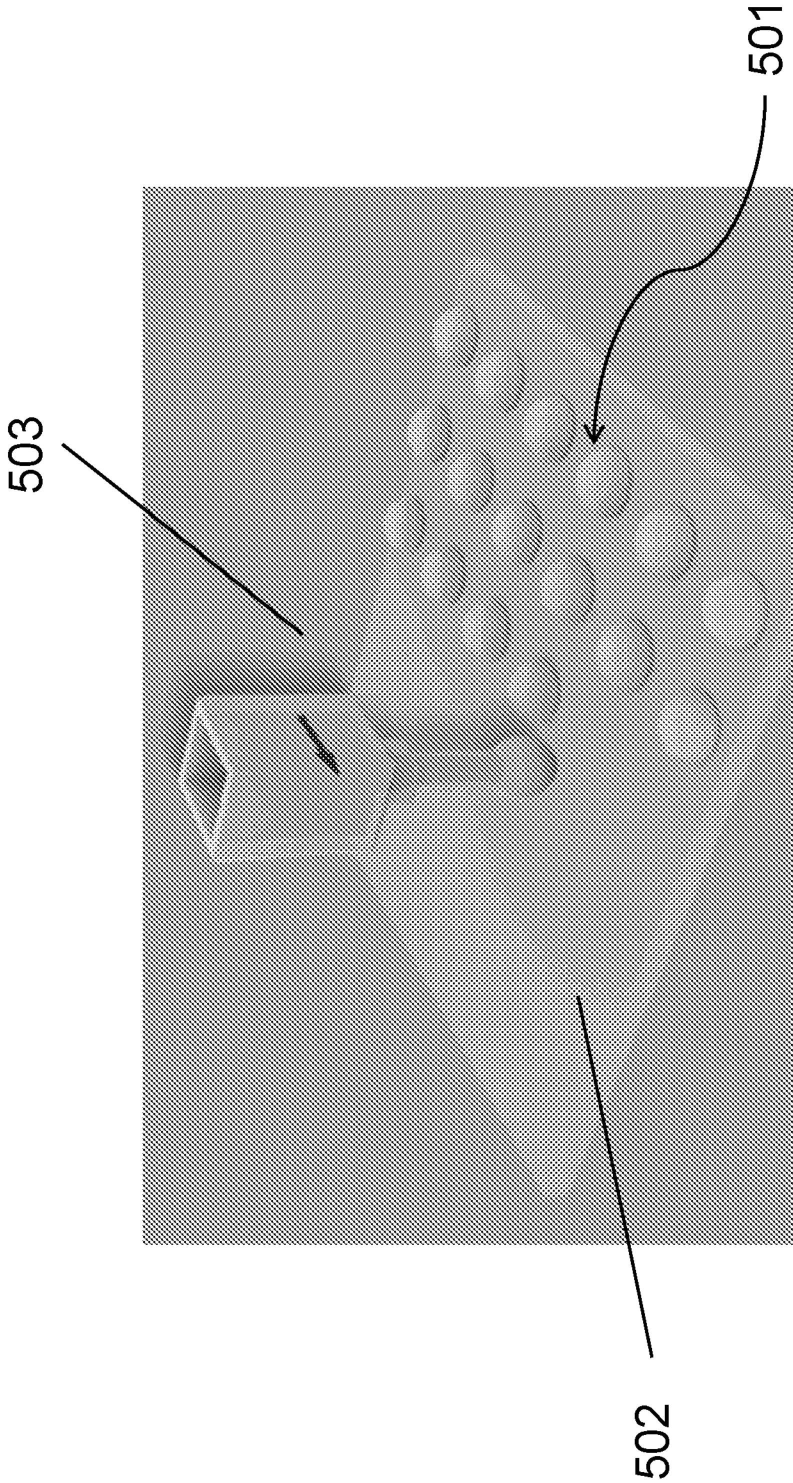

FIGURE 5

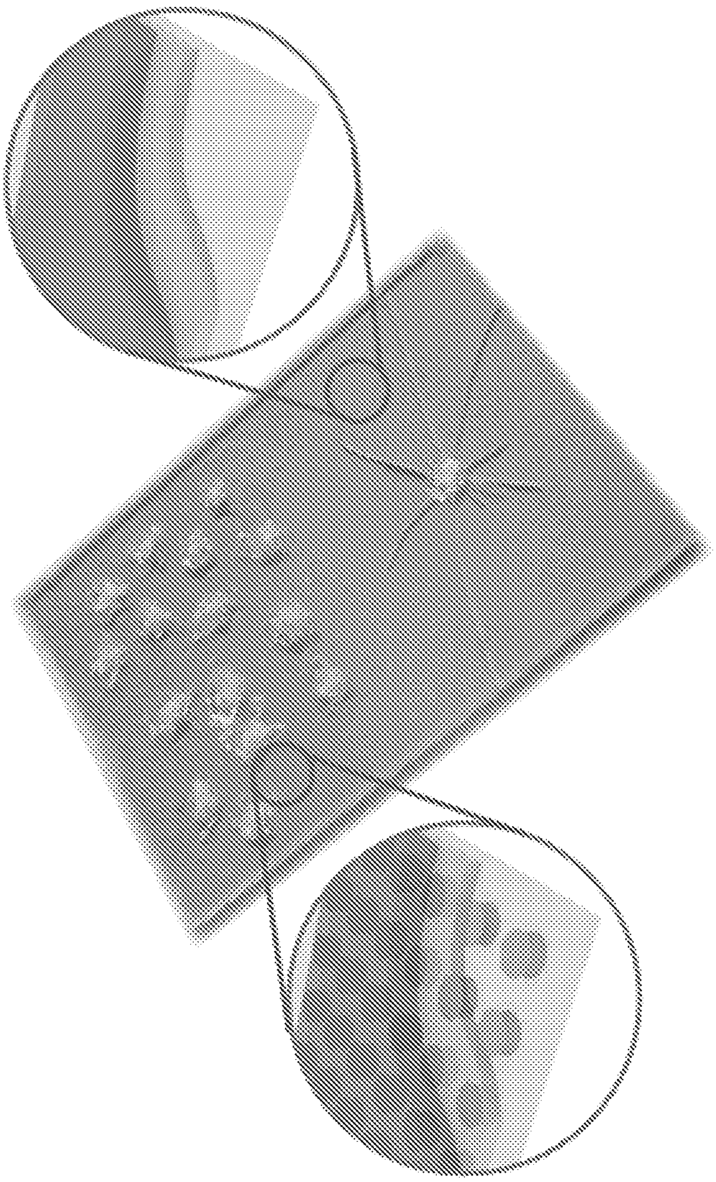

FIGURE 6

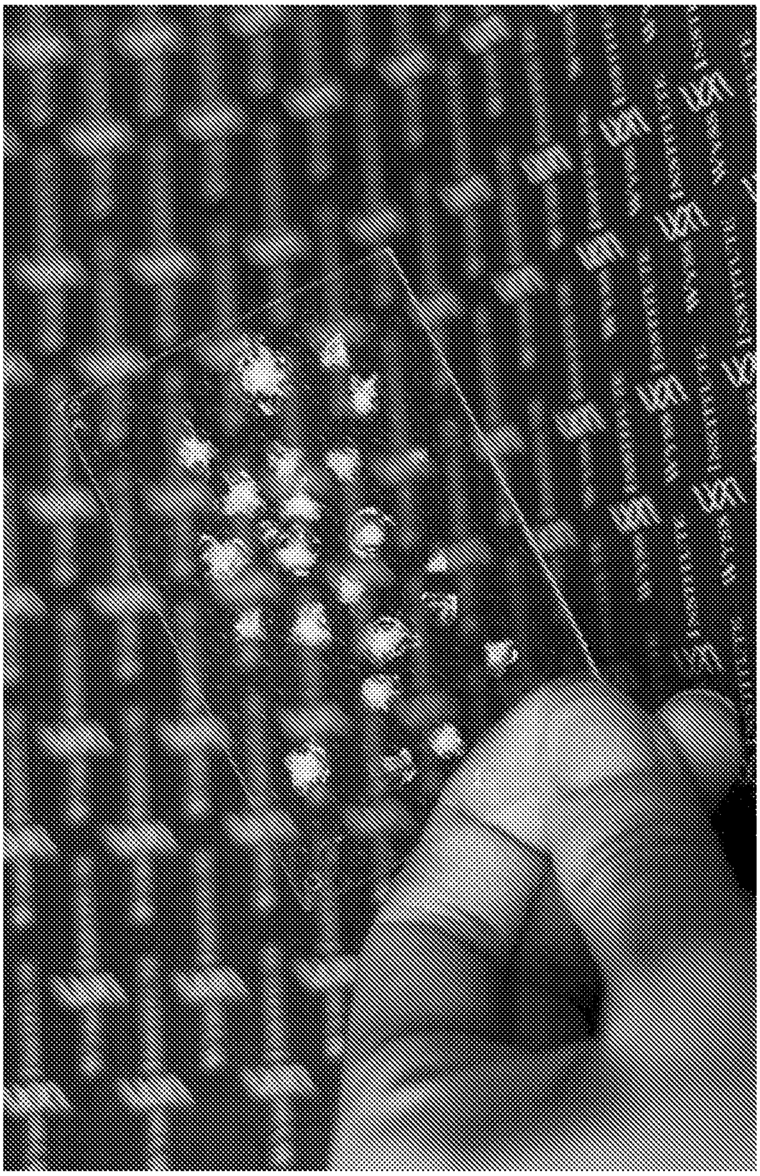

FIGURE 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/33466

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B32B 17/10; C03C 17/32; C03C 27/10 (2016.01)
CPC - B32B 17/10; B32B 17/10036; B32B 17/10807; B32B 17/10917; C03C 17/32; C03C 27/10
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8): B32B 17/10; C03C 17/32; C03C 27/10 (2016.01)
CPC: B32B 17/10; B32B 17/10036; B32B 17/10807; B32B 17/10917; C03C 17/32; C03C 27/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 156/99; 428/426

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Google Scholar, Google Patents, PatBase
Keywords used: glass, composite, laminate, layer, interlayer, adhesive, polymer, phase, continuous, discontinuous, disperse, phase separation polymer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,482,767 A (Karagiannis et al.) 09 January 1996 (09.01.1996); entire document, but especially: col 1 lines 33-34, col 1 lines 37-40, col 1 line 45, col 2 lines 4-6, col 2 lines 8-12, col 3 lines 61-65, col 4 lines 11-19, col 4 lines 29-34, col 5 line 67, col 6 lines 1-3, col 7 lines 35-37, col 7 lines 42-43, col 7 lines 47-51, fig. 1	1-4; 25-28; 35-36; 49; 51; 53; 55-56 --- 37
Y	US 2014/0242375 A1 (Mauro et al.) 28 August 2014 (28.08.2014); entire document, but especially: para [0008], para [0024]	37
A	US 2005/0136243 A1 (Fisher) 23 June 2005 (23.06.2005); entire document	1-4; 25-28; 35-37; 49; 51; 53; 55-56
A	US 5,530567A (Takei) 25 June 1996 (25.06.1996); entire document	1-4; 25-28; 35-37; 49; 51; 53; 55-56

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 July 2016 (13.07.2016)	16 AUG 2016

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/33466

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-24, 29-34, 38-48, 50, 52, 54, 57-58
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.