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POLISHING PADS WITH IMPROVED PLANARIZATION EFFICIENCY

BACKGROUND

Field

[0001] Embodiments of the present disclosure generally relate to polishing pads, and methods of manufacturing polishing pads, and more particularly, to polishing pads used for chemical mechanical polishing (CMP) of a substrate in an electronic device fabrication process.

Description of the Related Art

[0002] Chemical mechanical polishing (CMP) is commonly used in the manufacturing of high-density integrated circuits to planarize or polish a layer of material deposited on a substrate. A CMP process includes contacting the material layer to be planarized with a polishing pad and moving the polishing pad, the substrate, or both, to create relative movement between the material layer surface and the polishing pad, in the presence of a polishing fluid including abrasive particles, chemically active components, or both.

[0003] One common application of a CMP process in semiconductor device manufacturing is planarization of a bulk film, for example pre-metal dielectric (PMD) or interlayer dielectric (ILD) polishing, where underlying two or three-dimensional features create recesses and protrusions in the to be planarized material surface. Other common applications of CMP processes in semiconductor device manufacturing include shallow trench isolation (STI) and interlayer metal interconnect formation, where the CMP process is used to remove the via, contact, or trench fill material (overburden) from the exposed surface (field) of the material layer having the STI or metal interconnect features disposed therein.

[0004] Often, polishing pads used in CMP processes are selected based on material properties of the polishing pad and the suitability of those material properties for the desired CMP application. An example of material properties that affects the performance of a polishing pad for a desired CMP application are the tensile modulus and hardness of the material in polishing layer, which is the layer that includes a surface that is in contact with the surface of a substrate during a polishing process. Typically, a material's hardness is proportional to the tensile modulus of the material.

Generally, polishing pads formed of comparatively harder materials provide superior local planarization performance when compared to polishing pads formed of softer materials. However, polishing pads formed of harder materials are also associated with increased defectivity (e.g., number of defects per polished surface area) when compared with softer polishing pads. The higher defectivity found when using harder materials in the polishing layer is often attributed to undesirable scratches formed in a substrate surface due to asperities (e.g., high stress contact points) formed in the hard pad material at the polishing surface during a pad conditioning process. Unfortunately, conventional polishing pads also typically soften at the relatively high temperatures (e.g., $>40^{\circ}\text{C}$) achieved at the polishing pad surface due to friction, thereby reducing the polishing pad's ability to maintain a desirable hardness over a wide polishing process temperature range, which will typically range in temperature from about 20°C to about 90°C .

[0005] Accordingly, there is a need in the art for polishing pads that maintain their material properties and provide stable performance over a wide temperature range.

SUMMARY

[0006] Embodiments of the disclosure include a polishing pad for planarizing a surface of a substrate during a polishing process. The polishing pad includes a base layer, comprising a first material composition, and a polishing layer disposed over the base layer. The polishing layer includes a second material composition that is exposed at a polishing surface of the polishing pad, wherein the polishing surface is configured to contact the surface of the substrate during the polishing process. The second material composition includes a polishing layer material having a hardness that is greater than 50 on a Shore D scale, a yield point strength, a yield point strength strain, a break point strength, and an elongation at break point strain, wherein a magnitude of a difference between the elongation at break point strain and the yield point strength strain is greater than the magnitude of yield point strength strain when measured at room temperature.

[0007] Embodiments of the disclosure may further provide a polishing pad for planarizing a surface of a substrate during a polishing process. The polishing pad includes a base layer, comprising a first material composition, and a polishing layer disposed over the base layer. The polishing layer includes a second material

composition that is exposed at a polishing surface of the polishing pad, wherein the polishing surface is configured to contact the surface of the substrate during the polishing process. The second material composition comprises a polishing layer material having a hardness that is greater than 50 on a Shore D scale, and a mechanical strain ratio (ϵ_B/ϵ_Y) of greater than 2.

[0008] Embodiments of the disclosure may further provide a method of planarizing a surface of a substrate during a polishing process. The method can include conditioning a polishing surface of a polishing pad, delivering a ceria containing polishing slurry composition to the polishing surface of the polishing pad, and urging the surface of the substrate against the polishing surface of the polishing pad while the ceria containing polishing slurry composition is disposed across the polishing surface of the polishing pad. The polishing pad includes a base layer, comprising a first material composition, and a polishing layer disposed over the base layer. The polishing layer includes a second material composition that is exposed at the polishing surface of the polishing pad. The second material composition comprises a polishing layer material having: a hardness that is greater than 50 on a Shore D scale; a yield point strength; a yield point strength strain; a break point strength; and an elongation at break point strain, wherein a magnitude of a difference between the elongation at break point strain and the yield point strength strain is greater than the magnitude of yield point strength strain when measured at room temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only exemplary embodiments and are therefore not to be considered limiting of its scope, and may admit to other equally effective embodiments.

[0010] Figure 1 depicts a schematic top view of an exemplary chemical mechanical polishing system according to embodiments described herein.

[0011] Figure 2 depicts a schematic sectional view of an exemplary polishing station of the chemical mechanical polishing system from Figure 1 according to embodiments described herein.

[0012] Figure 3A depicts a schematic side view of an exemplary polishing pad and platen of the chemical mechanical polishing system from Figure 2 according to embodiments described herein.

[0013] Figure 3B is a schematic close up side view of a portion of the exemplary polishing pad depicted in Figure 3A according to embodiments described herein.

[0014] Figures 3C-3H are schematic plan views of various polishing pad designs which may be used in chemical mechanical polishing system from Figure 2 according to embodiments described herein.

[0015] Figures 4A-4B are scanning electron microscope (SEM) pictures of a polishing surface of a polishing pad after performing a pad conditioning process.

[0016] Figure 4C is a software rendered version of the polishing surface of the polishing pad depicted in Figure 4A.

[0017] Figure 4D is a software rendered version of the polishing surface of the polishing pad depicted in Figure 4B.

[0018] Figure 4E a grazing angle SEM partial section view picture of the polishing surface and internal portion of the polishing layer of the polishing pad depicted in Figure 4A.

[0019] Figures 5A-5B includes a plurality of engineering stress-strain curves that have been generated for different types of polymeric materials.

[0020] Figure 5C illustrates a surface roughness profile of a polishing surface of a portion of a polishing pad after a pad conditioning process.

[0021] Figure 5D includes a plurality of contact area versus texture depth curves that have been generated for polishing pad samples formed from different polymeric materials after performing a pad conditioning process.

[0022] Figures 5E-5G include scanning electron microscope (SEM) pictures of a polishing surface of the polishing pad samples used to form the contact area versus texture depth curves of Figure 5D.

[0023] Figure 5H includes a portion of the plurality of contact area versus texture depth curves illustrated in Figure 5D.

[0024] Figure 5I illustrates a plot of polishing rate versus contact ratio for a plurality of different polymeric material formulations.

[0025] Figure 6A is a schematic sectional view of an additive manufacturing system, which may be used to form the polishing pads described herein.

[0026] Figure 6B is a close-up cross-sectional view schematically illustrating a droplet disposed on a surface of a previously formed print layer according to embodiments described herein.

[0027] Figure 7 is a diagram setting forth a method of forming a polishing pad according to embodiments described herein.

[0028] Figure 8 is a schematic sectional view illustrating local planarization of a portion of a substrate following a chemical mechanical polishing (CMP) process using a conventional polishing pad.

[0029] To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements and features of one embodiment may be beneficially incorporated in other embodiments without further recitation.

DETAILED DESCRIPTION

[0030] In the following description, details are set forth by way of example to facilitate an understanding of the disclosed subject matter. It should be apparent to a person of ordinary skill in the field, however, that the disclosed implementations are exemplary and not exhaustive of all possible implementations. Thus, it should be understood that reference to the described examples is not intended to limit the scope of the disclosure. Any alterations and further modifications to the described devices, instruments, methods, and any further application of the principles of the present

disclosure are fully contemplated as would normally occur to one skilled in the art to which the disclosure relates. In particular, it is fully contemplated that the features, components, and/or steps described with respect to one implementation may be combined with the features, components, and/or steps described with respect to other implementations of the present disclosure. As used herein, the term "about" may refer to a +/-10% variation from the nominal value. It is to be understood that such a variation can be included in any value provided herein.

[0031] Embodiments described herein generally relate to polishing pads, and methods for manufacturing polishing pads, which may be used in a chemical mechanical polishing (CMP) process. In particular, the polishing pads described herein are able improve the polishing performance of a polishing pad during a CMP process by controlling the properties of the polishing layer of a polishing pad and/or the polishing layer and a base layer that supports the polishing layer. Typical properties that can be controlled to improve the polishing performance of a polishing pad, which are generally formed from a polymeric material, include a pad's mechanical properties and/or its physical properties. One aspect of a polishing pad's design that can be controlled to improve the polishing performance of a polishing pad is the mechanical and/or physical properties of a polishing layer material that is disposed at the polishing surface of the polishing pad during a polishing process, which is discussed further below. The physical properties of a portion of a polishing pad that may be of interest will generally include measurable properties of a material, such as, but not limited to, a material's density, melting point, conductivity, coefficient of thermal expansion, and glass transition temperature (T_g). The mechanical properties of a portion of a polishing pad that may be of interest will generally include properties that are exhibited when a load is applied to the material, such as, but not limited to, a tensile modulus (E) (or Young's modulus), storage modulus (E'), loss modulus (E''), yield strength, ultimate tensile strength, elongation at break, KEL, Tan Delta ($\tan\delta$), ductility, and wear resistance.

[0032] Undesirably poor local planarization performance is typically associated with conventional polishing pads that have a low hardness, often referred to as softer, elastomeric materials. An example of the effects that a low hardness material containing polishing surface region of a polishing pad has on a surface of a substrate

after a polishing process has been performed is schematically illustrated in Figure 8. Figure 8 is a schematic sectional view illustrating poor local planarization, e.g., erosion to a distance “e” and dishing to a distance “d”, following a CMP process to remove an overburden of metal fill material from the field, i.e., upper or outer, surface of a substrate 800. Here, the substrate 800 features a dielectric layer 802, a first metal interconnect feature 804 formed in the dielectric layer 802, and a plurality of second metal interconnect features 806 formed in the dielectric layer 802. The plurality of second metal interconnect features 806 are closely arranged to form a region 808 of relatively high feature density. Typically, the metal interconnect features 804, 806 are formed by depositing a metal fill material onto the dielectric layer 802 and into corresponding openings formed therein. The material surface of the substrate 800 is then planarized using a CMP process to remove the overburden of fill material from the field surface 810 of the dielectric layer 802. If a polishing pad that is selected for a CMP process provides relatively poor local planarization performance, such as found when using soft polishing pads (e.g., polishing pads having a hardness of <60 on Shore D scale), the resulting upper surface of the metal interconnect feature 804 may be recessed a distance “d” from the surrounding surfaces of the dielectric layer 802, otherwise known as dishing.

[0033] Poor local planarization performance of a polishing pad may also result in undesirable recessing of the dielectric layer 802 in the high feature density region 808, e.g., distance “e”, where the upper surfaces of the dielectric layer 802 in the region 808 are recessed from the plane of the field surface 810, otherwise known as erosion. Polishing processes that are used during semiconductor fabrication processes will experience significant metal loss due to poor planarization performance, due to dishing and/or erosion, which can cause undesirable variation in the effective resistance of the metal interconnect features 804, 806 formed therefrom thus affecting device performance and reliability of the formed IC devices.

[0034] Another measure of a pad's polishing performance is a pad's local planarization efficiency (PE), which is a measure determined by subtracting the vertical distance from an average position of a top polished surface of a polished substrate to an average low point (or formed depression) in the polishing surface (D_{tip}) divided by the distance from the average position of a top polished surface of a

polished substrate to the surface of a layer (D_{tsi}) on which the polishing process is to be stopped (e.g., underlying dielectric layer top surface in a metal CMP process) from one (i.e., $PE = 1 - (D_{tlp}/D_{tsi})$). A pad's local planarization efficiency is typically measured over a one square centimeter (cm^2) area, and the average low points are typically formed over embedded features, such as vias or trenches formed in the surface of the substrate.

[0035] Embodiments described herein will reduce dishing and erosion types of defects over a wide range of feature sizes compared to conventional polishing pad materials, due to the materials, and/or materials and structure, of the polishing pad disclosed herein. In addition, embodiments described herein have more stable or consistent dishing and erosion performance compared to conventional polishing pad materials. In some embodiments described herein provide polishing pads with segmented polishing elements (Figures 3B-3H) that are disposed on a relatively more compliant foundation layer. Also, the various embodiments described herein will include improved non-uniformity results as compared to conventional pad materials, such as, for example, the IC1000™, Visionpad™ and Ikonix™ types of polishing pads available from DuPont and Epic™ polishing pads available from Cabot Corporation, even though one would expect an increase in polishing non-uniformity due to the significantly harder polishing pad materials being less compliant to the surface of the substrate.

[0036] Although embodiments described herein are generally related to chemical mechanical polishing (CMP) pads used in semiconductor device manufacturing, the polishing pads and manufacturing methods thereof are also applicable to other polishing processes using at least one of chemically active polishing fluids, chemically inactive polishing fluids and polishing fluids free from abrasive particles. In addition, embodiments described herein, alone or in combination, may be used in at least the following industries: aerospace, ceramics, hard disk drive (HDD), MEMS and Nano-Tech, metalworking, optics and electro-optics manufacturing, and semiconductor device manufacturing, among others.

Polishing System Overview

[0037] Figure 1 is a top plan view illustrating one embodiment of a chemical mechanical polishing (CMP) system 100 that can be adapted to perform a polishing process on a substrate using a polishing pad described herein, which can be used to improve the polishing process results achieved on the substrate over conventional polishing processes. The CMP system 100 includes a factory interface module 102, a cleaner 104, and a polishing module 106. A wet robot 108 is provided to transfer substrates 115 between the factory interface module 102 and the polishing module 106. The wet robot 108 may also be configured to transfer the substrates 115 between the polishing module 106 and the cleaner 104. The factory interface module 102 includes a dry robot 110 which is configured to transfer the substrates 115 between one or more cassettes 114, one or more metrology stations 117, and one or more transfer platforms 116. In some embodiments, as shown in Figure 1, four substrate storage cassettes 114 are shown. The dry robot 110 within the factory interface 102 has sufficient range of motion to facilitate transfer between the four cassettes 114 and the one or more transfer platforms 116. Optionally, the dry robot 110 may be mounted on a rail or track 112 to position the robot 110 laterally within the factory interface module 102. The dry robot 110 is also configured to receive the substrates 115 from the cleaner 104 and return the clean polished substrates to the substrate storage cassettes 114.

[0038] Still referring to Figure 1, the polishing module 106 includes a plurality of polishing stations 124 on which the substrates 115 are polished while being retained in a carrier head 210. The polishing stations 124 are sized to interface with one or more carrier heads 210 so that polishing of a substrate 115 may occur in a single polishing station 124. The carrier heads 210 are coupled to a carriage (not shown) that is mounted to an overhead track 128 that is shown in phantom in Figure 1. The overhead track 128 allows the carriage to be selectively positioned around the polishing module 106 which facilitates positioning of the carrier heads 210 selectively over the polishing stations 124 and load cup 122. In some embodiments, as shown in Figure 1, the overhead track 128 has a circular configuration which allows the carriages retaining the carrier heads 210 to be selectively and independently rotated over and/or clear of the load cups 122 and the polishing stations 124.

[0039] In some embodiments, as shown in Figure 1, three polishing stations 124 are shown located in the polishing module 106. At least one load cup 122 is in the corner of the polishing module 106 between the polishing stations 124 closest to the wet robot 108. The load cup 122 facilitates transfer between the wet robot 108 and the carrier heads 210.

[0040] Each polishing station 124 includes a polishing pad 204 having a polishing surface (e.g., a polishing surface 204A in Figure 2) capable of polishing a substrate 115. Each polishing station 124 includes one or more carrier heads 210, a conditioning assembly 132 and a polishing fluid delivery module 135. During the operation of the polishing assembly 200, the pad 204 is subject to compression, shear and friction, which produce heat and wear, as a slurry and substrate are urged against the polishing surface 204A by the one or more carrier heads 210. The slurry and abraded material from the substrate and pad are pressed into the surface and pores of the pad material, which causes the pad material, and pores formed in the pad material to become matted and even partially fused. These effects created at the polishing surface 204A are sometimes referred to as "glazing," and reduce the pad's ability to have a desirable polishing rate and provide fresh slurry to the substrate during processing. In some embodiments, the conditioning assembly 132 may comprises a conditioning disk 133 of a pad conditioning assembly 140, which dresses the polishing surface of the polishing pad 204 by removing polishing debris, remove any "glazing" formed on the polishing pad 204, which occurs after extended use of the pad. Generally, the bottom surface of the conditioning disk 133 contacts and abrades the polishing surface 204A of the polishing pad 204 during a pad conditioning process. During a pad conditioning process, the arm 132B of the pad conditioning assembly 140, provides translational motion to the conditioning disk 133 so that the conditioning disk 133 may contact and abrade the entire polishing surface of the polishing pad 204. A typical pad conditioning process includes applying a down force to the conditioning disk 133 relative to the polishing surface 204A of the polishing pad 204 in a range between about 0.1 psi and about 30 psi, such as , between about 0.7 psi to about 2.0 psi, to achieve an down force of between about 3 and 6 pounds. During a pad conditioning process the conditioning disk 133 is rotated about the axis 235 at a rotation speed of typically between about 30 RPM to about 120 RPM, for example, between about 30 RPM to about 100 RPM, or even between about 40 RPM to about

70 RPM, while a rotational actuator causes the conditioning arm 132B to cause the conditioning disk 133 to translate across the polishing surface 204A of the polishing pad 204 as the polishing pad 204 is being rotated about the axis 216 at a rotation speed of typically between about 20 RPM to about 120 RPM, for example, between about 40 RPM to about 85 RPM. The abrasive action applied by the conditioning disk 133 to the surface of the polishing pad 204 will intentionally cause damage to the polishing layer material at the polishing surface 204A to assure that any "glazing" and other unwanted debris is removed. The pad conditioning process can also be used to open pores formed in the polishing pad 204, when they are present at or near in the polishing surface 204A.

[0041] Referring to Figure 2, the conditioning disk 133 typically has a plurality of abrasive regions (not shown) on its lower face, in which abrasive particles (e.g., diamond or silicon carbide particles) are secured. The abrasive particles are disposed on a surface of a backing plate portion of the conditioning disk 133 to provide a structure capable of enabling the removal of the material on the polishing surface 204A of the polishing pad 204. The abrasive particles can be attached to the lower surface of the conditioning disk 133 by way of known electroplating and/or electrodeposition processes, or by way of organic binding, brazing or welding processes. Each individual abrasive particle can have one or more cutting points, ridges or mesas. In some configurations, the abrasive diamond particles are between 60 micrometers (μm) and 250 μm in size, which can provide superior conditioning of the material used in 3D printed polishing pads, e.g., a low wear rate while maintaining uniform surface roughness across the pad.

[0042] In other embodiments, the polishing fluid delivery module 135 may comprise a fluid delivery arm 134 to deliver a slurry. Each polishing station 124 comprises a pad conditioning assembly 132. In some embodiments, the fluid delivery arm 134 is configured to deliver a fluid stream (e.g., a fluid 222 in Figure 2) to a polishing station 124. The polishing pad 204 is supported on a platen (e.g., a platen 202 in Figure 2) which rotates the polishing surface during processing. The platen 202 includes a body 203 that has a pad supporting surface 203A. The CMP system 100 is coupled with a power source 180.

[0043] In some embodiments, the substrates 115, such as a silicon wafer having one or more layers deposited thereon, are loaded into the CMP system 100 via a cassette 114. During processing, the factory interface module 102 extracts the substrate 115 from the cassette 114 to begin processing while a controller 190 coordinates operations of the CMP system 100. The dry robot 110 within the factory interface module 102 then transfers the substrate 115 to the metrology station 117, which in some cases measures a thickness profile of the substrate 115. The dry robot 110 then transfers the substrate 115 to the transfer platforms 116, and the wet robot 108 transfers the substrates through subsequent processing components including the CMP system 100.

[0044] The substrate 115 is then transferred by the wet robot 108 to a load cup 122 so that a carrier head 210 can pick-up and transport the substrate 115 to each of the one or more polishing stations 124 to undergo a CMP process according to the polishing parameters selected. Each polishing station includes a polishing pad 204 secured to a rotatable platen 202. Different types of polishing pads 204 may be used at different polishing stations 124 to control the material removal of the substrate 115.

[0045] During CMP, the controller 190 controls aspects of the polishing stations 124. In some embodiments, the controller 190 is one or more programmable digital computers executing digital control software. The controller 190 can include a processor 192 situated near the polishing apparatus, e.g., a programmable computer, such as a personal computer. The controller can include a memory 194 and support circuits 196. The controller 190 can, for example, coordinate contact between the substrate 115 and the polishing pad 204 at differing rotational speeds such that a selective removal profile is aligned with indices of residue locations on the substrate 115, such as an asymmetric thickness profile of the substrate 115. Aligning these profiles ensures the thickest part of the substrate 115 has the most material removed and reduces the asymmetry of the substrate 115 during polishing. The controller 190 may include a plurality of separate controllers that are connected via network.

[0046] After polishing in at least one of the polishing stations 124, the carrier head 210 (Figure 2) transports the substrate 115 to the load cup 122, and then the wet robot 108 transports the substrate 115 from the load cup 122 to a cleaning chamber in the cleaner 104, where slurry and other contaminants that have accumulated on the

substrate surface during polishing are removed. In the embodiment depicted in Figure 1, the cleaner 104 includes two pre-clean modules 144, two megasonic cleaner modules 146, two brush box modules 148, a spray jet module 150, and two dryers 152. The dry robot 110 then removes the substrate 115 from the cleaner 104 and transfers the substrate 115 to the metrology station 117 to be measured again. In certain embodiments, the post-polish layer measurements can be used to adjust the polishing process parameters for a subsequent substrate. Finally, the dry robot 110 returns the substrate 115 to one of the cassettes 114.

Polishing Station Overview

[0047] Figure 2 depicts a schematic sectional view of a polishing station 124 of the CMP system 100 from Figure 1 that comprises a polishing assembly 200 having a polishing pad 204 formed according to embodiments described herein. In particular, Figure 2 shows how a carrier head 210 is positioned relative to the polishing pad 204. A coordinate system 201, having an x-axis, a y-axis, and a z-axis, shows the orientation of the different components of the polishing assembly 200 in this and subsequent figures. The coordinate system 201 shows positive directions of the x, y, and z-axes and positive direction for rotation about the z-axis, which is in a counter-clockwise direction. The opposite directions (not shown) are negative directions.

[0048] In some embodiments, the polishing pad 204 is secured to the pad supporting surface 203A of the platen 202 using an adhesive layer 220 (Figure 3A), such as a pressure sensitive adhesive (PSA) layer, as shown in Figure 3A, disposed between the polishing pad 204 and the pad supporting surface 203A of the platen 202. In some embodiments, the PSA layer can include a rubber resin, acrylic or silicone containing material.

[0049] The carrier head 210, facing the platen 202 and the polishing pad 204 mounted thereon, includes a flexible diaphragm 212 configured to impose different pressures in different regions of the flexible diaphragm 212 against a surface of a substrate 115 that is disposed between the carrier head 210 and the polishing pad 204. The carrier head 210 includes a carrier ring 218 surrounding the substrate 115, which holds the substrate in place. The carrier head 210 rotates about a carrier head axis 216 while the flexible diaphragm 212 urges a to-be-polished surface of the

substrate 115, such as a device side of the substrate 115, against a polishing surface 204A of the polishing pad 204. During polishing, a downforce on the carrier ring 218 urges the carrier ring 218 against the polishing surface 204A to improve the polishing process uniformity and prevent the substrate 115 from slipping out from under the carrier head 210.

[0050] In some embodiments, the polishing pad 204 rotates about a platen axis 205. The polishing pad 204 has a polishing pad axis 206 that is typically collinear with the platen axis 205. In some embodiments, the polishing pad 204 rotates in the same rotational direction as the rotational direction of the carrier head 210. For example, the polishing pad 204 and carrier head 210 both rotate in a counter-clockwise direction. As shown in Figure 2, the polishing pad 204 has a surface area that is greater than the to-be-polished surface area of the substrate 115. However, in some embodiments, the polishing pad 204 has a surface area that is less than the to-be-polished surface area of the substrate 115.

[0051] In some embodiments, an endpoint detection (EPD) system 224 detects reflected light that is directed towards the substrate 115 from a light source, through a platen opening 226 and an optically transparent window feature 227 of the polishing pad 204 disposed over the platen opening 226, and then back through these components to a detector (not shown) within the EPD system 224 during processing to detect properties of a layer formed on a surface of the substrate during polishing. The EPD system 224 can allow a thickness and/or residue location measurement, of the substrate 115 to be taken while the polishing assembly 200 is in use. In some embodiments, an eddy current probe is used to measure the thickness of conductive layers formed on a region of a surface of the substrate 115 by the comparison of the relative angle and position of the notch of the substrate 115, or carrier head 210, to the EPD system 224 within the platen 202.

[0052] During polishing, a fluid 222 is introduced to the polishing pad 204 through the fluid delivery arm 134 portion of the polishing fluid delivery module 135, which is positioned over the polishing surface 204A of the polishing pad 204. In some embodiments, the fluid 222 is a polishing fluid, a polishing slurry, a cleaning fluid, or a combination thereof. In some embodiments, the polishing fluid may include water based chemistries that include abrasive particles. The fluid 222 may also include a

pH adjuster and/or chemically active components, such as an oxidizing agent, to enable CMP of the material surface of the substrate 115 in conjunction with the polishing pad 204. The fluid 222 removes material from the substrate as the carrier head 210 urges the substrate against the polishing pad 204.

[0053] Figure 3A is an enlarged side view of a portion of the polishing pad 204, carrier head 210 and the platen 202 of the CMP system according to some embodiments. In some embodiments, as shown in Figure 3A, the polishing pad 204 includes a foundation layer region 204C and a polishing layer region 204B. The polishing layer region 204C is also often referred to herein as simply the “polishing layer”, and the foundation layer region 204C is also often referred to herein as the “base layer.” The polishing layer region 204C will typically include a plurality of polishing features 204G that are formed on or bonded to the foundation layer region 204C, or are an inseparable part that is positioned on the foundation layer region 204C. In some embodiments, the foundation layer region 204C and the polishing layer region 204C of the polishing pad 204 are formed layer-by-layer using a 3D printing process, which is described further below. In some embodiments, the polishing layer region 204C includes a material that has different mechanical and/or chemical properties from the material found in the foundation layer region 204C. In one example, the polishing layer region 204C includes a polymeric material that has hardness and tensile modulus that is greater than the material found in the foundation layer region 204C.

[0054] Figure 3B is an enlarged side view of a portion of the polishing layer region 204B illustrated in Figure 3A, according to some embodiments of the disclosure. As illustrated in Figure 3B, the polishing surface 204A of the polishing elements 204G of the polishing layer region 204B includes a plurality of asperities 207 that are formed on the polishing surface 204A during a pad conditioning process. During a polishing process the roughness of the polishing surface 204A and material properties of the material at the surface of the polishing elements 204G will, as previously discussed, affect the planarization efficiency and defectivity of a polished substrate.

[0055] Figures 3C-3H are schematic plan views of various polishing pad designs according to embodiments of the present disclosure. Each of the Figures 3C-3H include pixel charts having white regions (regions in white pixels) that represent the

polishing features 204G of the polishing layer region 204B of the polishing pads 204, for contacting and polishing a substrate, and black regions (regions in black pixels) that represent the foundation layer region 204C. As similarly discussed herein, the white regions generally protrude over the black regions so that channels are formed between the white regions. Figures 3C-3H provide examples of various arrangements of the polishing features 204G within a polishing pad 204. In some embodiments, the polishing pads 204 shown in Figures 3C-3H are formed by depositing a plurality of layers of materials using an additive manufacturing process, such as described below in conjunction with Figures 6A-6B. Each of the plurality of layers formed during an additive manufacturing process may include two or more materials to form portions of the polishing layer region 204B and/or the foundation layer region 204C. In one embodiment, the foundation layer region 204C may be thicker than the polishing layer region 204B in a direction normal to a plane that is parallel to the plurality of layers of materials. Figure 3C illustrates a polishing pad that has a plurality of concentric polishing features 204G that are separated a channel. Figure 3D illustrates a polishing pad that has a plurality of segmented polishing elements 204G arranged in concentric circles. Figure 3E illustrates a polishing pad that has a plurality of spiral polishing elements 204G disposed over the foundation layer region 204C. In Figure 3E, the polishing pad 204 has four spiral polishing elements 204G extending from a center of the polishing pad to an edge of the polishing pad. Figure 3F illustrates a polishing pad that has a plurality of segmented polishing elements 204G arranged in a spiral pattern over the foundation layer region 204C. The polishing pad 204 illustrated in Figure 3F is similar to the polishing pad in Figure 3E except that the first polishing elements 204G are segmented and the radial pitch of the first polishing elements 204G varies. Figure 3G illustrates a polishing pad that has a plurality of discrete first polishing elements 204G formed over the foundation layer region 204C. In one embodiment, each of the plurality of first polishing elements 204G may be a cylindrical post type structure. In some embodiments, the plurality of cylindrical first polishing elements 204G may be arranged in concentric circles, in a regular 2D pattern relative to the plane of the polishing surface, or other desirable pattern. Figure 3H illustrates a polishing pad that has a plurality of discrete polishing elements 204G formed over the foundation layer region 204C. The polishing pad of Figure 3F is similar to the polishing pad of Figure 3G except that some first polishing elements 204G in Figure 3H may be connected to form one or more closed circles. The polishing elements

204G in the designs of Figures 3C-3H may be formed from an identical material or identical compositions of materials. Alternatively, the material composition and/or material properties of the polishing elements 204G in the designs of Figures 3C-3H may vary from polishing feature to polishing feature. Individualized material composition and/or material properties allows polishing pads to be tailored for specific needs.

Polishing Pad Properties

[0056] As discussed above, the tensile modulus, and/or hardness, of the material disposed at the polishing surface 204A of the polishing pad 204 has a significant effect on the performance of a polishing pad during a CMP process. As discussed briefly above, polishing pads formed of comparatively harder materials provide superior local planarization performance when compared to polishing pads formed of softer materials. However, polishing pads formed of harder materials are also associated with an increased defectivity when compared with softer polishing pads. In general, polishing pads that include harder materials at the polishing surface 204A of a polishing pad will generate a higher number of scratches and other surface defects than a softer pad material. The higher scratch related defectivity found when using harder materials in the polishing layer can often be attributed to the asperities 207 (Figure 3B) formed in the hard pad material at the polishing surface 204A during a pad conditioning process. There is a need for a polishing pad that includes a polishing layer material disposed at the polishing surface 204A of the polishing pad 204 that will have a desirable hardness over a wide polishing process temperature range (e.g., temperature range of between about 20°C and about 90°C) and have a low defectivity. Moreover, it is desirable to form a polishing pad that includes a polishing layer material that has desirable mechanical properties and/or its physical properties that will allow the polishing pad to achieve a low defectivity, improved local and global planarization performance, improved planarization efficiency and improved dishing performance over conventional polishing pads. However, one will note that embodiments of the disclosure provided herein can also include a pad structure that when used in combination with a desired polishing layer material is able further improve the polishing performance of the polishing pad 204. In some configurations, for example, a desirable polishing pad structure will include a desired physical structure of the

polishing elements 204G (e.g., shape, surface area, size, etc.), distribution of the polishing elements 204G in a plane that is parallel to the polishing surface 204A, and the composition of the material in the foundation layer region 204C of the polishing pad 204.

[0057] It has been found that polishing pads 204 that include a polishing layer material that has desirable properties, such as a high hardness and/or high tensile modulus, and a desirable mechanical strain ratio (ϵ_B/ϵ_Y), can be formed by combining precursor components during a desired polishing pad fabrication process. In some embodiments, as will be discussed further below, the polishing layer material can be formed by use of an additive manufacturing process that allows the material at and within a region near the polishing surface 204A of the polishing layer region 204B to be engineered so that polishing layer material has desired physical and mechanical properties. In some embodiments, the polishing layer region 204B and/or the foundation layer region 204C are both formed by use of an additive manufacturing process in which two or more compositions of precursors are positioned within each layer of a multilayer stack, and, in some cases, at least partially combined to form the polishing layer material. While the ability to and benefits of engineering the properties of different portions of a polishing pad by use of an additive manufacturing process can be easily appreciated, in some cases it may be possible to form a polishing layer material that has desirable properties by use of two or more compositions of precursors that are formed into a useable configuration by use of a conventional casting or molding process, which is currently used to form conventional polishing pads today.

[0058] Figure 4A is scanning electron microscope (SEM) view of a surface of a polishing layer material that has been conditioned during a pad conditioning process that utilized a pad conditioning disk 133. Figure 4B is scanning SEM view of a surface of a high hardness polymeric material that has been conditioned using a similar process to the one used to condition the surface of the polishing layer material illustrated in Figure 4A. As shown, the surface of the polishing layer material in Figure 4A has a much smoother pad conditioned surface versus the pad conditioned surface of the high hardness polymeric material illustrated in Figure 4B. The term “smoother” as used herein is intended to describe a surface that has fewer surface features, or

stated another way has a "higher contact area" that can be placed against a surface of a substrate during a polishing process. The term smoother as used herein is intended to describe a surface that has a reduced roughness or surface undulations that will affect the contact area of the polishing surface of the polishing pad to the surface of the substrate. In some cases, a measure of a surface texture is useful to gauge a relative amount of surface contact area. In some cases, a measure of a surface's "Areal Material Ratio" ($Smr(c)$), as defined in ISO 25178, can be used as a gauge of a surface's relative smoothness or amount of contact area. The $Smr(c)$ -ISO 25178 parameter can be used to determine the amount of bearing area remaining after a certain depth of material is removed from the surface, such the material removed from the polishing surface of the polishing pad after performing a pad conditioning operation. The Areal Material Ratio, $Smr(c)$ is the ratio (expressed as a percentage) of the cross sectional area of the surface at a height (c) relative to the evaluation cross sectional area. The height (c) may be measured from the best fitting least squares mean plane or as a depth down from the maximum point of an Areal Material Ratio Curve.

[0059] One will note that amount of contact area of similarly configured surfaces is proportional to the tensile modulus material, and thus will decrease as the tensile modulus increases. The surface of the high hardness polymeric material illustrated in Figure 4B includes a number of regions that include small high roughness areas that are believed to be created by the brittle fracture of the high hardness polymeric material as the abrasive components of the pad conditioning disk 133 are moved across the polishing surface of the polishing pad 204 during a pad conditioning process. It is believed that these areas of high roughness can form asperities 207 that have a high enough contact force during a substrate polishing process to generate scratches on the surface of the substrate. However, due to the desirable physical and mechanical properties of the polishing layer material illustrated in Figure 4A, which can include its hardness, elongation at break, and mechanical strain ratio, the polishing surface 204A is smoother after a pad conditioning process, which is believed to be due in part to yielding and plastic deformation properties of the polishing layer material found in the polishing pad. The smoother polishing surface 204A of the polishing layer material will minimize and/or prevent scratches from being formed on the substrate during polishing and improves the actual contact area that the polishing

elements 204G have with the surface of a substrate during polishing and thus will improve the polishing rate of the CMP process. By way of comparison, Figures 4C and 4D, which are each software rendered versions of the polishing surfaces illustrated in Figures 4A and 4B, respectively, graphically illustrate a difference in the amount of relative smoother surfaces of the polishing layer material shown in Figure 4A versus the high hardness polymeric material illustrated in Figure 4B. Based on the software analysis of the surfaces, the polishing layer material illustrated in Figure 4A is about 39% smoother than the surface of the high hardness polymeric material illustrated in Figure 4B due to the smaller number of surface features, which will include the asperities 207.

[0060] Figure 4E is a grazing angle SEM partial section view of the polishing surface and internal portion 204B of the polishing layer of the polishing pad depicted in Figure 4A. In some embodiments of a polishing pad 204, the polishing surface 204A can include a plurality of porosity features 452 and asperity-free features 451, which have been formed during a pad conditioning process due to the desirable physical and mechanical properties of the polishing layer material. The plurality of porosity features 452 can be formed within layers of the polishing pad 204 by use of an additive manufacturing process as described herein.

[0061] For ease and clarity of discussion purposes, a polishing layer material that exhibits the desirable properties as discussed in relation to Figure 4A above, and further described below will be referred to herein as a “rigid polymeric material.” However, the use of the phrase “rigid polymeric material” is not intended to be limiting and is only intended to provide a name for a material that exhibits the various properties and contains one or more chemical components that are described herein.

[0062] Figure 5A includes plots of engineering stress-strain curves for four different classes of polymeric materials that can be used to form a polishing pad. For general classification purposes, the four classes of materials that are discussed herein include a brittle polymer C₁, a ductile polymer C₂, a tough polymer C₃, and an elastomeric polymer C₄. Figure 5B includes plots of stress-strain curves for three different polymeric materials that can be used to form a polishing pad, according to an embodiment of the disclosure provided herein. Stress-strain curves represented herein can be generated using an ASTM testing standard, such as ASTM D638-10.

Other testing methodologies that may be used to obtain one or more of the properties of the polymeric materials can include ASTM D412 and ASTM 4065-20.

[0063] The first class of materials, or brittle polymers C_1 , are characterized by a high tensile modulus (i.e., slope of the linear portion C_{1R1} of the stress-strain curve) with very little plastic deformation before the brittle material fractures at the breaking point B_1 , which coincides with a relatively high breaking strength stress σ_{B1} and low break point strain ϵ_{B1} at the breaking point B_1 . Brittle fractures are generally characterized by the formation of jagged features at the fracture surface due to the low amount of plastic deformation found in the material.

[0064] The second class of materials, or ductile polymer C_2 , are characterized by a moderately high tensile modulus, which is seen by slope of the linear portion C_{2R1} of the stress-strain curve. The ductile polymer C_2 materials will include plastic deformation region that includes a yield point Y_2 that is followed by a plastic deformation region C_{2R2} that includes a relatively small plastic deformation strain before the ductile material fractures at the breaking point B_2 , which coincides with a relatively high breaking strength stress σ_{B2} and moderate break point strain ϵ_{B2} at the breaking point B_2 . It is believed that the high hardness polymeric material, which is associated with the material shown in Figures 4B and 4D, is believed to fall somewhere between the first and second classes of materials due to the significant proportion of brittle fracturing regions.

[0065] The third class of materials, or tough polymer C_3 , are also characterized by a moderately high tensile modulus, which is seen by slope of the linear portion C_{3R1} of the stress-strain curve. The tough polymer C_3 materials will include a large plastic deformation region that includes a yield point Y_3 that is followed by a relatively large plastic deformation region and elongation before the tough material fractures at the breaking point B_3 , which coincides with a relatively moderate breaking strength stress σ_{B3} and large break point strain ϵ_{B3} at the breaking point B_3 . As shown in Figure 5A, the tough materials C_3 include a plastic deformation region C_{3R2} that drops down from a peak yield level stress σ_{Y2} at the yield stress point Y_3 that may then be followed by strain hardening or strain softening as the load is continually applied. For the tough polymer C_3 materials, a material composition that experiences strain hardening will typically include a stress-strain curve that is characterized by the stress level

increasing after it dips below the yield point Y_3 (see curves C_3 and C_7 in Figures 5A and 5B). For the tough polymer C_3 materials, a material composition that experiences strain softening will typically include a stress-strain curve that is characterized by the stress level decreasing or remaining relative flat after the stress-strain curve dips below the yield point Y_3 (see curve C_8 in Figure 5B).

[0066] The forth class of materials, or elastomeric polymer C_4 are characterized by a low tensile modulus, which is seen by slope of the linear portion C_{4R1} of the stress-strain curve. The elastomeric polymer C_4 materials will generally not include a yield point and will not contain much of a plastic deformation region, since the elastomeric material will generally have the same stress-strain curve if it is loaded to a point before its breaking point B_4 and then unloaded. The material of an elastomeric polymer C_4 is also characterized by an increasing stress level from its initial loading until the material fractures at the break point B_4 , as seen the positive slope in the regions C_{4R1} and C_{4R2} of the curve C_4 illustrated in Figure 5A. The elastomeric polymers C_4 will generally include a low breaking strength stress σ_{B4} and a large break strain ϵ_{B4} at the breaking point. It has been found that most polyurethane materials, which are produced in a polymerization reaction between diols (or polyols: alcohols with two or more reactive hydroxyl $-OH$ groups) and diisocyanates (or polyisocyanates: isocyanates with two or more reactive isocyanate $-NCO$ groups), typically fall within the fourth class of materials. An example of a conventional polyurethane containing IC1000 polishing pad's stress-strain curve and properties is discussed in an article by Ashraf-F. Bastawros et al. (2019 ECS J. Solid State Sci. Technol. 8 P3145), which similarly includes the attributes illustrated in curve C_4 of Figure 5A. The conventional polyurethane elastomeric polymer pads, such as the IC1000 and IC1010 polishing pads are available from Dupont or Dow/Rohm Haas.

Rigid Polymeric Materials

[0067] It has been found that rigid polymeric materials, hereafter "rigid materials", which generally fall within the third class of materials are the preferred material for use as a polishing layer material due to at least their higher relative hardness than conventional polishing pads, their improved dishing and planarization performance, and desirable defectivity results after performing one or more pad conditioning processes. Rigid materials that include a yield point that is followed by a significant

elongation until the material breaks has been found to provide these desirable polishing pad performance results.

[0068] As will be discussed further below, the pre-polymer compositions that are used to form the “rigid material” may include a mixture of one or more of functional polymers, functional oligomers, functional monomers, functional cross-linkers, reactive diluents, additives, and photoinitiators. Examples of suitable functional polymers which may be used to form one or more of the at least two pre-polymer compositions that are used to form the rigid material can include multifunctional acrylate including di, tri, tetra, and higher functionality acrylates, such as 1,3,5-triacryloylhexahydro-1,3,5-triazine or trimethylolpropane triacrylate, dipropylene glycol diacrylate or dimethacrylate. Other examples of pre-polymer compositions are discussed further below.

[0069] Figure 5B includes engineering stress-strain curves for various rigid materials that fall within the desired third class of materials. Each of the stress-strain curves C_5 , C_6 and C_7 include a linear region in which stress (σ) is proportional to the amount of strain (ϵ), which is noted by the regions C_{5R1} , C_{6R1} and C_{7R1} , respectively. Each of the stress-strain curves C_5 , C_6 and C_7 also include a yield point Y_5 , Y_6 , and Y_7 (i.e., peak of the regions C_{5R1} , C_{6R1} and C_{7R1}) that each occur at a yield point strain ϵ_{Y5} , ϵ_{Y6} , and ϵ_{Y7} , respectively. The stress-strain curves C_5 , C_6 and C_7 also include a plastic deformation region C_{5R2} , C_{6R2} and C_{7R2} , respectively, in which the amount of stress created in the material initially drops from the peak found at the yield point Y_5 , Y_6 , and Y_7 . The plastic deformation region C_{5R2} , C_{6R2} and C_{7R2} of each of the stress-strain curves C_5 , C_6 and C_7 then extend out to a fracture point, or break point B_5 , B_6 , and B_7 that each occur at a break point strain ϵ_{B5} , ϵ_{B6} , and ϵ_{B7} , respectively. In some configurations of a desirable rigid material, the plastic deformation region C_{5R2} , C_{6R2} and C_{7R2} , include a portion that includes strain hardening, which is characterized by the stress level increasing after it dips below the yield point (e.g., second half of the plastic deformation region C_{7R2} of the stress-strain curve C_7), or strain softening, which is characterized by the stress level decreasing and/or remaining relative flat after the stress-strain curve drops an amount below the yield point (e.g., plastic deformation region C_{6R2} of the stress-strain curve C_6). In some embodiments, in either case of strain softening or strain hardening of the rigid material due to the applied load, the

stress level (σ_B) at the break point is always less than the stress level (σ_Y) achieved at the yield point.

[0070] It has been additionally found that rigid materials that exhibit a desirable mechanical strain ratio (ϵ_B/ϵ_Y) are able to achieve an improved dishing and planarization performance, and a desirable substrate defectivity result. Due to the ability of the rigid material to have a relatively high level of hardness (or high tensile modulus) and yet plastically deform a significant amount before break is believed to be a significant factor in the improved polishing pad performance results. As discussed above, the ability of the rigid material to plastically deform during the pad conditioning process will cause the rigid material at the polishing surface 204A to be smoothed versus creating brittle fracture regions for similarly hard polymeric materials during the pad conditioning process. One measure used to characterize a rigid material that is able to achieve the desirable polishing process performance is the mechanical strain ratio (ϵ_B/ϵ_Y), which is a ratio of the measured strain at the breaking point minus the measure strain at the yield point divided by the measured strain at the yield point. For example, the mechanical strain ratios (ϵ_B/ϵ_Y) for the material illustrated by curves C₅, C₆ and C₇ in Figure 5B, are described in equations (1), (2) and (3), respectively, as shown below.

$$\frac{\epsilon_B}{\epsilon_Y} = \frac{\epsilon_{B5} - \epsilon_{Y5}}{\epsilon_{Y5}} = \frac{S52}{S51} \quad (1)$$

$$\frac{\epsilon_B}{\epsilon_Y} = \frac{\epsilon_{B6} - \epsilon_{Y6}}{\epsilon_{Y6}} = \frac{S62}{S61} \quad (2)$$

$$\frac{\epsilon_B}{\epsilon_Y} = \frac{\epsilon_{B7} - \epsilon_{Y7}}{\epsilon_{Y7}} = \frac{S72}{S71} \quad (3)$$

It has been found that hard materials that yield and have a long elongation at break are able to achieve desirable dishing, planarization, and defectivity performance when used in a standard CMP polishing process. In some embodiments, the rigid material includes a mechanical strain ratio (ϵ_B/ϵ_Y) that is greater than 1.0, such as greater than 2.0, greater than 2.2, greater than 2.5, greater than 3.0, greater than 5.0, greater than 8.0, greater than 10, greater than 20 or even greater than 25. In some embodiments, the rigid material also has an elongation at break of at least 20%, such as greater than 40%, or even greater than 100%. In some embodiments, the rigid material also

includes a hardness of at least 50 on the Shore D scale, a hardness of at least 60 on the Shore D scale, a hardness of at least 65 on the Shore D scale, a hardness of at least 68 on the Shore D scale, or even a hardness greater than 70 on the Shore D scale. In some embodiments, the rigid material includes a hardness in a range from 60 to 80 on the Shore D scale, such as a range from 65 to 80 on the Shore D scale, or even in a range from 68 to 78 on the Shore D scale. In some embodiments, the rigid material also has a tensile modulus of at least 1000 megapascals (MPa), such as greater than 1200 MPa, or even greater than 2000 MPa, or even from 1000 to 2000 MPa. In some embodiments, the rigid material also has a yield strength of at least 30 megapascals (MPa), such as greater than 40 megapascals (MPa), or even greater than 60 megapascals (MPa), or even from 30 to 60 MPa. In some embodiments, the rigid material also has a glass transition temperature (T_g) of at least 40°C, such as greater than 50°C, or even greater than 60°C.

[0071] In some example, the rigid material has a hardness that is between 62 and 80 on the Shore D scale, a tensile modulus of between 1000 and 2000 MPa and a mechanical strain ratio (ϵ_B/ϵ_Y) that is at least greater than 2. In another example, the rigid material has a hardness that is between 65 and 78 on the Shore D scale, a tensile modulus of between 1000 and 2000 MPa and a mechanical strain ratio (ϵ_B/ϵ_Y) that is at least greater than 2.

[0072] It has been found that rigid material formulations that include a hardness that is between 60 and 80 on the Shore D scale, a tensile modulus of between 1000 and 2000 MPa and a mechanical strain ratio (ϵ_B/ϵ_Y) that is at least greater than 2 are able to achieve a reduced defectivity and improved planarization efficiency over conventional formulations after the same pad conditioning process had been performed on the different formulations. More conventional formulations, such as the brittle polymers C_1 and ductile polymers C_2 formulations illustrated in Figure 4B and 4D, have an undesirably low contact ratio (e.g., measure of surface smoothness and contact area) as determined by use of the "Areal Material Ratio" ($S_{mr}(c)$) measurement as compared to the tough polymer C_3 formulations, such as the rigid material formulations disclosed herein. It has been found that $S_{mr}(c)$ determined contact ratios of greater than 0.8%, such as greater than 2.0% contact ratios at a measurement depth (c) of 3 micrometers (μm) have provided an improved level of

defectivity versus brittle polymers C₁ and ductile polymers C₂ formulations that form contact ratios less than 0.8% after the same pad conditioning process has been performed on each of the materials. It has thus been found that formulations that fall within the tough polymer C₃ class of materials have a lower defectivity and improved planarization efficiency as compared to the brittle polymers C₁ and ductile polymers C₂ formulations, and an improved local and global planarization performance and improved dishing performance over conventional polishing pads that include the an elastomeric polymer C₄ formulations. It has been found, for example, that rigid material formulations that have [1.] a hardness that is between 60 and 80 on the Shore D scale, such as between 65 and 78 on the Shore D scale, [2.] a tensile modulus of between 1000 and 2000 MPa, [3.] a mechanical strain ratio (ϵ_B/ϵ_Y) that is at least greater than 2, and [4.] is able to achieve a contact ratio of greater than 0.8%, such as greater than 2.0% contact ratios at a measurement depth (c) of 3 micrometers (μm) after performing a pad conditioning process similar to the processes disclosed herein, has achieved a significant improvement in defectivity, planarization efficiency, local and global planarization performance and improved dishing performance over more conventional pad formulations.

[0073] Figure 5C illustrates an example of a surface roughness profile of a polishing surface of a portion of a polishing pad after a pad conditioning process has been performed on the polishing pad. It has been found that by use of an optical microscope and confocal laser analysis techniques, such as available in products made by Keyence Corporation for example, a contact ratio and profile of the surface of a polishing pad can be determined. As will described below, the effect of the material properties of the rigid material formulations versus other material formulations in relation to the contact ratio and profile of the surface of a polishing pad have been analyzed. In general, a contact ratio (A_c/A_e) is defined as the ratio of a contact area (A_c) of the pad surface that contacts a surface of a substrate during polishing to the measurement area (A_e) of the measurement region on the surface of the polishing pad. The contact area (A_c) can be determined by use of the optical microscope and confocal laser analysis techniques at a plane positioned at a measurement depth (D_M) within the measurement area (A_e) of the measurement region. The contact ratio of a pad conditioned surface of a polishing pad can be measured across the polishing surface of a polishing pad by use an optical measurement method, such as a $S_{mr}(c)$ -

ISO 25178 method. The measurement technique includes measuring the contact ratio at a measurement depth (D_M) that is measured from a peak asperity (T1), and when viewed in two dimensions (2D), as shown in Figure 5C, would be a measure of the area of the horizontal contacting regions within a horizontal plane (e.g., portions highlighted by the dark horizontal lines at the measurement depth (D_M)) versus the total area of the portion of a horizontal plane that is within the measurement region. In practice, the actual contact ratio of a horizontal portion of a polishing pad (e.g., polishing surface 204A illustrated in Figures 2 and 3A-3B) during a polishing process will vary as a function of a pressure applied to the surface of polishing pad by a "body" (e.g., 300mm SEMI™ standard monocrystalline silicon wafer), the rigidity of the "body," and the mechanical properties of the polishing pad, which includes the material properties of the rigid material that is in contact with the body. It is typically assumed that the rigidity of the body (e.g., wafer) will have a very small to negligible effect on the actual contact ratio of a pad conditioned surface of a polishing pad.

[0074] Figure 5D includes a plurality of contact area versus texture depth curves that have been generated for material layers used to form the polishing surface 204A of a polishing pad after performing a pad conditioning process. The plurality of contact area versus texture depth curves were generated for three different polymeric material samples by use of the Smr(c)-ISO 25178 measurement method. The two of the three different polymeric material samples (i.e., samples 552 and 553) were created by an additive manufacturing process, as described herein, to form the solid material layer samples that were exposed to the same pad conditioning process. In one example, a "standard" pad conditioning process included abrading the surface of the samples by sweeping a 4 inch (~102 millimeter (mm)) diameter pad conditioning disk that includes 60-100 μm sized diamond abrasive particles at a rotation speed of 100 RPM and a downforce of about 4.5 pounds at an abrasive disk sweep rate of 19 radial sweeps per minute (sweeps/min) while the platen on which the samples were positioned was rotating 85 RPM. The standard pad conditioning process is typically performed on a new polishing pad (e.g., break-in process) for a time between about 30 minutes to about 60 minutes, such as about 45 minutes. The standard pad conditioning process is typically performed while the polishing surface is maintained in a "wet" state, and thus a flow of DI water and/or polishing slurry (e.g., conventional ceria containing slurry) are provided to the polishing surface at a sufficient rate to

lubricate the polishing surface (e.g., prevent polymeric material(s) from overheating and becoming glazed) and sweep-away the abraded material created during the pad conditioning process. The three different polymeric material samples shown in Figure 5D include a first sample 552, a second sample 553 and a conventional sample 551, which were taken from a mid-radius position of a 40 inch diameter platen after the pad conditioning process had been performed. In one example, the standard pad conditioning process utilizes a pad conditioning disk that is available from Saesol Diamond Ind. Co. LTD, such as conditioning disk Part No. AB45 that includes about 40 μm diamond abrasive particle protrusions and have diamond density of about 950 per square centimeter (cm^2) and diamond tip size of about 180 μm . Similar pad conditioning disks can also be purchased from 3M or Entegris. The conventional sample 551 includes a portion of a conventional IC1010 polishing pad available from Dupont. The rigid material samples, or the first sample 552 and the second sample 553 which fall within the tough polymer C₃ class of materials, each comprise an aromatic monofunctional acrylate, a low viscosity aliphatic trifunctional monomer, a trifunctional aliphatic acrylate, and a monofunctional aliphatic acrylamide, which is discussed in further detail below. In this example, the first sample 552 and second sample 553 included a porous structure that has a pore density that was about 16%, and the porosity of the conventional sample 551 was about 30%. Figures 5E, 5F and 5G are SEM views of the surface of the conventional sample 551, the first sample 552 and the second sample 553, respectively, that has been conditioned by the pad conditioning process. Figure 5H is close up view of a portion of the contact area versus texture depth curves of Figure 5D that illustrates a difference in the contact ratio of each of the three samples at a measurement depth (D_M) of 4 μm . It has been empirically found that correlations between contact ratio and polishing performance (e.g., planarization efficiency, polishing rate, and planarization performance) performed at measurement depths (D_M) of about 4 μm are useful as a baseline for understanding the effect of contact ratio on the various polishing performance parameters due in part to the typical mechanical properties of the typical polymeric materials used to form the polishing surface of a polishing pad.

[0075] Referring back to Figures 5D and 5H, the contact area versus texture depth curves illustrate the effect of material composition the contact ratio on a pad conditioned surface. As shown in Figures 5D and 5H, contact ratio of a pad

conditioned surface increases greatly at the shallower measurement depth (D_M) versus the conventional sample 551, and thus it is believed that the rigid material formulations found in the first sample 552 and second sample 553 have a greater tendency to plastically deform due to the interaction of the surface of the pad conditioning disk during a pad conditioning operations and thus form a smoother surface that has a reduced roughness, or reduced number of surface undulations, versus the material compositions similar to the conventional samples 551, which fall within the elastomeric polymer C4 class of materials. By comparison, as shown in Figure 5H, the second sample 553 has a contact ratio of about 5.3%, the first sample 552 has a contact ratio of about 0.8%, and the conventional sample 551 has a contact ratio of about 0.03% when measured at a measurement depth (D_M) of 4 μm , as illustrated in Figure 5H. Similar to Figures 4C and 4D, the plots 551B, 552B, and 553B in Figure 5H are each software rendered versions of the polishing surfaces that graphically illustrates the relative amount of surface area at a given measurement depth (D_M) of 4 μm and the distribution of the surface area at the 4 μm depth for the conventional sample 551, the first sample 552 and the second sample 553, respectively, within the measurement areas.

[0076] Comparing the SEM images of the surfaces 551A, 552A, and 553A of the conventional sample 551, the first sample 552 and the second sample 553, respectively, in Figures 5E, 5F and 5G, and their associated distribution of the pad surface versus depth plots (right side of SEM images), it is apparent that surface of the conventional sample 551, the first sample 552 and the second sample 553 become increasing smooth when viewed in that order. The distribution of the pad surface versus depth plots for each of the respective Figures 5E, 5F and 5G, illustrate the distribution of the position of the polishing surface as a function of depth of the pad conditioned surface from a peak region of the pad conditioned surface for the conventional sample 551, the first sample 552 and the second sample 553. In Figures 5E, 5F and 5G, the peak value and distribution of the position of the polishing surface as a function of depth decreases when comparing the conventional sample 551 with the rigid materials of the first sample 552 and the second sample 553, respectively. For example, the conventional sample 551 has a surface depth distribution that extends from zero to a value that is greater than 45 μm and has a peak value at about 28 μm versus the second sample 553 that has a surface depth distribution that

extends from zero to a value of about 28 μm and has a peak value at about 10 μm . It is believed that a narrower distribution of the depth of the pad conditioned surface from a peak value will increase the amount of a polishing pad's contact with the surface of a "body" (e.g., wafer or substrate) that is being urged against the polishing surface of the polishing pad, which will increase the polishing rate and reduce defectivity of a polished body.

[0077] Figure 5I illustrates a plot of polishing rate versus contact ratio for a plurality of different polymeric material formulations. The data shown in Figure 5I includes data taken using a polishing process that included the use of a ceria containing slurry that was performed during a dielectric material polishing process (i.e., SiO_2) performed in a Reflexion® LK Prime® CMP tool available from Applied Materials Inc. of Santa Clara, California. Conventional ceria based slurries are available from Solvay S.A., Inochem, and AGC Inc. In one example, the ceria slurry can include cerium oxide (ceria) nanoparticles (e.g., 10-30 wt% in suspension (10nm-60nm sized particles)), an amine, DI water, and optionally TMAH. It has been found that the rigid material formulation described herein, which are used to form the polishing surface of a polishing pad, achieve greatly improved polishing process results when used with ceria based slurries versus other common slurry compositions (e.g., alumina, titania, zirconia, germania, or silica based slurries). It is believed that polishing processes that are more chemically driven, such as ceria slurry based polishing processes, will benefit significantly versus the more mechanical abrasion dominated CMP processes, which utilize the other common types of slurry compositions. The added benefit provided to the more chemically driven processes is believed at least in-part to be due to the increased contact area of the pad conditioned polishing surface's increased ability to interact with and remove the chemical reaction components formed at the surface of the substrate during a polishing process, and thus increase the interaction of the fresh and unreacted polishing chemistry with the newly exposed substrate surface that recently interacted with a portion of the pad conditioned polishing surface.

[0078] As illustrated in Figure 5I, the polishing rate (angstroms ($\text{\AA}$)/minute) increases as the contact ratio (%) increases, as illustrated by the data collected for the three different types of samples that are described above. In this example, the conventional sample 551 polishing process data is illustrated by an open circle, first

sample 552 polishing process data is illustrated by the open square data point, and second sample 553 polishing process data is illustrated by the open and closed triangle data points. One will also note that the polishing rate also increases as the down force applied to the substrate during a polishing process increases (e.g., 4.0 psi to 4.5 psi) for at least the ceria based polishing processes described herein. It is believed that most ceria, and non-ceria, based polishing processes that utilize the rigid material compositions disclosed herein will have an increased polishing rate as the down force is increased, due in some part to the improved elongation/deformation of the material that contacts the surface of the substrate during polishing. However, it has been found that ceria based processes see a significant increase in benefit over the other non-ceria polishing processes due to the use of rigid material chemistries disclosed herein.

[0079] It has been found that the rigid material formulations described herein are beneficially configured to achieve contact ratios that are at least greater than 0.8%, such as greater than 1.0%, or greater than 2.0%, or greater than 2.5%, or greater than 4.0%, or even greater than 5.0% when measured at a measurement depth (D_M) of about 4 μm after performing a standard pad conditioning process as described herein. The increased contact ratios over convention pad materials will provide a significant benefit relating to the planarization efficiency and defectivity of a polished substrate, along with an increase in polishing rate of a substrate during various polishing processes, such as ceria based polishing processes.

Formulation and Material Examples

[0080] As briefly discussed above, in some embodiments, a polishing layer region 204B that includes the rigid material is formed from a mixture of two or more pre-polymer compositions that are at least partially mixed and cured to cause at least partial polymerization, e.g., cross-linking, of the pre-polymer composition(s) to form a continuous polymer phase. In some embodiments, by use of an additive manufacturing process, which is described further below, the formed continuous polymer phase forms the structural elements of the polishing pad 204, such as the polishing features 204G of the polishing layer region 204B. Pre-polymer compositions of the present disclosure may include a mixture of one or more of functional polymers,

functional oligomers, functional monomers, functional cross-linkers, reactive diluents, additives, and photoinitiators.

[0081] Examples of suitable functional polymers which may be used to form one or both of the at least two pre-polymer compositions include multifunctional acrylates including di, tri, tetra, and higher functionality acrylates, such as 1,3,5-triacryloylhexahydro-1,3,5-triazine or trimethylolpropane triacrylate, dipropylene glycol diacrylate or dimethacrylate.

[0082] Examples of suitable functional oligomers which may be used to form one or both of the at least two pre-polymer compositions include monofunctional and multifunctional oligomers, acrylate oligomers, such as aliphatic urethane acrylate oligomers, aliphatic hexafunctional urethane acrylate oligomers, diacrylate, aliphatic hexafunctional acrylate oligomers, multifunctional urethane acrylate oligomers, aliphatic urethane diacrylate oligomers, aliphatic urethane acrylate oligomers, aliphatic polyester urethane diacrylate blends with aliphatic diacrylate oligomers, or combinations thereof, for example bisphenol-A ethoxylate diacrylate or polybutadiene diacrylate, tetrafunctional acrylated polyester oligomers, aliphatic polyester based urethane diacrylate oligomers and aliphatic polyester based acrylates and diacrylates.

[0083] Examples of suitable monomers which may be used to form one or both of the at least two pre-polymer compositions include both mono-functional monomers and multifunctional monomers. Suitable mono-functional monomers include tetrahydrofurfuryl acrylate (e.g. SR285 from Sartomer®), tetrahydrofurfuryl methacrylate, vinyl caprolactam, isobornyl acrylate, isobornyl methacrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, 2-(2-ethoxyethoxy)ethyl acrylate, isooctyl acrylate, isodecyl acrylate, isodecyl methacrylate, lauryl acrylate, lauryl methacrylate, stearyl acrylate, stearyl methacrylate, cyclic trimethylolpropane formal acrylate, 2-[[[(Butylamino) carbonyl]oxy]ethyl acrylate (e.g. Genomer 1122 from RAHN USA Corporation), cycloaliphatic acrylate (e.g. SR217 from Sartomer®), 3,3,5-trimethylcyclohexyl acrylate, or mono-functional methoxylated PEG (350) acrylate. Suitable multifunctional monomers include diacrylates or dimethacrylates of diols and polyether diols, such as propoxylated neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate,

alkoxylated aliphatic diacrylate (e.g., SR9209A from Sartomer®), diethylene glycol diacrylate, diethylene glycol dimethacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, triethylene glycol dimethacrylate, alkoxylated hexanediol diacrylates, or combinations thereof, for example SR508, SR562, SR563, SR564 from Sartomer®.

[0084] Typically, the reactive diluents used to form one or more of the pre-polymer compositions are least monofunctional, and undergo polymerization when exposed to free radicals, Lewis acids, and/or electromagnetic radiation. Examples of suitable reactive diluents include monoacrylate, 2-ethylhexyl acrylate, octyldecyl acrylate, cyclic trimethylopropane formal acrylate, caprolactone acrylate, isobornyl acrylate (IBOA), or alkoxylated lauryl methacrylate. In some examples, reactive diluents may include Genocure series products, such as PBZ, or Genomer series products, such as Genomer 5142, each manufactured by Rahn AG of Zurich, Switzerland.

[0085] Examples of suitable additives include surface modifiers such as surfactants to control surface tension. Some example additives may include ethoxylated polydimethylsiloxanes, such as BYK series products, such as BYK-307, manufactured by BYK-Chemie GmbH of Wesel, Germany.

[0086] Examples of suitable photoinitiators used to form one or more of the at least two different pre-polymer compositions include polymeric photoinitiators and/or oligomer photoinitiators, such as benzoin ethers, benzyl ketals, acetyl phenones, alkyl phenones, phosphine oxides, benzophenone compounds and thioxanthone compounds that include an amine synergist, or combinations thereof. In some examples, photoinitiators may include Irgacure® series products, such as Irgacure® 819, manufactured by BASF of Ludwigshafen, Germany.

[0087] Examples of polishing pad materials formed of the pre-polymer compositions described above typically include at least one of oligomeric and, or, polymeric segments, compounds, or materials selected from the group consisting of: polyamides, polycarbonates, polyesters, polyether ketones, polyethers, polyoxymethylenes, polyether sulfone, polyetherimides, polyimides, polyolefins, polysiloxanes, polysulfones, polyphenylenes, polyphenylene sulfides, polyurethanes, polystyrene, polyacrylonitriles, polyacrylates, polymethylmethacrylates, polyurethane acrylates, polyester acrylates, polyether acrylates, epoxy acrylates, polycarbonates,

polyesters, melamines, polysulfones, polyvinyl materials, acrylonitrile butadiene styrene (ABS), halogenated polymers, block copolymers, and random copolymers thereof, and combinations thereof.

Rigid Material Examples

[0088] A rigid material that can be used to form a desirable polishing layer is formed from at least two different materials that are formed from the pre-polymer compositions that contain “resin precursor components” that include, but are not restricted to functional polymers, functional oligomers, monomers, reactive diluents, flow additives, curing agents, photoinitiators, and cure synergists.

[0089] In some embodiments, the rigid material is formed from a composition that includes an aromatic monofunctional acrylate, a low viscosity aliphatic trifunctional monomer, a trifunctional aliphatic acrylate, and a monofunctional aliphatic acrylamide. In one example, the rigid material is formed from a pre-polymer composition that includes (by weight ratio) 34.2% of a IBXA diluted Oligomer, 8% of DEAA, 3.8% of SR351H, 21.1% of TMCHA, 30.9% of IBXA, and 2% of Omnirad 819. In this example, the rigid material had a mechanical strain ratio (ϵ_B/ϵ_Y) of about 2, a hardness of about 75 on the Shore D scale, a tensile modulus of about 1500 megapascals (MPa), a yield strength of at least 30 megapascals (MPa), and an elongation at break of about 8%.

[0090] In a second example, the resin precursor components used to form the rigid material may include, an oligomer, such as tri functional urethane, one or more monomers, such as difunctional polyether acrylate, a reactive diluent, such as monofunctional urethane acrylate, flow additives, curing agents, and photoinitiators. In this example, the rigid material had a mechanical strain ratio (ϵ_B/ϵ_Y) of about 8, a hardness of about 68 on the Shore D scale, a tensile modulus of about 1200 megapascals (MPa), a yield strength of at least 26 megapascals (MPa), and an elongation at break of about 60%.

[0091] In a third example, the resin precursor components used to form the rigid material may include, an oligomer, such as difunctional polyester acrylate, one or more monomers, such as difunctional epoxy acrylate, a reactive diluent, such as monofunctional methacrylate, flow additives, curing agents, and photoinitiators. In this example, the rigid material had a mechanical strain ratio (ϵ_B/ϵ_Y) of about 10, a

hardness of about 60 on the Shore D scale, a tensile modulus of about 1000 megapascals (MPa), a yield strength of at least 22 megapascals (MPa), and an elongation at break of about 80%.

Pore Forming Features

[0092] In some embodiments of the polishing pad 204, pore-features are formed into a region at and/or just below the polishing surface 204A of the polishing pad 204. The pore-features can be formed by use of a sacrificial material precursor that is deposited in desired locations within the layers used to form the polishing layer of the polishing pad by use of an additive manufacturing process, which is described below. The sacrificial material precursor can include water-soluble materials, such as, glycols (e.g., polyethylene glycols), glycol-ethers, and amines. Examples of suitable sacrificial material precursors which may be used to form the pore forming features described herein include ethylene glycol, butanediol, dimer diol, propylene glycol-(1,2) and propylene glycol-(1,3), octane-1,8-diol, neopentyl glycol, cyclohexane dimethanol (1,4-bis-hydroxymethylcyclohexane), 2-methyl-1,3-propane diol, glycerine, trimethylolpropane, hexanediol-(1,6), hexanetriol-(1,2,6) butane triol-(1,2,4), trimethyloethane, pentaerythritol, quinitol, mannitol and sorbitol, methylglycoside, also diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols, dibutylene glycol, polybutylene glycols, ethylene glycol, ethylene glycol monobutyl ether (EGMBE), diethylene glycol monoethyl ether, ethanolamine, diethanolamine (DEA), triethanolamine (TEA), and combinations thereof.

[0093] In some embodiments, the sacrificial material precursor includes a water soluble polymer, such as 1-vinyl-2-pyrrolidone, vinylimidazole, polyethylene glycol diacrylate, acrylic acid, sodium styrenesulfonate, Hitenol BC10®, Maxemul 6106®, hydroxyethyl acrylate and [2-(methacryloyloxy)ethyltrimethylammonium chloride, 3-allyloxy-2-hydroxy-1-propanesulfonic acid sodium, sodium 4-vinylbenzenesulfonate, [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide, 2-acrylamido-2-methyl-1-propanesulfonic acid, vinylphosphonic acid, allyltriphenylphosphonium chloride, (vinylbenzyl)trimethylammonium chloride, E-SPERSE RS-1618, E-SPERSE RS-1596, methoxy polyethylene glycol monoacrylate, methoxy polyethylene glycol diacrylate, methoxy polyethylene glycol triacrylate, or combinations thereof.

Additive Manufacturing Process and System

[0094] Figure 6A is a schematic sectional view of an additive manufacturing system, which may be used to form the polishing pads described herein, according to some embodiments. Here, the additive manufacturing system 600 features a movable manufacturing support 602, a plurality of dispense heads 604 and 606 disposed above the manufacturing support 602, a curing source 608, and a system controller 610. In some embodiments, the dispense heads 604, 606 move independently of one another and independently of the manufacturing support 602 during the polishing pad manufacturing process. Here, the first and second dispense heads 604 and 606 are respectively fluidly coupled to a first pre-polymer composition source 612 and a sacrificial material source 614. Typically, the additive manufacturing system 600 features at least one more dispense head (e.g., a third dispense head, not shown) which is fluidly coupled to a second pre-polymer composition source used to form a foundation layer. In some embodiments, the additive manufacturing system 600 includes as many dispense heads as desired to each dispense a different pre-polymer composition or sacrificial material precursor composition. In some embodiments, the additive manufacturing system 600 further includes pluralities of dispense heads where two or more dispense heads are configured to dispense the same pre-polymer compositions or sacrificial material precursor compositions.

[0095] Here, each of dispense heads 604, 606 features an array of droplet ejecting nozzles 616 configured to eject droplets 630, 632 of the respective pre-polymer composition 612 and sacrificial material composition 614 delivered to the dispense head reservoirs. Here, the droplets 630, 632 are ejected towards the manufacturing support 602 and thus onto the manufacturing support 602 or onto a previously formed print layer 618 disposed on the manufacturing support 602. Typically, each of dispense heads 604, 606 is configured to fire (control the ejection of) droplets 630, 632 from each of the nozzles 616 in a respective geometric array or pattern independently of the firing of other nozzles 616 thereof. Herein, the nozzles 616 are independently fired according to a droplet dispense pattern for a print layer to be formed, such as the print layer 624, as the dispense heads 604, 606 move relative to the manufacturing support 602. Once dispensed, the droplets 630 of the pre-polymer composition 612 and/or the droplets 632 of the sacrificial material composition 614

are at least partially cured by exposure to electromagnetic radiation, e.g., UV radiation 626, provided by the curing source 608, e.g., an electromagnetic radiation source, such as a UV radiation source to form a print layer, such as the partially formed print layer 624.

[0096] Here, the additive manufacturing system 600 shown in Figure 6A further includes the system controller 610 to direct the operation thereof. The system controller 610 includes a programmable central processing unit (CPU) 634 which is operable with a memory 635 (e.g., non-volatile memory) and support circuits 636. The support circuits 636 are conventionally coupled to the CPU 634 and include cache, clock circuits, input/output subsystems, power supplies, and the like, and combinations thereof coupled to the various components of the additive manufacturing system 600, to facilitate control thereof. The CPU 634 is one of any form of general purpose computer processor used in an industrial setting, such as a programmable logic controller (PLC), for controlling various components and sub-processors of the additive manufacturing system 600. The memory 635, coupled to the CPU 634, is non-transitory and is typically one or more of readily available memories such as random access memory (RAM), read only memory (ROM), floppy disk drive, hard disk, or any other form of digital storage, local or remote.

[0097] Typically, the memory 635 is in the form of a computer-readable storage medium containing instructions (e.g., non-volatile memory), which when executed by the CPU 634, facilitates the operation of the manufacturing system 600. The instructions in the memory 635 are in the form of a program product such as a program that implements the methods of the present disclosure.

[0098] The program code may conform to any one of a number of different programming languages. In one example, the disclosure may be implemented as a program product stored on computer-readable storage media for use with a computer system. The program(s) of the program product define functions of the embodiments (including the methods described herein).

[0099] Illustrative computer-readable storage media include, but are not limited to: (i) non-writable storage media (e.g., read-only memory devices within a computer such as CD-ROM disks readable by a CD-ROM drive, flash memory, ROM chips or

any type of solid-state non-volatile semiconductor memory) on which information is permanently stored; and (ii) writable storage media (e.g., floppy disks within a diskette drive or hard-disk drive or any type of solid-state random-access semiconductor memory) on which alterable information is stored. Such computer-readable storage media, when carrying computer-readable instructions that direct the functions of the methods described herein, are embodiments of the present disclosure. In some embodiments, the methods set forth herein, or portions thereof, are performed by one or more application specific integrated circuits (ASICs), field-programmable gate arrays (FPGAs), or other types of hardware implementations. In some other embodiments, the polishing pad manufacturing methods set forth herein are performed by a combination of software routines, ASIC(s), FPGAs and, or, other types of hardware implementations.

[00100] Here, the system controller 610 directs the motion of the manufacturing support 602, the motion of the dispense heads 604 and 606, the firing of the nozzles 616 to eject droplets of pre-polymer compositions therefrom, and the degree and timing of the curing of the dispensed droplets provided by the UV radiation source 608. In some embodiments, the instructions used by the system controller to direct the operation of the manufacturing system 600 include droplet dispense patterns for each of the print layers to be formed. In some embodiments, the droplet dispense patterns are collectively stored in the memory 635 as CAD-compatible digital printing instructions.

[00101] In some embodiments, dispensed droplets of the pre-polymer compositions, such as the dispensed droplets 630 of the pre-polymer composition 612, are exposed to electromagnetic radiation to physically fix the droplet before it spreads to an equilibrium size such as set forth in the description of Figure 6B. Typically, the dispensed droplets are exposed to electromagnetic radiation to at least partially cure the pre-polymer compositions thereof within 1 second or less of the droplet contacting a surface, such as the surface of the manufacturing support 602 or of a previously formed print layer 618 disposed on the manufacturing support 602.

[00102] Figure 6B is a close up cross-sectional view schematically illustrating a droplet 630 disposed on a surface 618a of a previously formed layer, such as the previously formed layer 618 described in Figure 6A, according to some embodiments.

In a typical additive manufacturing process, a droplet of pre-polymer composition, such as the droplet 630, spreads and reaches an equilibrium contact angle α with the surface 618a of the previously formed layer within about one second from the moment in time that the droplet 630 contacts the surface 618a. The equilibrium contact angle α is a function of at least the material properties of the pre-polymer composition and the energy at the surface 618a (surface energy) of the previously formed layer. In some embodiments, it is desirable to at least partially cure the dispensed droplet before it reaches an equilibrium size in order to fix the droplet's contact angle with the surface 618a of the previously formed layer. In those embodiments, the fixed droplet's 630a contact angle θ is greater than the equilibrium contact angle α of the droplet 630b (shown in phantom) of the same pre-polymer composition, which was allowed to spread to its equilibrium size.

[00103] Herein, at least partially curing a dispensed droplet causes at least partial polymerization, e.g., cross-linking, of the pre-polymer composition(s) within the droplets and with adjacently disposed droplets of the same or different pre-polymer compositions to form a continuous polymer phase. In some embodiments, the pre-polymer compositions are dispensed and at least partially cured to form a well about a desired pore before a sacrificial material composition is dispensed thereinto.

[00104] Figure 7 is a flow diagram setting forth a method of forming a printed layer of a polishing pad according to embodiments described herein. Embodiments of the method 700 may be used in combination with one or more of the systems and system operations described herein, such as the additive manufacturing system 600 of Figure 6A and the fixed droplets of Figure 6B. Further, embodiments of the method 700 may be used to form any one or combination of embodiments of the polishing pads shown and described herein.

[00105] At activity 710, the method 700 includes dispensing droplets of a pre-polymer composition onto a surface of a previously formed print layer according to a predetermined droplet dispense pattern. In this configuration, activity 710 will include a process of dispensing droplets of a pre-polymer composition and dispensing droplets of a sacrificial material composition onto a surface of a previously formed print layer according to a predetermined droplet dispense pattern to form a layer within the polishing pad 204.

[00106] At activity 720, the method 700 includes at least partially curing the dispensed droplets of the pre-polymer composition to form a print layer that includes the rigid material. In some embodiments, the rigid material layer may also include a plurality of pore-features that include the sacrificial material composition.

[00107] In some embodiments, the method 700 further includes sequential repetitions of activities 710 and 720 to form a plurality of print layers stacked in a Z-direction, i.e., a direction orthogonal to the surface of the manufacturing support or a previously formed print layer disposed thereon. The predetermined droplet dispense pattern used to form each print layer may be the same or different as a predetermined droplet dispense pattern used to form a previous print layer disposed there below.

[00108] In some embodiments of the method 700, the plurality of print layers include a polishing layer having a plurality of pores, or pore-features, formed therein. In some embodiments, the plurality of print layers include a polishing layer having a plurality of pore-forming features formed therein in which the plurality of pore-forming features include the sacrificial material composition.

[00109] The preceding description is provided to enable any person skilled in the art to practice the various embodiments described herein. The examples discussed herein are not limiting of the scope, applicability, or embodiments set forth in the claims. Various modifications to these embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments. For example, changes are made in the function and arrangement of elements discussed without departing from the scope of the disclosure. Various examples may omit, substitute, or add various procedures or components as appropriate. For instance, the methods described may be performed in an order different from that described, and various steps may be added, omitted, or combined. Also, features described with respect to some examples may be combined in some other examples. For example, an apparatus may be implemented or a method may be practiced using any number of the aspects set forth herein. In addition, the scope of the disclosure is intended to cover such an apparatus or method that is practiced using other structure, functionality, or structure and functionality in addition to, or other than, the various aspects of the disclosure set forth herein. It should be understood

that any aspect of the disclosure disclosed herein may be embodied by one or more elements of a claim.

[00110] The methods disclosed herein comprise one or more steps or actions for achieving the methods. The method steps and/or actions may be interchanged with one another without departing from the scope of the claims. In other words, unless a specific order of steps or actions is specified, the order and/or use of specific steps and/or actions may be modified without departing from the scope of the claims. Further, the various operations of methods described above may be performed by any suitable means capable of performing the corresponding functions. The means may include various hardware and/or software component(s) and/or module(s), including, but not limited to a circuit, an application specific integrated circuit (ASIC), or processor. Generally, where there are operations illustrated in figures, those operations may have corresponding counterpart means-plus-function components with similar numbering.

[00111] While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is claimed is:

1. A polishing pad for planarizing a surface of a substrate during a polishing process, comprising:
 - a base layer, comprising a first material composition; and
 - a polishing layer disposed over the base layer, wherein
 - the polishing layer comprises a second material composition that is exposed at a polishing surface of the polishing pad,
 - the polishing surface is configured to contact the surface of the substrate during the polishing process,
 - the second material composition comprises a polishing layer material having:
 - a hardness that is greater than 50 on a Shore D scale;
 - a yield point strength;
 - a yield point strength strain;
 - a break point strength; and
 - an elongation at break point strain,
 - wherein a magnitude of a difference between the elongation at break point strain and the yield point strength strain is greater than the magnitude of yield point strength strain when measured at room temperature.
2. The polishing pad of claim 1, wherein the break point strength is less than the yield point strength.
3. The polishing pad of claim 2, wherein the hardness of the second material composition is greater than 60 on a Shore D scale.
4. The polishing pad of claim 1, wherein the hardness of the second material composition is in a range from 65 to 78 on a Shore D scale.

5. The polishing pad of claim 1, wherein the magnitude of the difference between the elongation at break point strain and the yield point strength strain is at least 2 times greater than the magnitude of yield point strength strain.
6. The polishing pad of claim 5, wherein the polishing layer material further includes:
- a glass transition temperature (T_g) of between about 60-80 C;
 - a tensile Modulus of about 100-2,000 MPa at 40 C; and
 - an E' ratio at 30C-90C of between about 1 and 5.
7. The polishing pad of claim 1, wherein the polishing surface of the polishing layer material comprises:
- a contact ratio of at least 0.8% at a measurement depth (D_M) of 4 μm after performing a standard pad conditioning process.
8. The polishing pad of claim 1, wherein the polishing surface of the polishing layer material comprises:
- a contact ratio of at least 2% at a measurement depth (D_M) of 4 μm after performing a standard pad conditioning process.
9. A polishing pad for planarizing a surface of a substrate during a polishing process, comprising:
- a base layer, comprising a first material composition; and
 - a polishing layer disposed over the base layer, wherein
 - the polishing layer comprises a second material composition that is exposed at a polishing surface of the polishing pad,
 - the polishing surface is configured to contact the surface of the substrate during the polishing process, and
 - the second material composition comprises a polishing layer material having:
 - a hardness that is greater than 50 on a Shore D scale; and
 - a mechanical strain ratio (ϵ_B/ϵ_Y) of greater than 2.

10. The polishing pad of claim 9, wherein the polishing layer material has a hardness that is greater than 65 on the Shore D scale.
11. The polishing pad of claim 9, wherein
the hardness is between 65 and 78 on the Shore D scale, and
the polishing layer material has a tensile modulus of between 1000 and 2000 MPa and an elongation at break of greater than about 60%.
12. The polishing pad of claim 9, wherein resin precursor components used to form the polishing layer material comprise an oligomer, one or more monomers, and a reactive diluent.
13. The polishing pad of claim 12, wherein
the oligomer comprises a tri-functional urethane;
the one or more monomers comprise a difunctional polyether acrylate; and
the reactive diluent comprises a monofunctional urethane acrylate.
14. The polishing pad of claim 12, wherein
the oligomer comprises a difunctional polyester acrylate;
the one or more monomers comprise a difunctional epoxy acrylate; and
the reactive diluent comprises a monofunctional methacrylate.
15. The polishing pad of claim 12, wherein the polishing layer material comprises an aromatic monofunctional acrylate, a low viscosity aliphatic trifunctional monomer, a trifunctional aliphatic acrylate, and a monofunctional aliphatic acrylamide.
16. The polishing pad of claim 15, wherein the polishing surface of the polishing layer comprises:
a contact ratio of at least 0.8% at a measurement depth (D_M) of 4 μm after performing a standard pad conditioning process.
17. The polishing pad of claim 10, wherein the second material composition has a break point strength that is less than its yield point strength.

18. A method of planarizing a surface of a substrate during a polishing process, comprising:

conditioning a polishing surface of a polishing pad;

delivering a ceria containing polishing slurry composition to the polishing surface of the polishing pad; and

urging the surface of the substrate against the polishing surface of the polishing pad while the ceria containing polishing slurry composition is disposed across the polishing surface of the polishing pad,

wherein the polishing pad comprises:

a base layer, comprising a first material composition; and

a polishing layer disposed over the base layer, wherein

the polishing layer comprises a second material composition that is exposed at the polishing surface of the polishing pad, and

the second material composition comprises a polishing layer material having:

a hardness that is greater than 50 on a Shore D scale;

a yield point strength;

a yield point strength strain;

a break point strength; and

an elongation at break point strain,

wherein a magnitude of a difference between the elongation at break point strain and the yield point strength strain is greater than the magnitude of yield point strength strain when measured at room temperature.

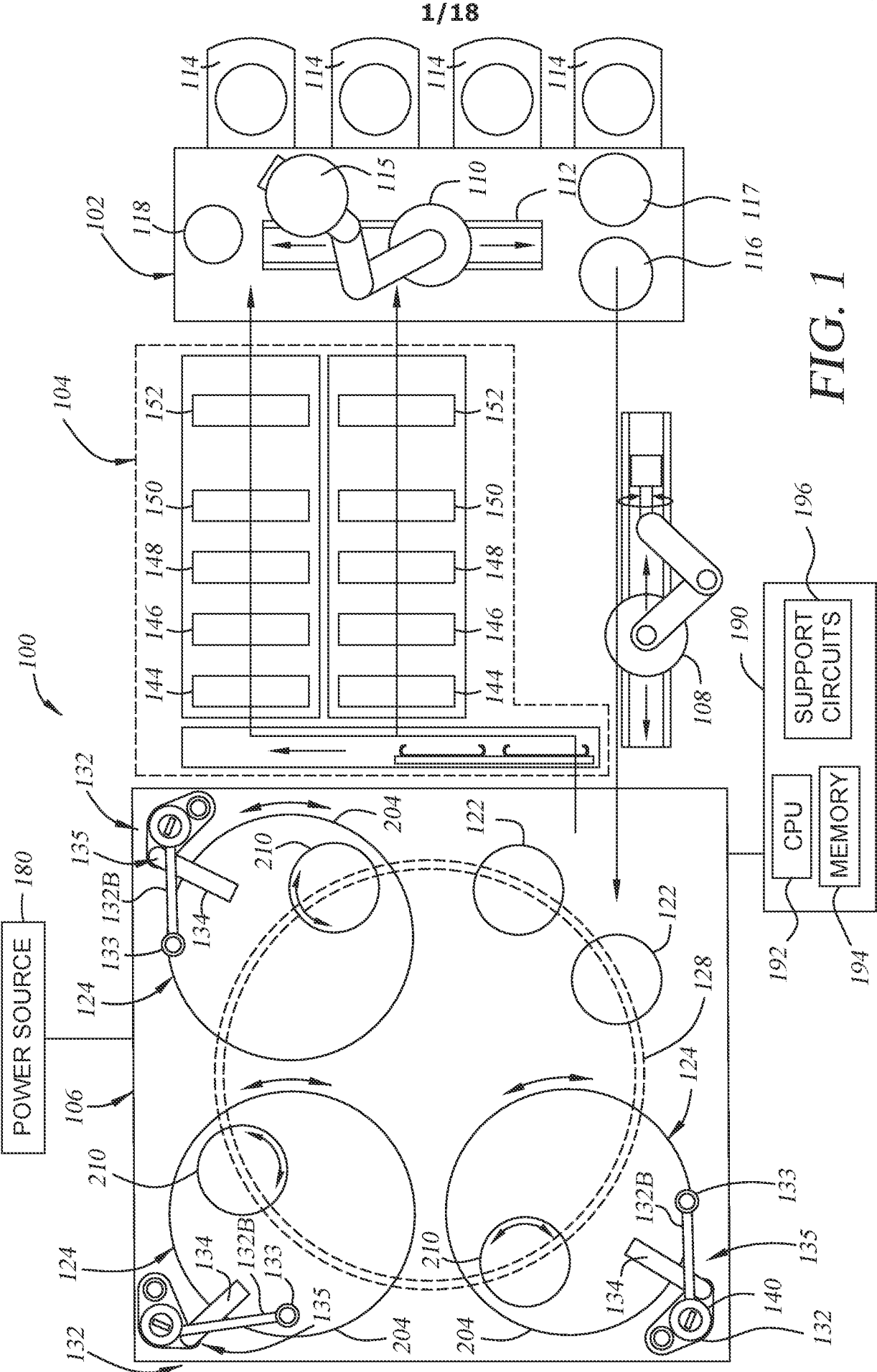
19. The method of claim 18, wherein the second material composition further comprises:

a hardness that is greater than 68 on a Shore D scale; and

a mechanical strain ratio (ϵ_B/ϵ_Y) of greater than 2.

20. The method of claim 19, wherein the polishing surface of the polishing layer comprises:

a contact ratio of at least 0.8% at a measurement depth (D_M) of 4 μm after conditioning the polishing surface of the polishing pad using a standard pad conditioning process.



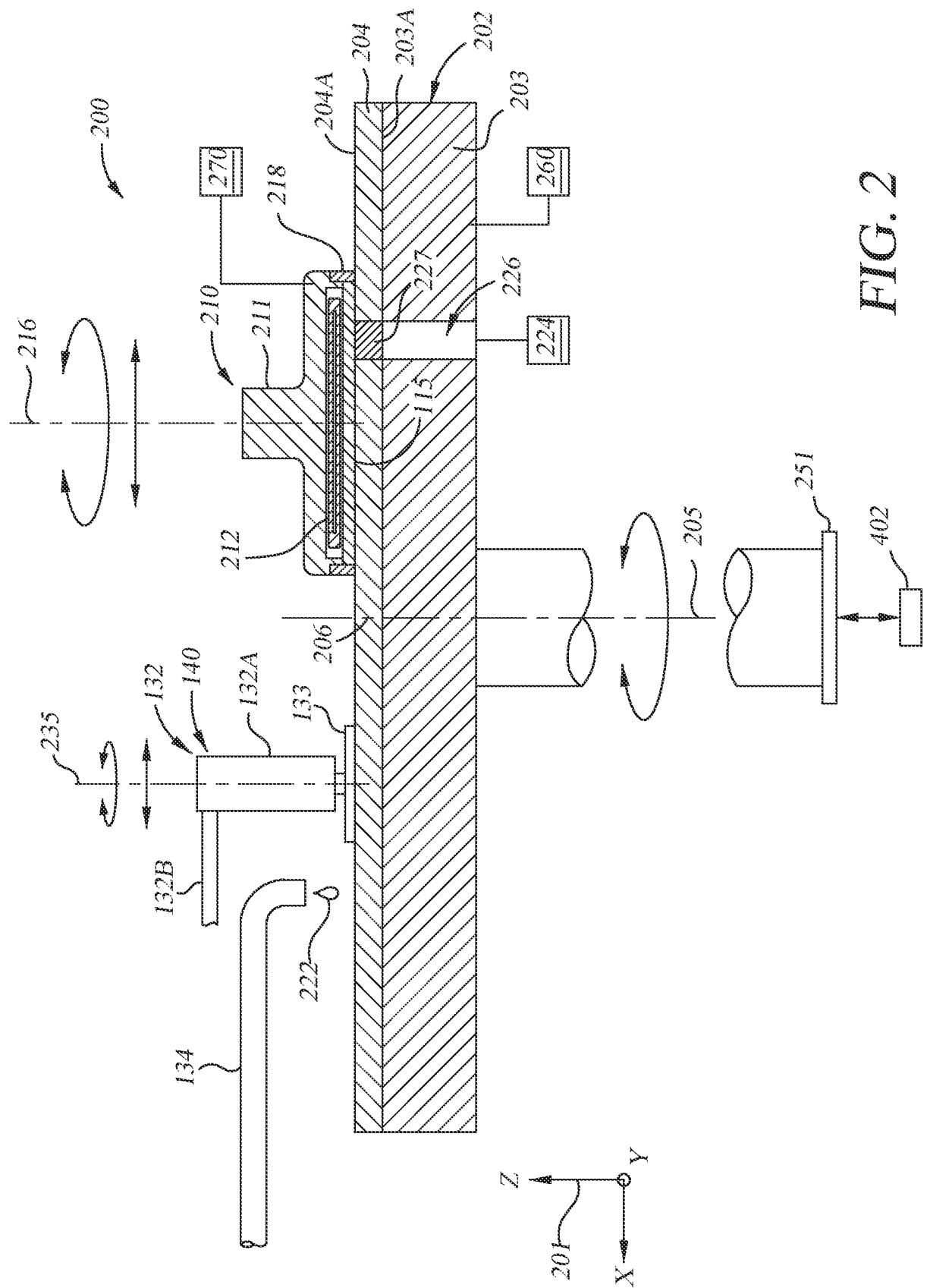
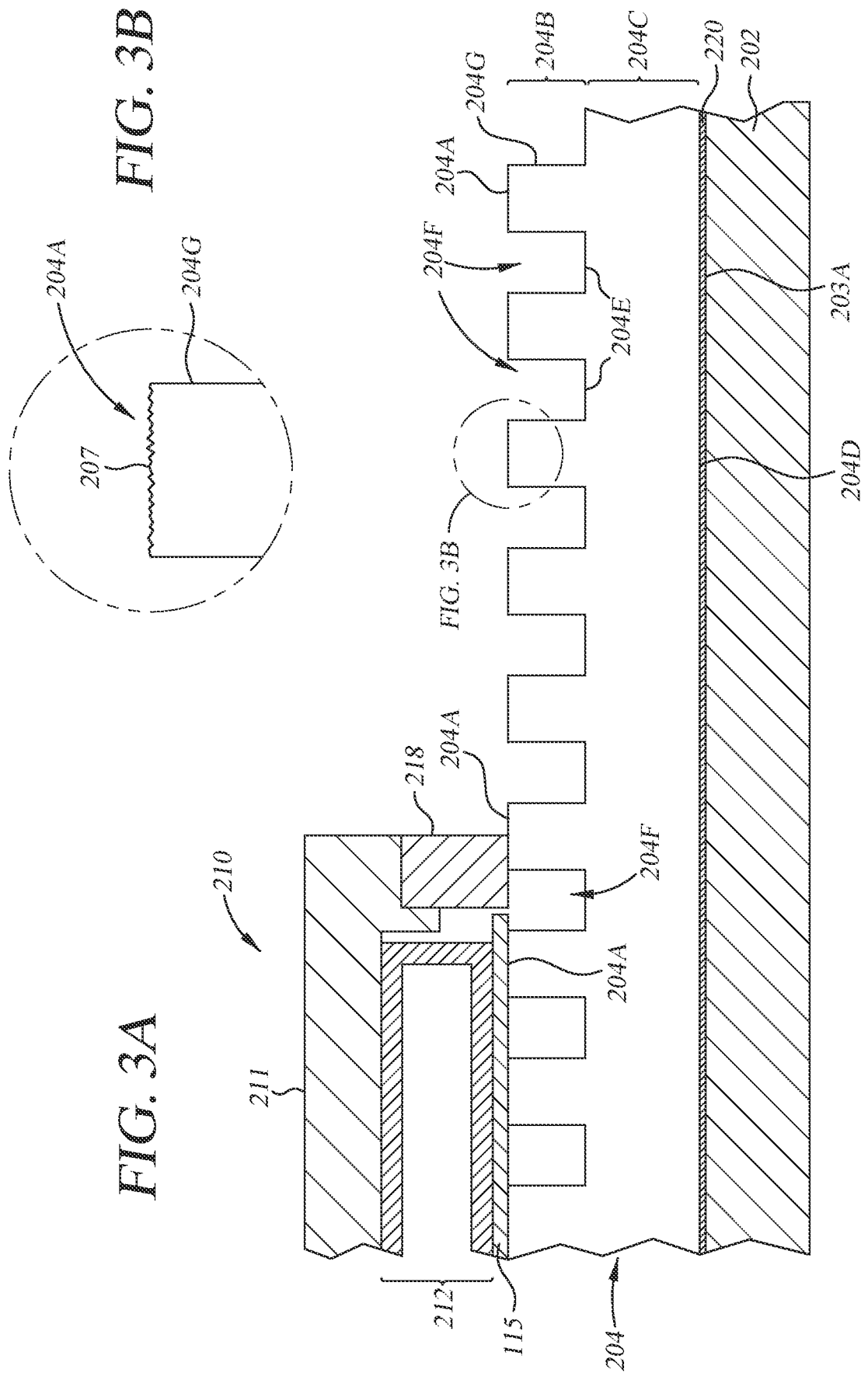


FIG. 2



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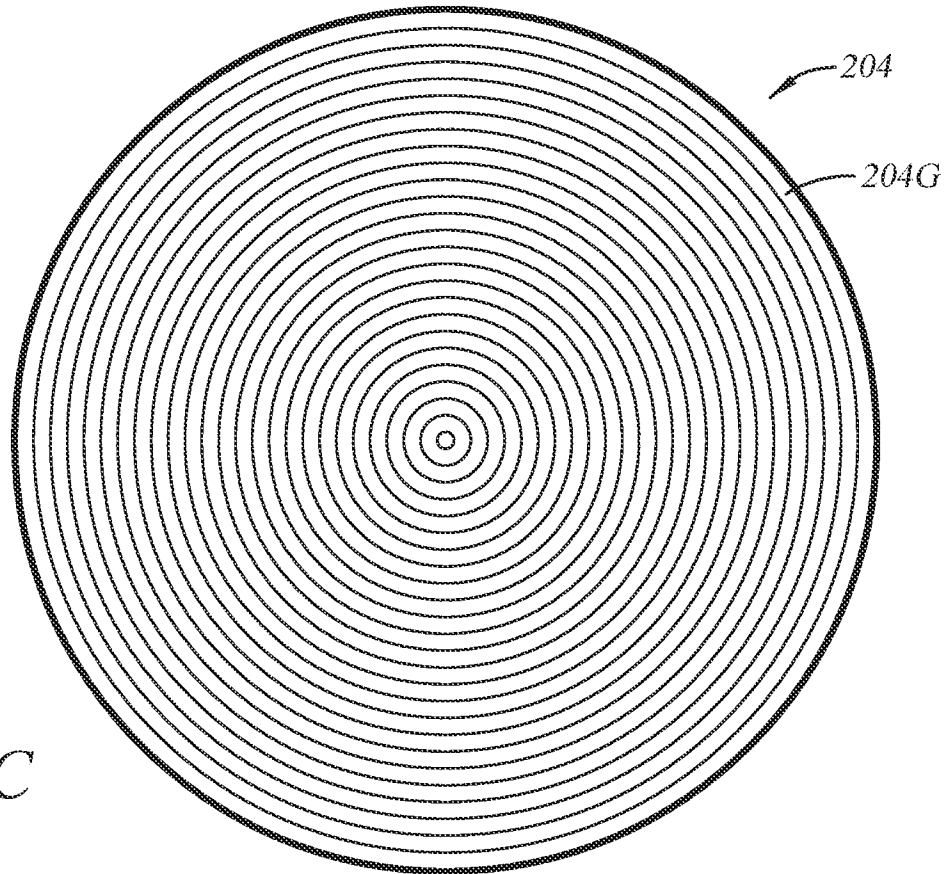


FIG. 3C

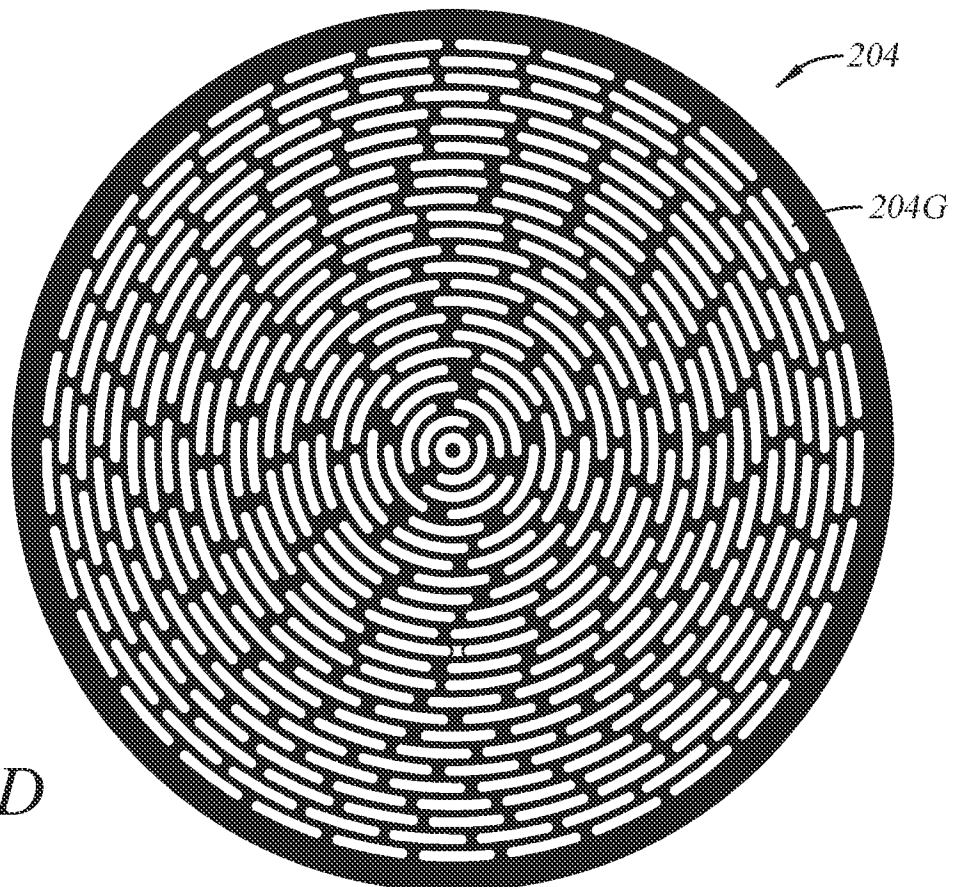


FIG. 3D

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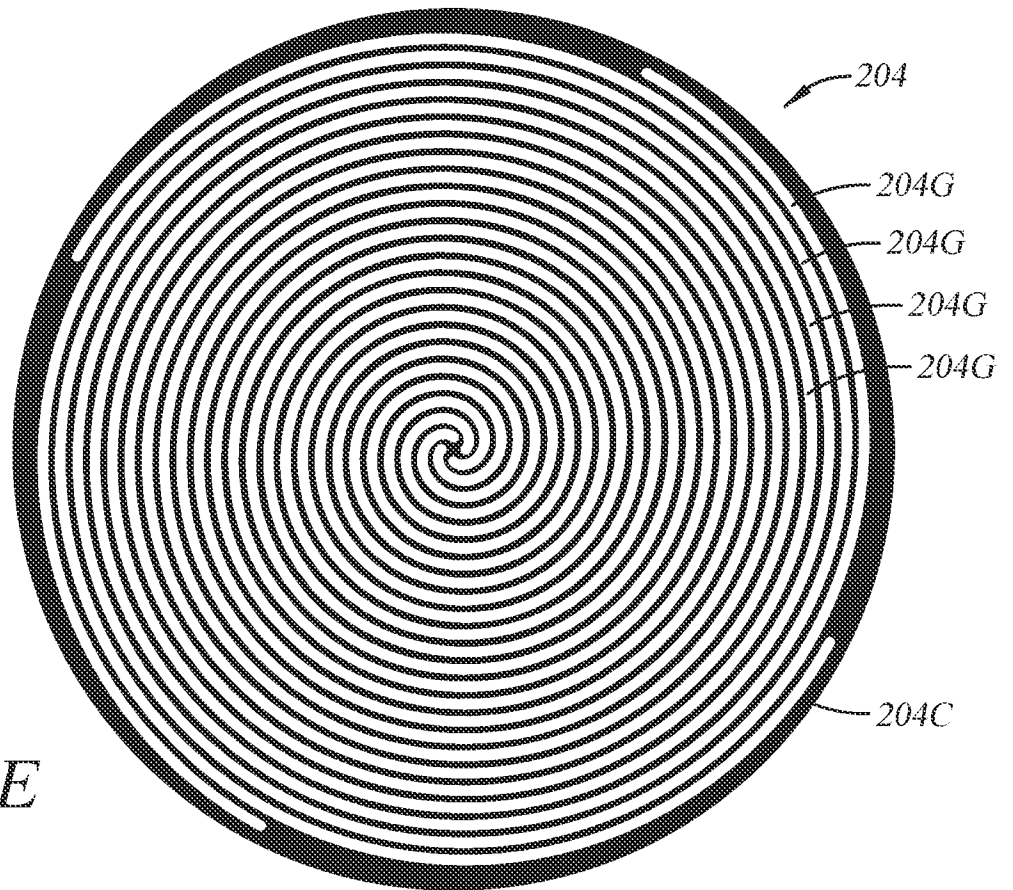


FIG. 3E

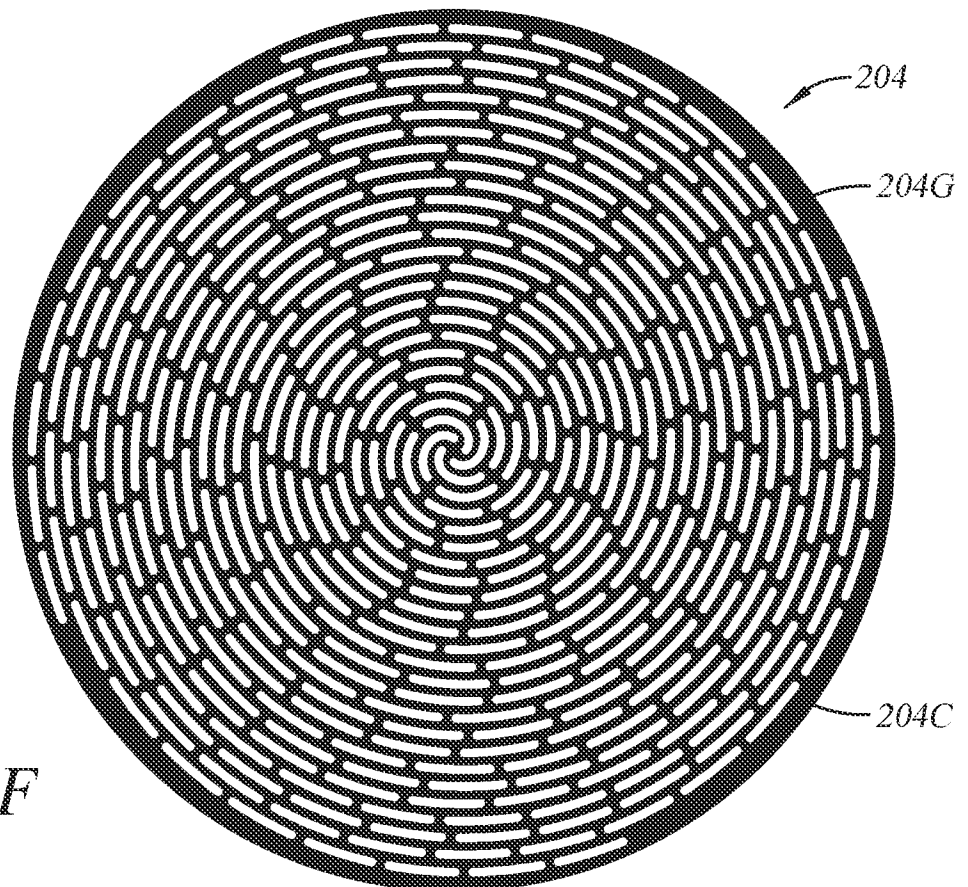


FIG. 3F

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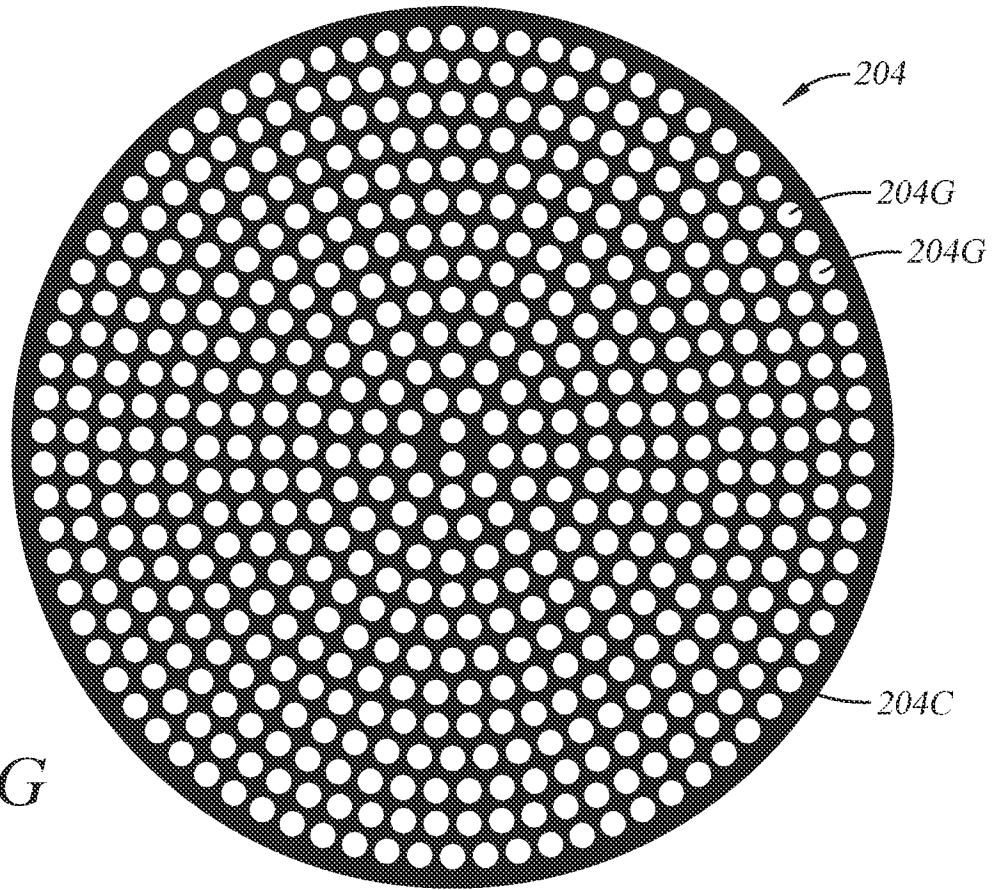


FIG. 3G

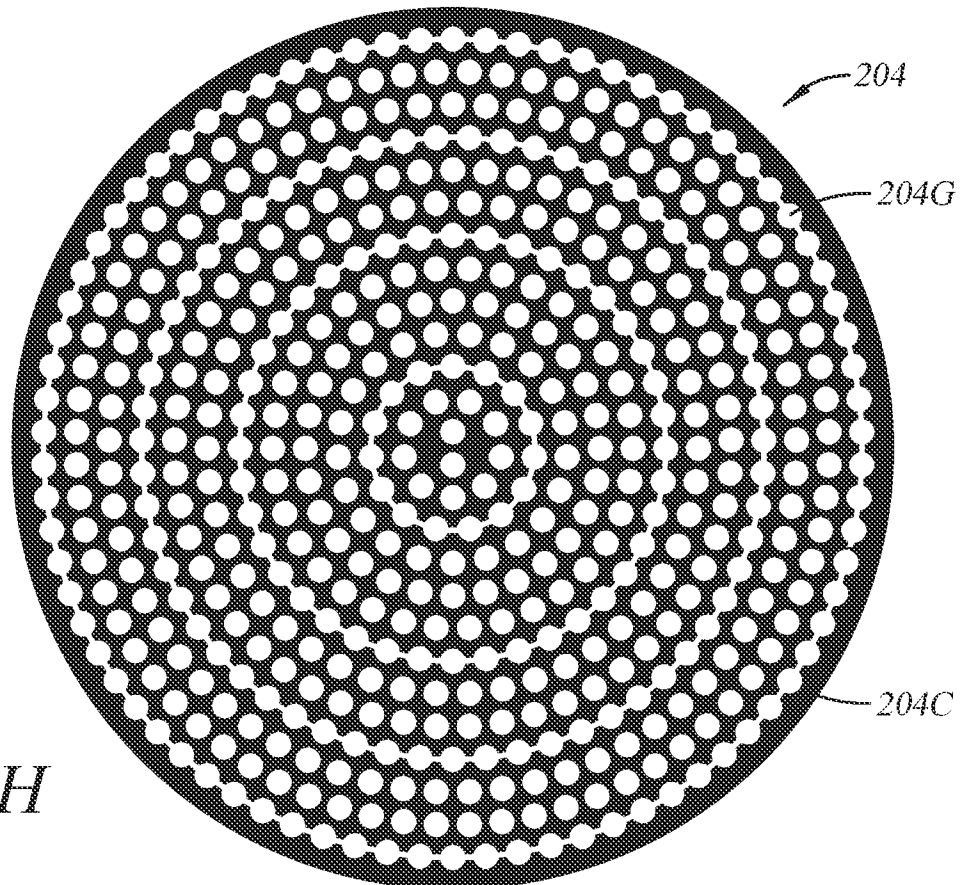
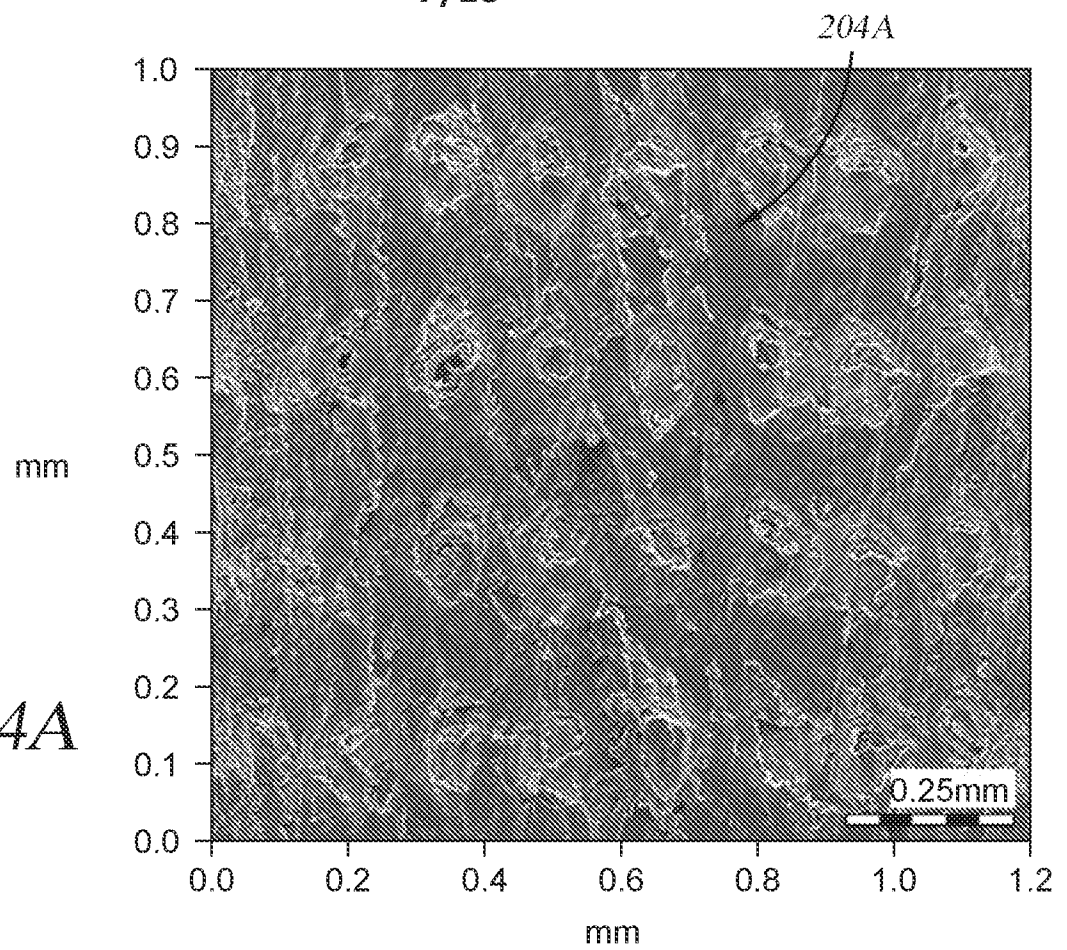
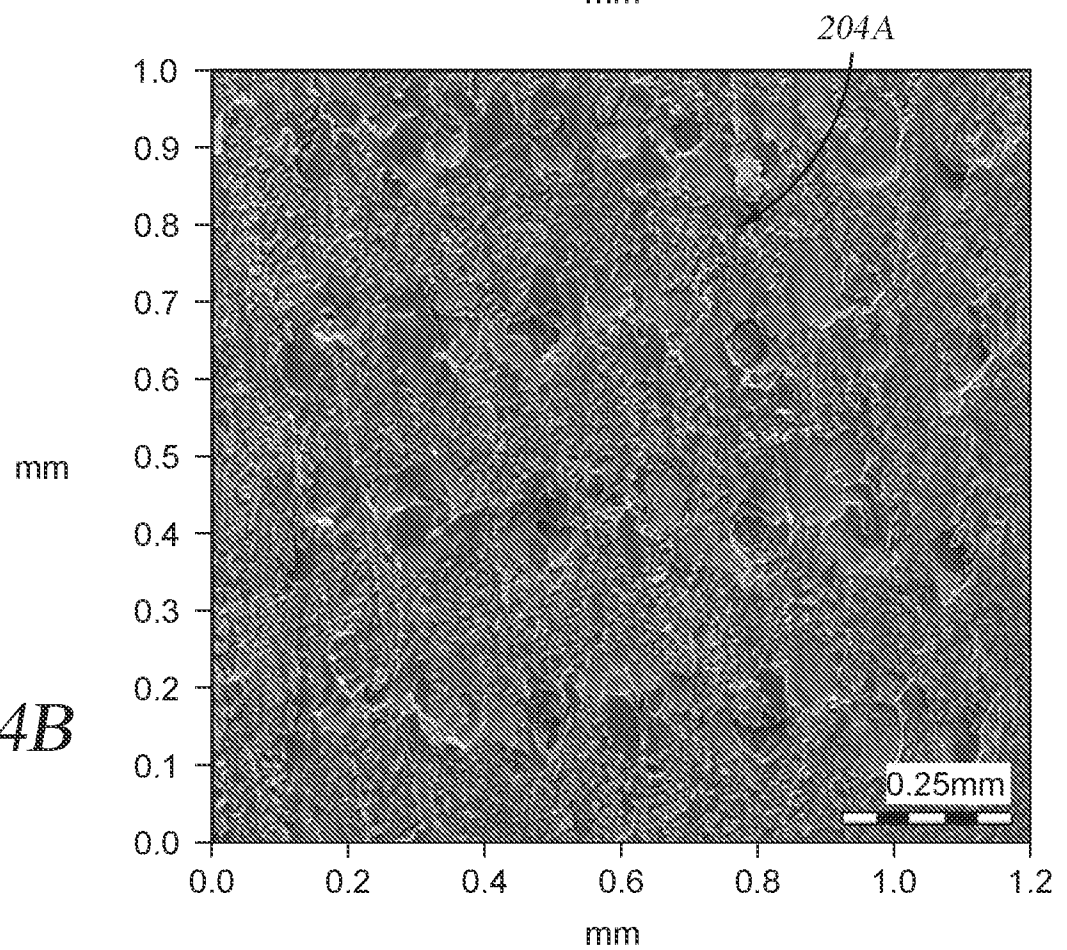
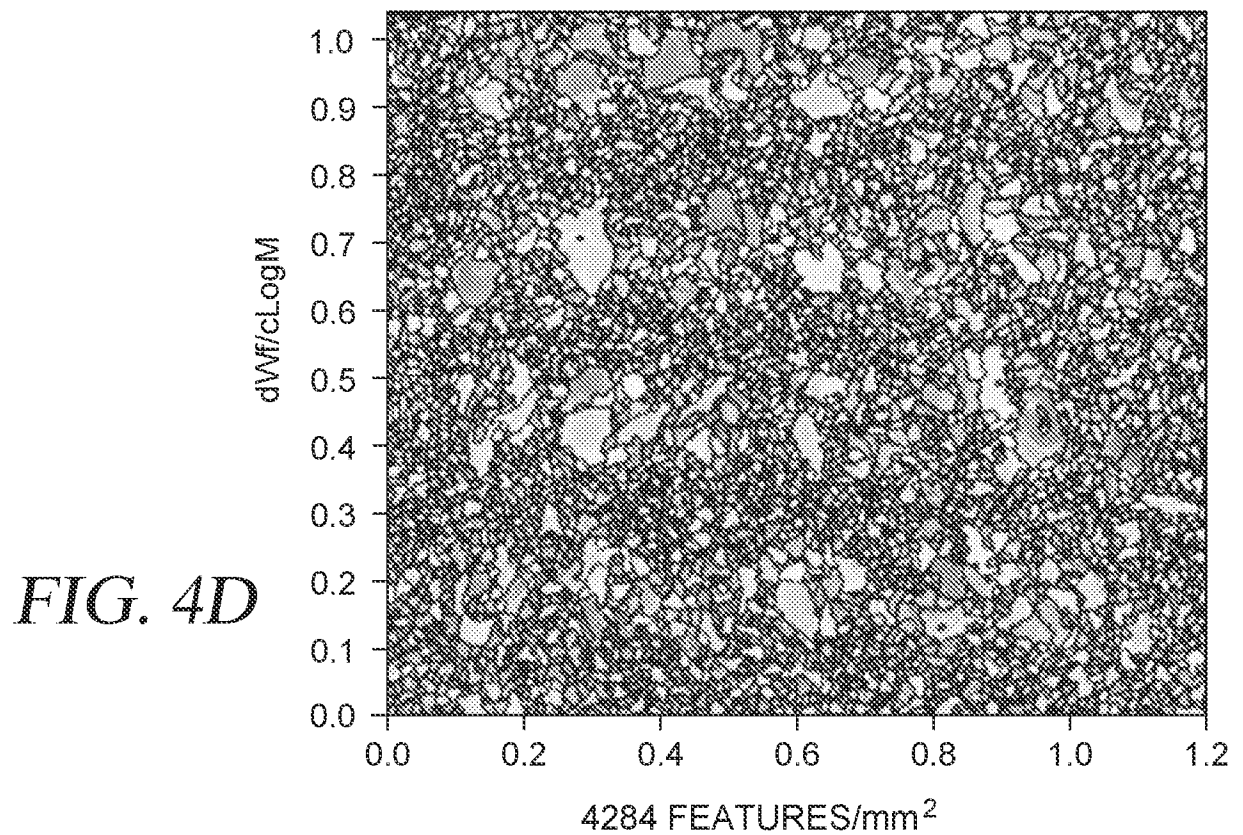
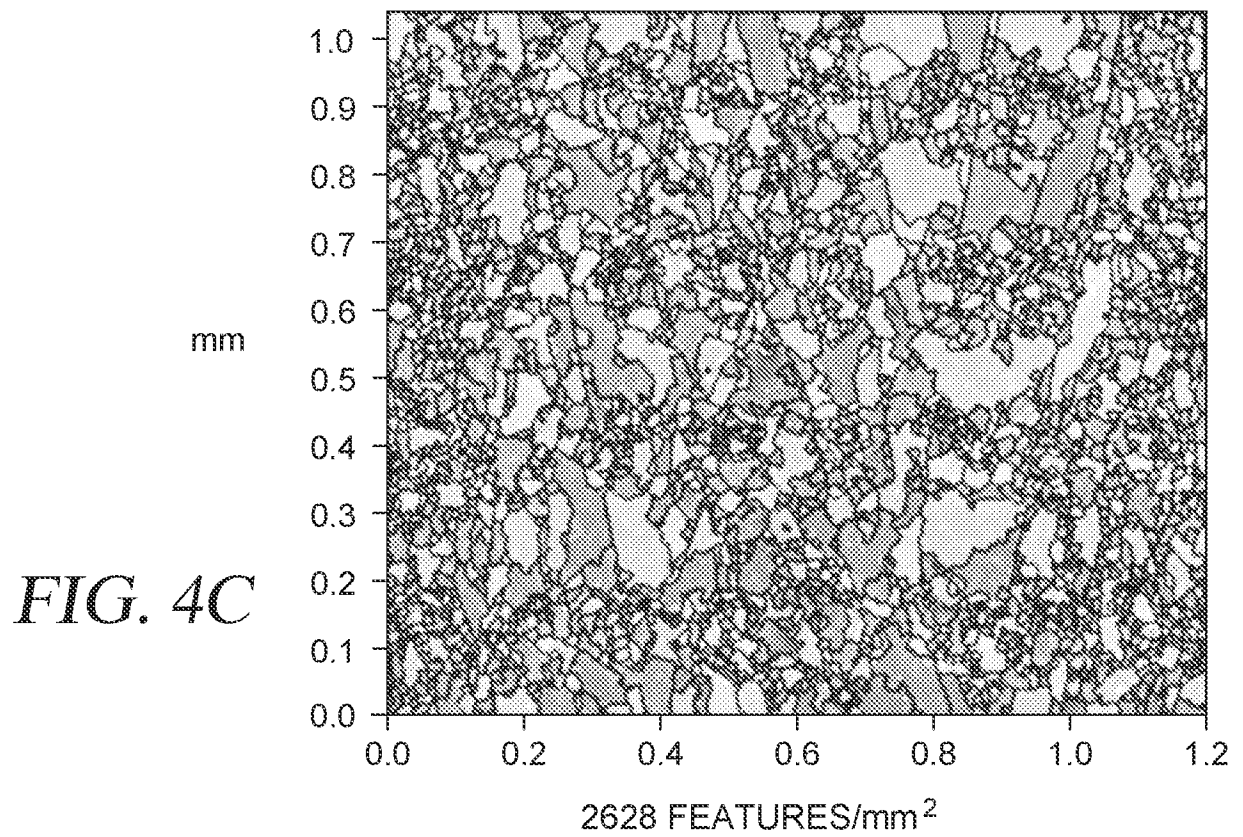


FIG. 3H

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FIG. 4A*FIG. 4B*

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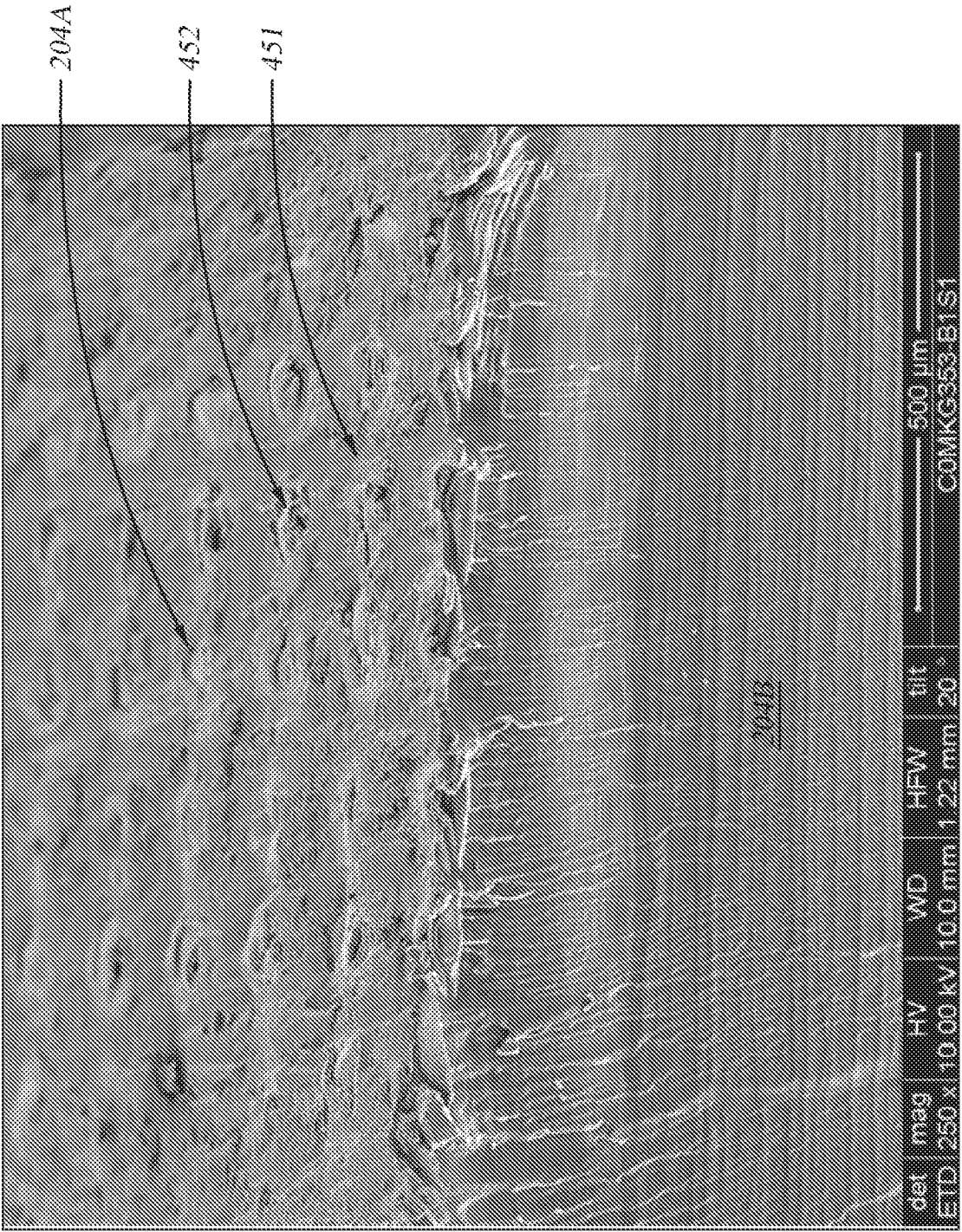
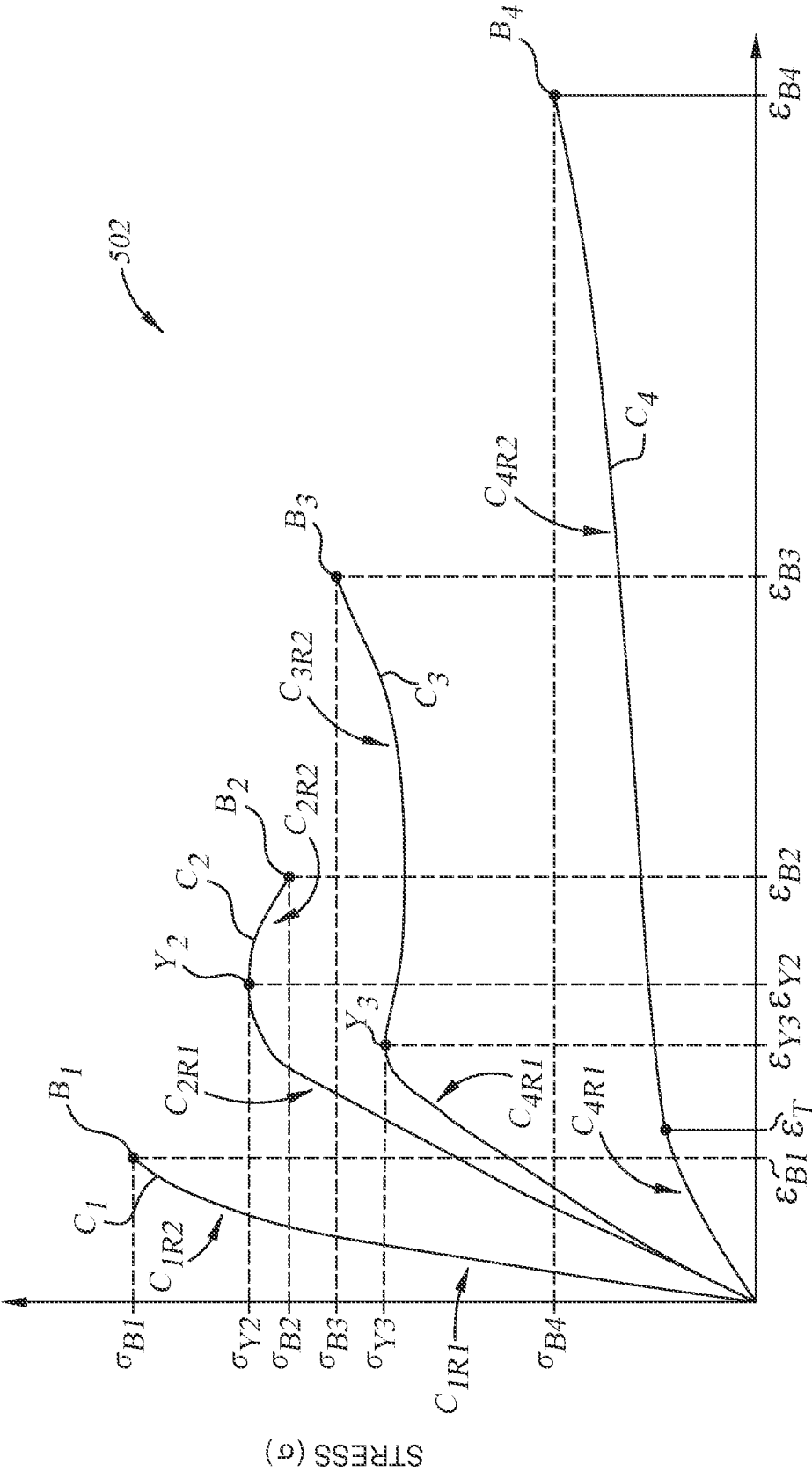


FIG. 4E



STRAIN (ϵ)
FIG. 5A

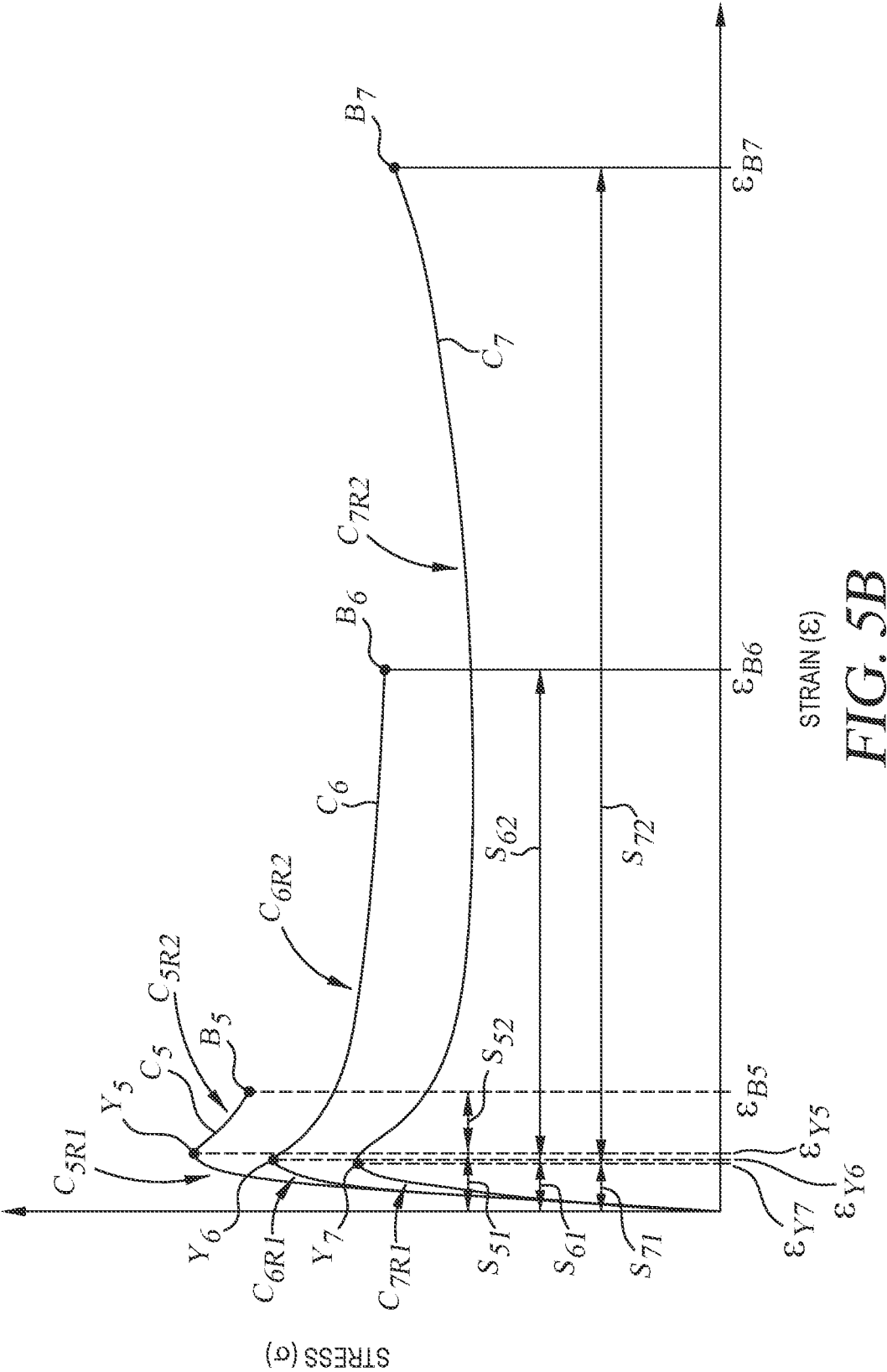
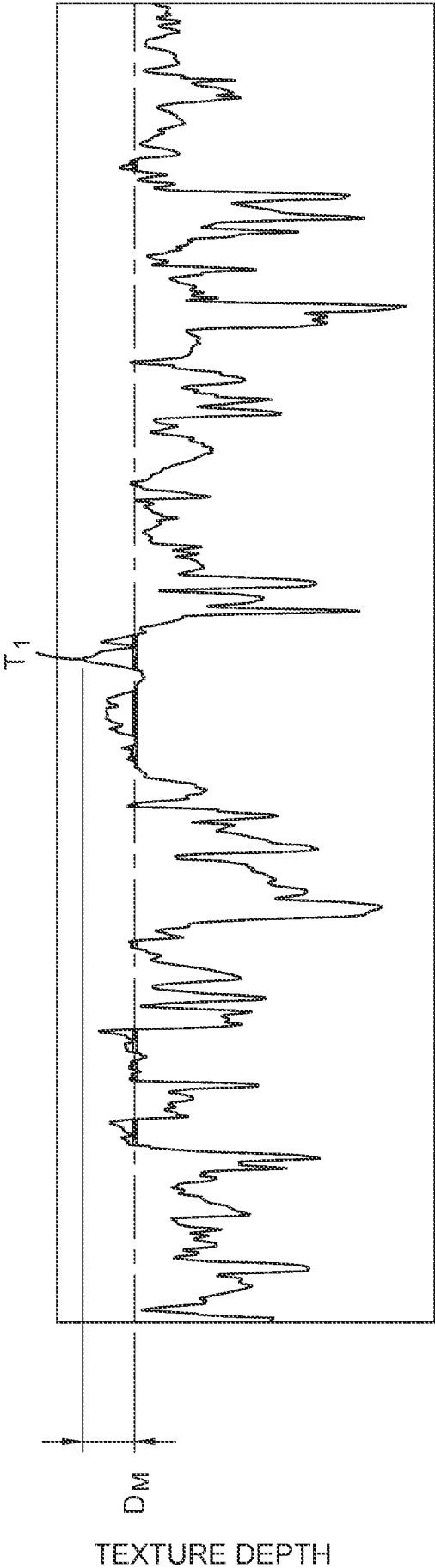
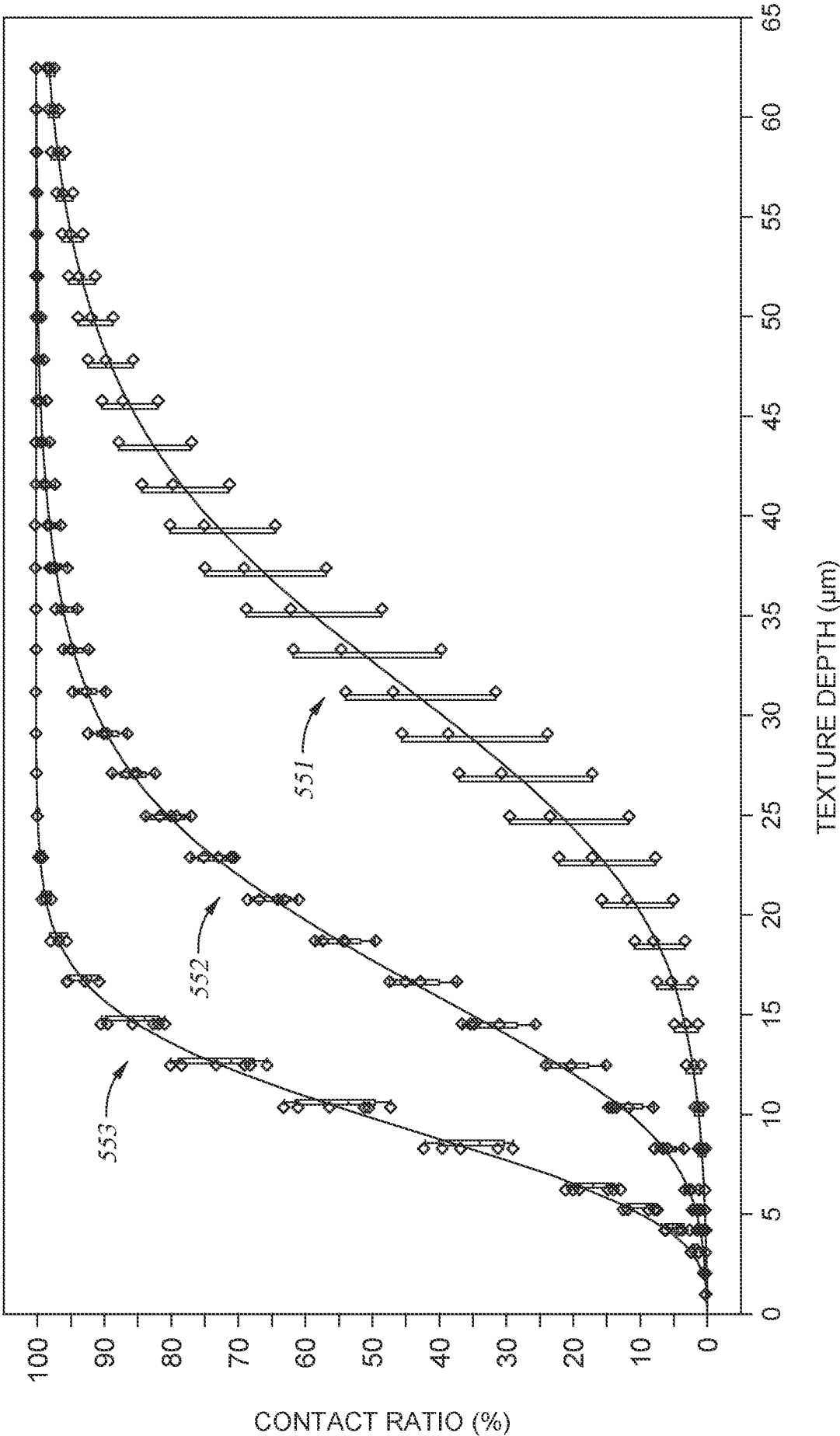


FIG. 5B



HORIZONTAL DIMENSION

FIG. 5C



TEXTURE DEPTH (μm)

FIG. 5D

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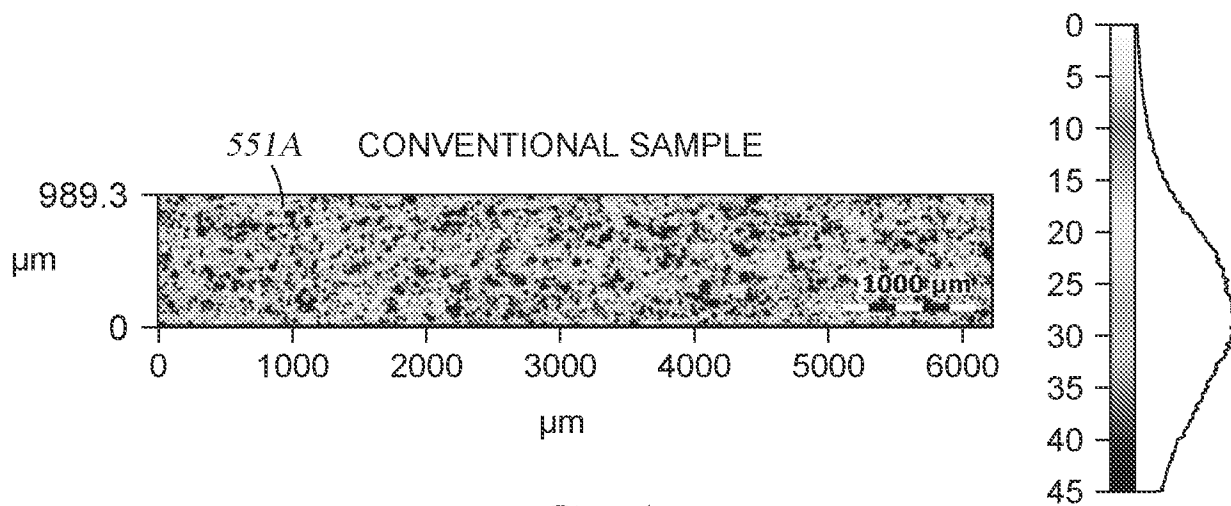


FIG. 5E

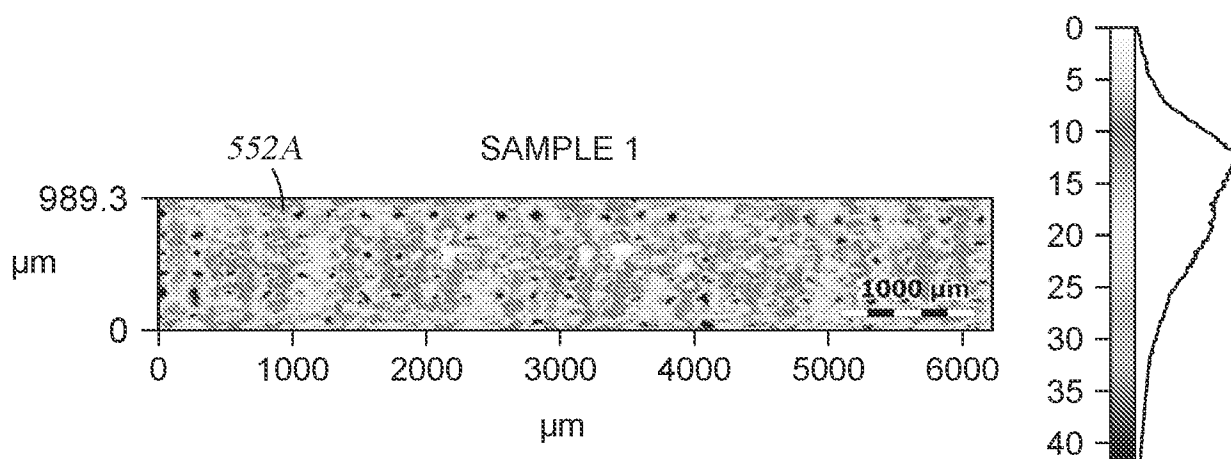


FIG. 5F

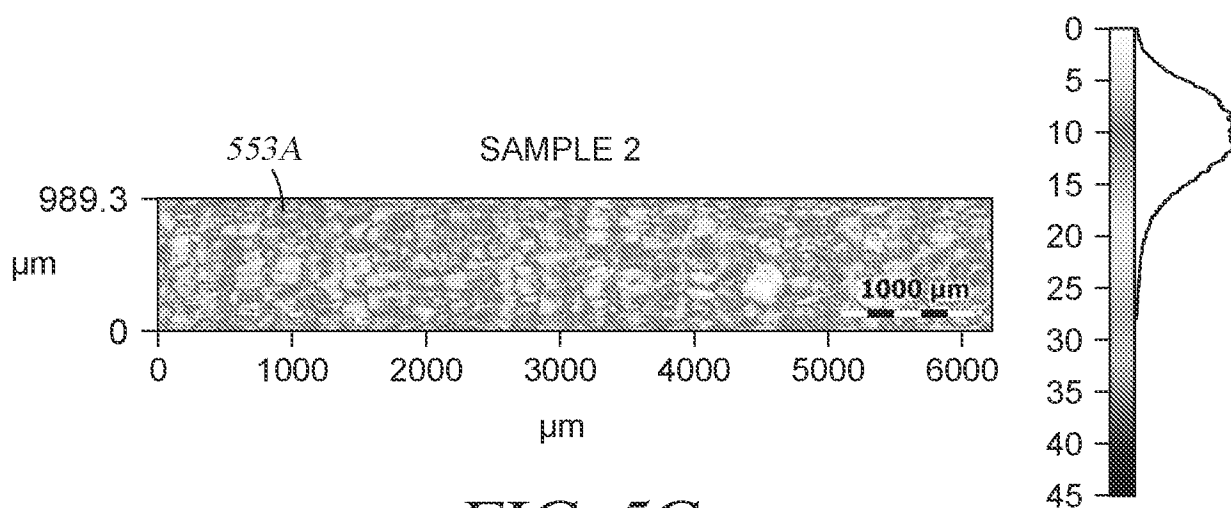


FIG. 5G

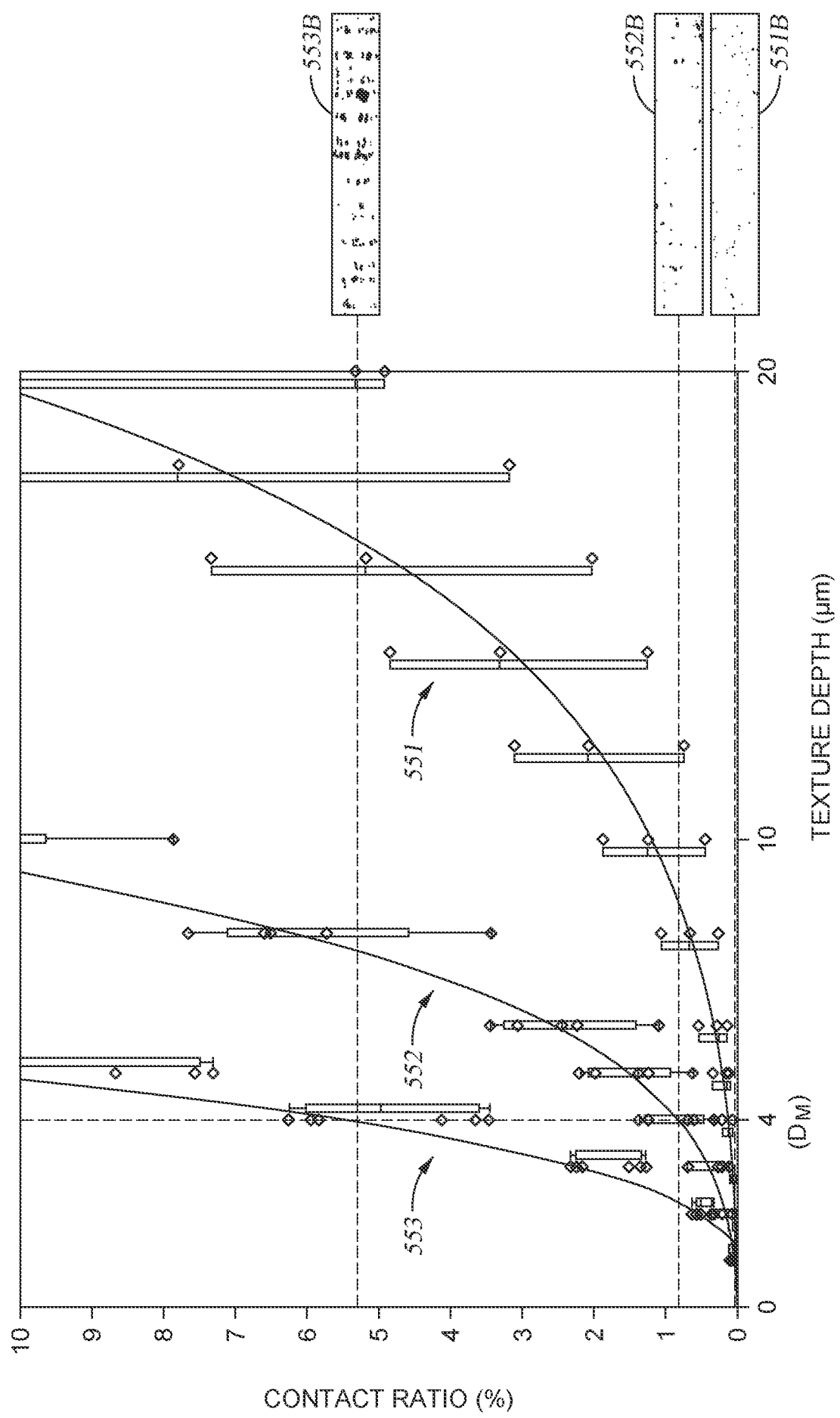
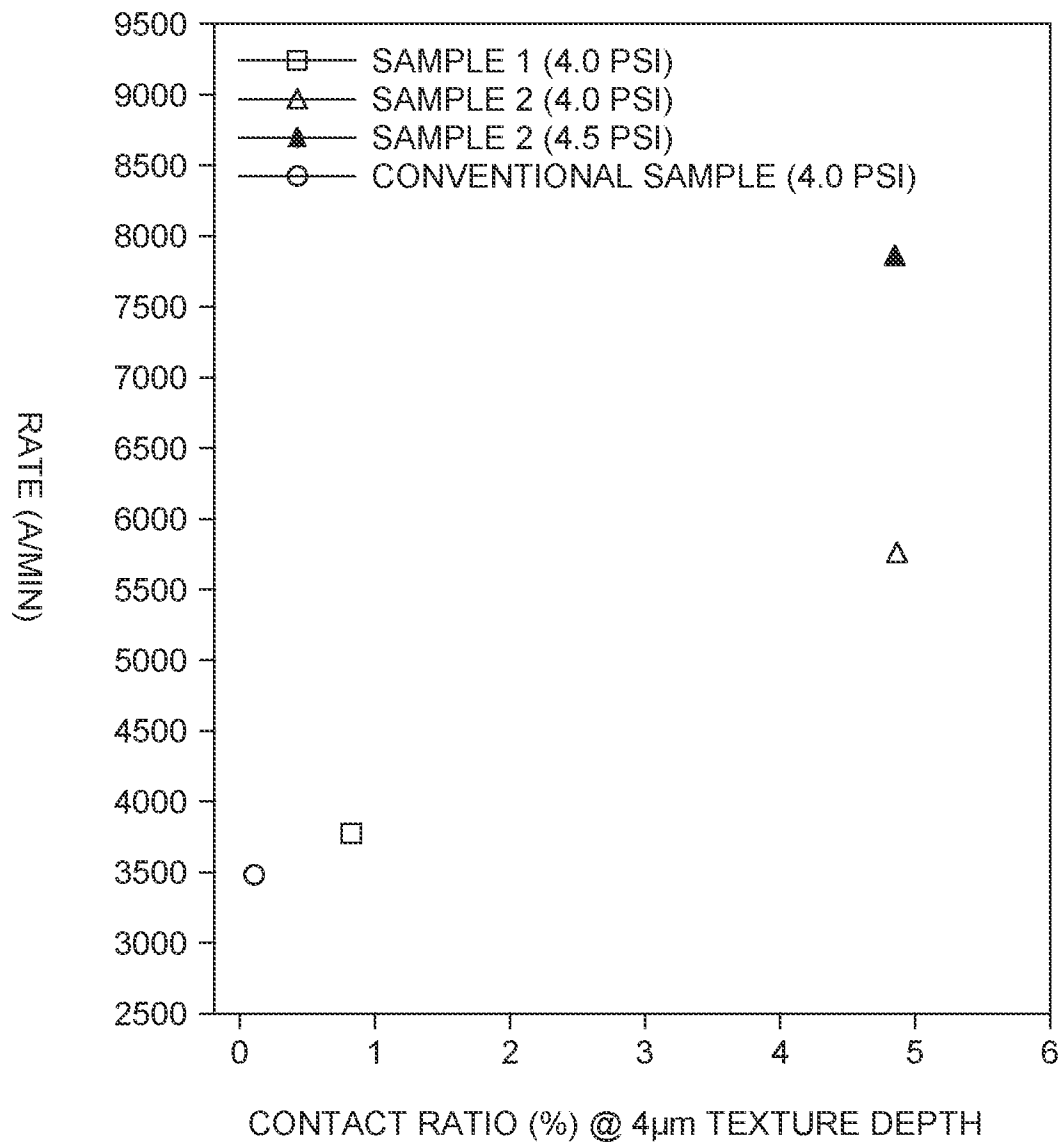


FIG. 5H

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*FIG. 5I*

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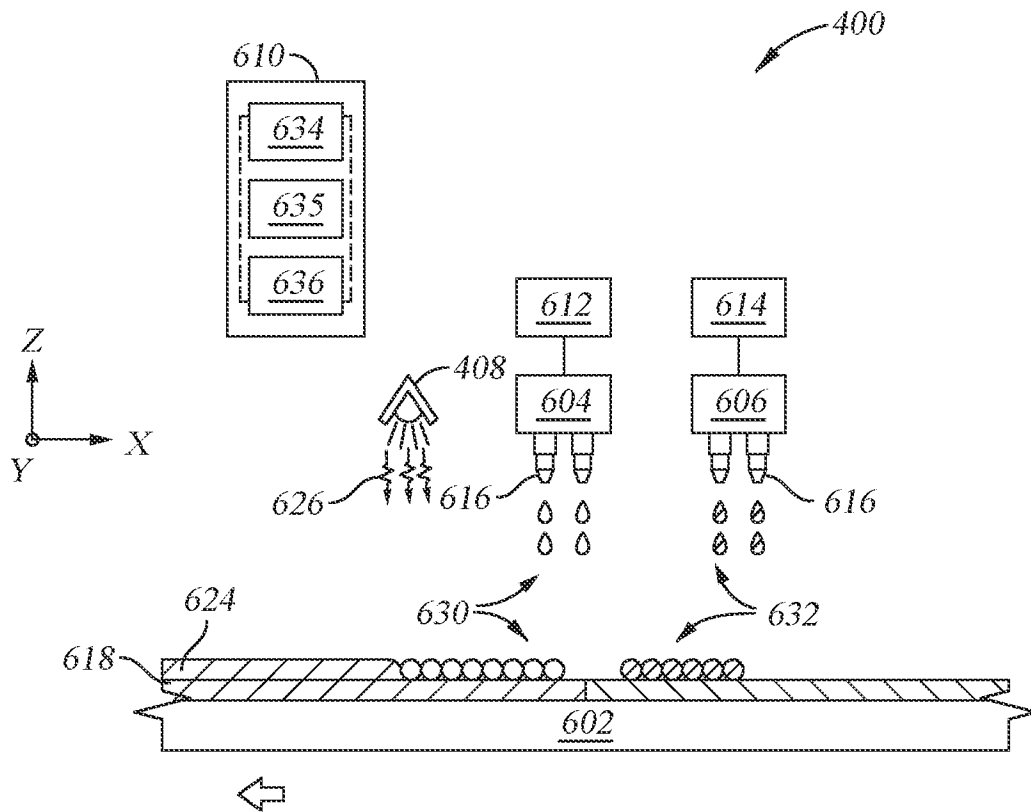


FIG. 6A

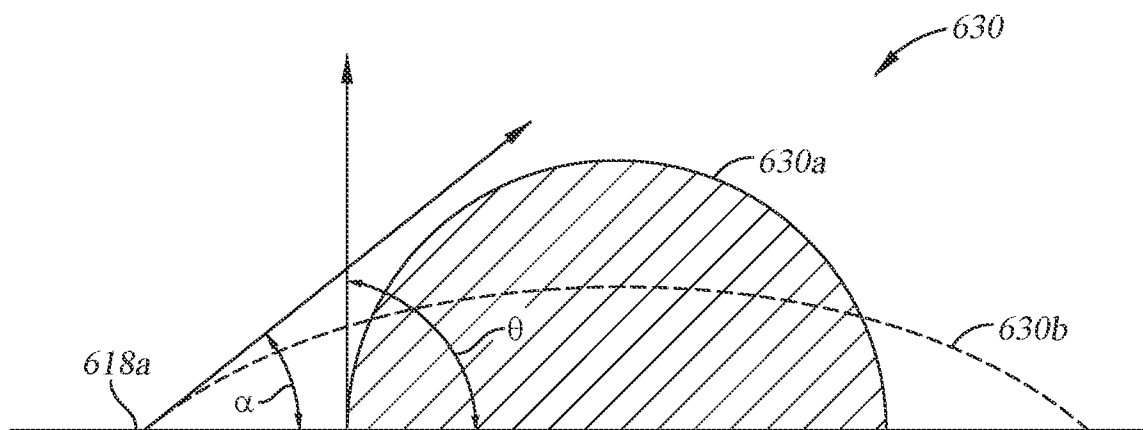
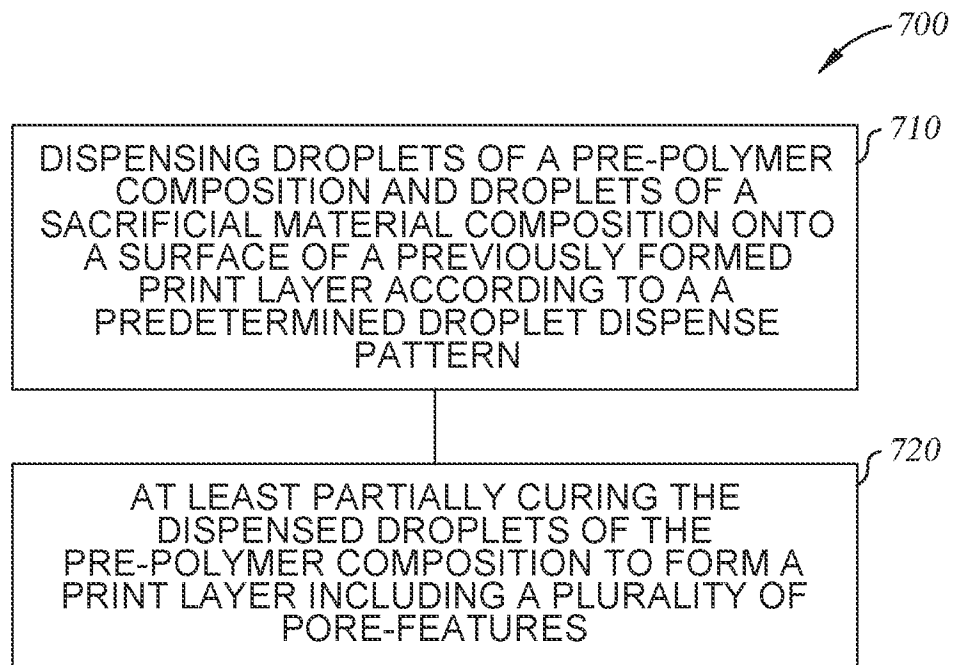
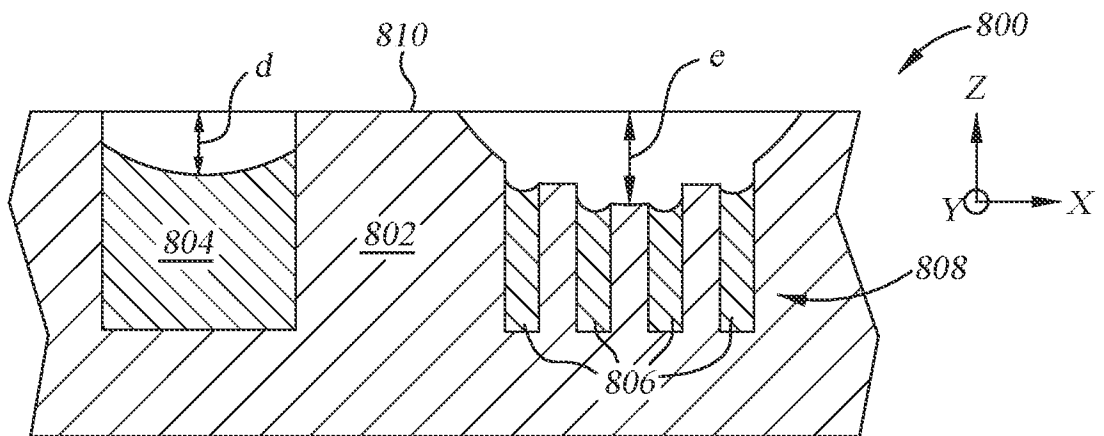


FIG. 6B

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*FIG. 7**FIG. 8*

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2023/019583

A. CLASSIFICATION OF SUBJECT MATTER**B24B 37/22**(2012.01)i; **B24B 37/24**(2012.01)i; **B24B 53/017**(2012.01)i; **H01L 21/67**(2006.01)i

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)

B24B 37/22(2012.01); B24B 37/20(2012.01); B24B 37/24(2012.01); B24B 37/26(2012.01); B29C 64/112(2017.01); H01L 21/304(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: polishing pad, yield point, elongation, break point, fracture point, stress, strain, oligomer, monomer, reactive diluent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	WO 2015-182757 A1 (NITTA HAAS INCORPORATED) 03 December 2015 (2015-12-03) paragraph [0011], claim 1, table 2 and figures 1-2	1,4-5,9-14,18-19 2-3,6-8,15-17,20
Y	US 2017-0203408 A1 (APPLIED MATERIALS, INC.) 20 July 2017 (2017-07-20) paragraphs [0071]-[0072], [0135], [0203]-[0204], [0231], [0233], claim 11, tables 3-4 and figures 1A, 2A	1,4-5,9-14,18-19
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A	US 6843712 B2 (ROBERTS et al.) 18 January 2005 (2005-01-18) claim 1	1-20



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See patent family annex.

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Date of the actual completion of the international search

27 July 2023

Date of mailing of the international search report

27 July 2023

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Information on patent family members

International application No.

PCT/US2023/019583

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