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(54) POLISHING PADS HAVING IMPROVED PORE STRUCTURE

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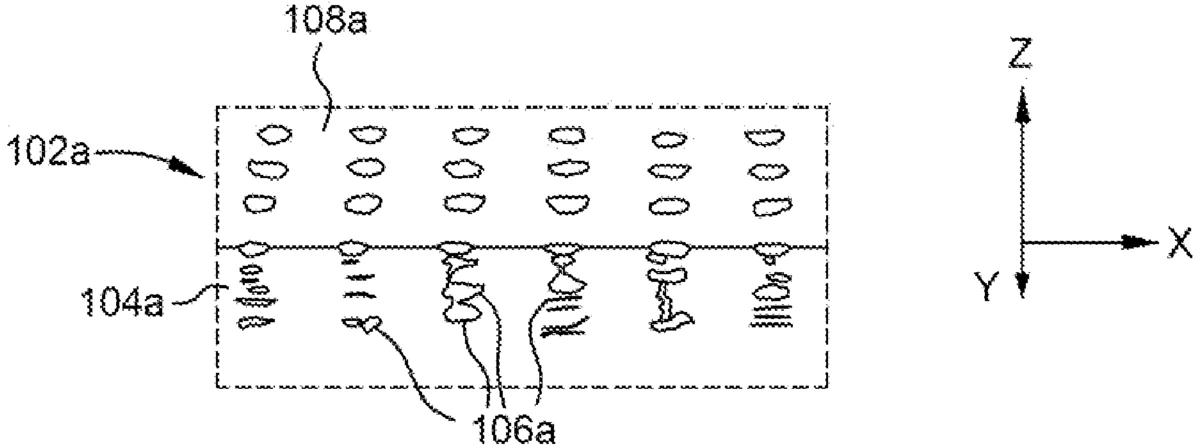
(57) ABSTRACT

Embodiments herein generally relate to polishing pads and methods of forming polishing pads. A method of forming a polishing pad includes (a) dispensing droplets of a pre-polymer composition and droplets of a sacrificial material composition onto a surface of a previously formed print layer according to a predetermined droplet dispense pattern. The method includes (b) at least partially curing the dispensed droplets of the pre-polymer composition to form a print layer. The method includes (c) sequentially repeating (a) and (b) to form a polishing layer having a plurality of pore-features formed therein. The pre-polymer composition includes a multifunctional acrylate component. A curing rate of the dispensed droplets of the pre-polymer composition including the multifunctional acrylate component when exposed to a first dose of electromagnetic radiation is greater than a curing rate of the pre-polymer composition without the multifunctional acrylate component when exposed to the same first dose of electromagnetic radiation.



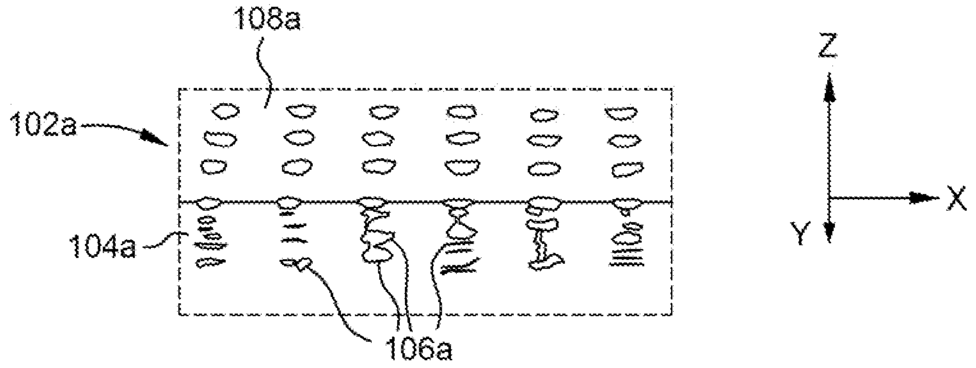


FIG. 1A

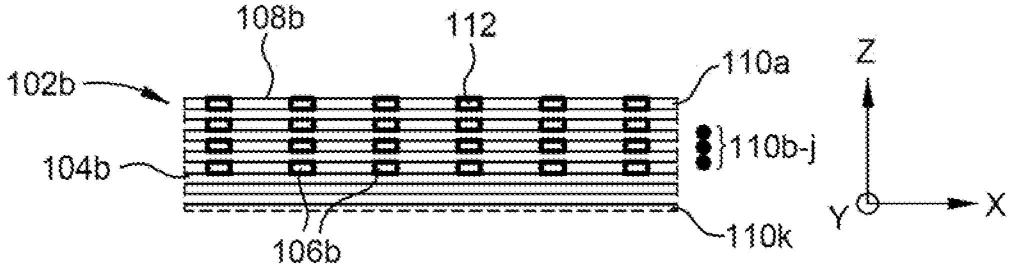


FIG. 1B

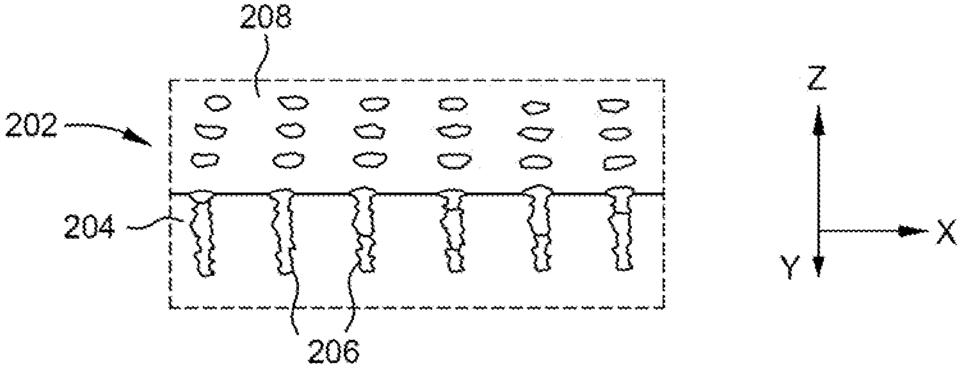


FIG. 2

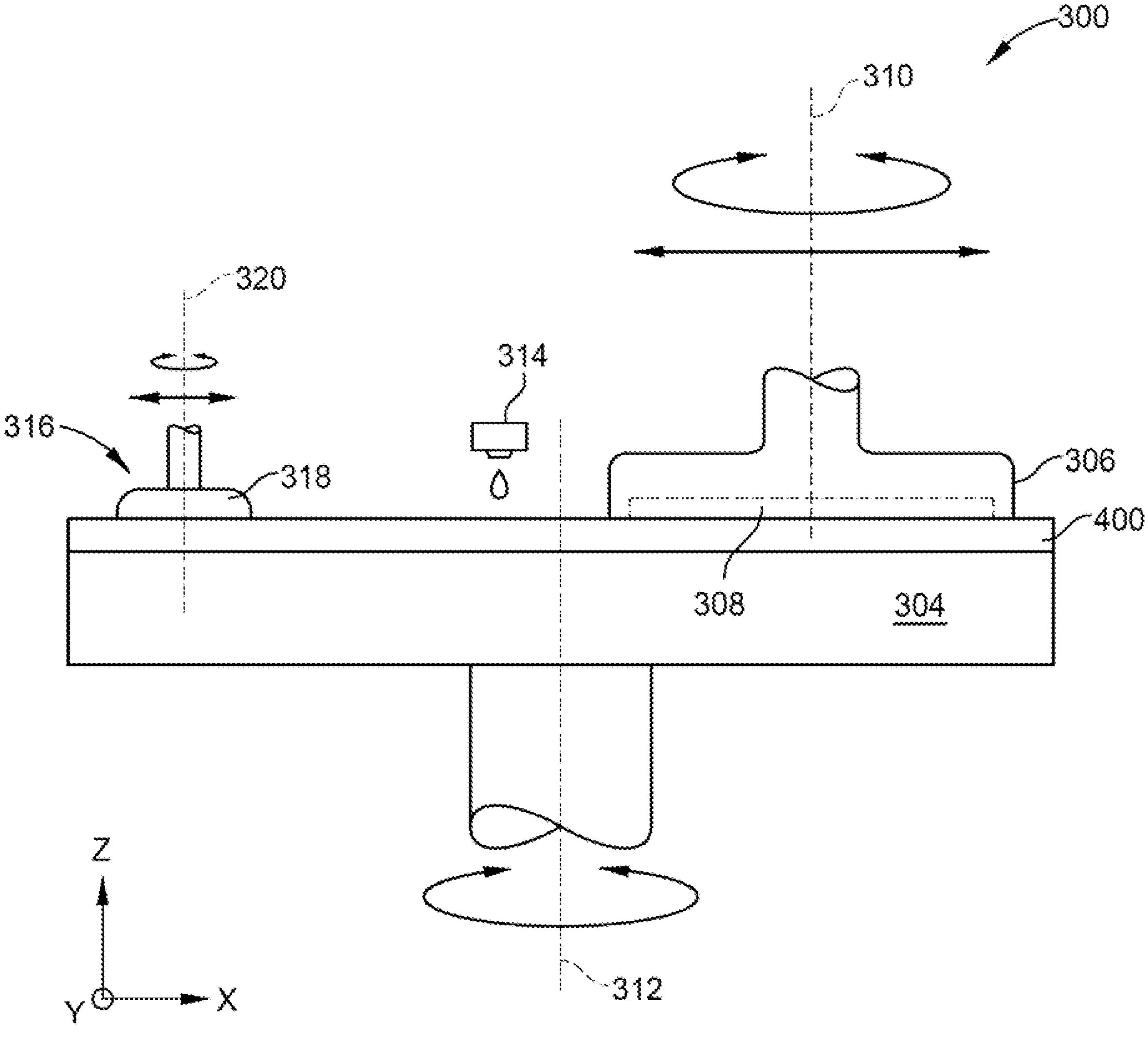


FIG. 3

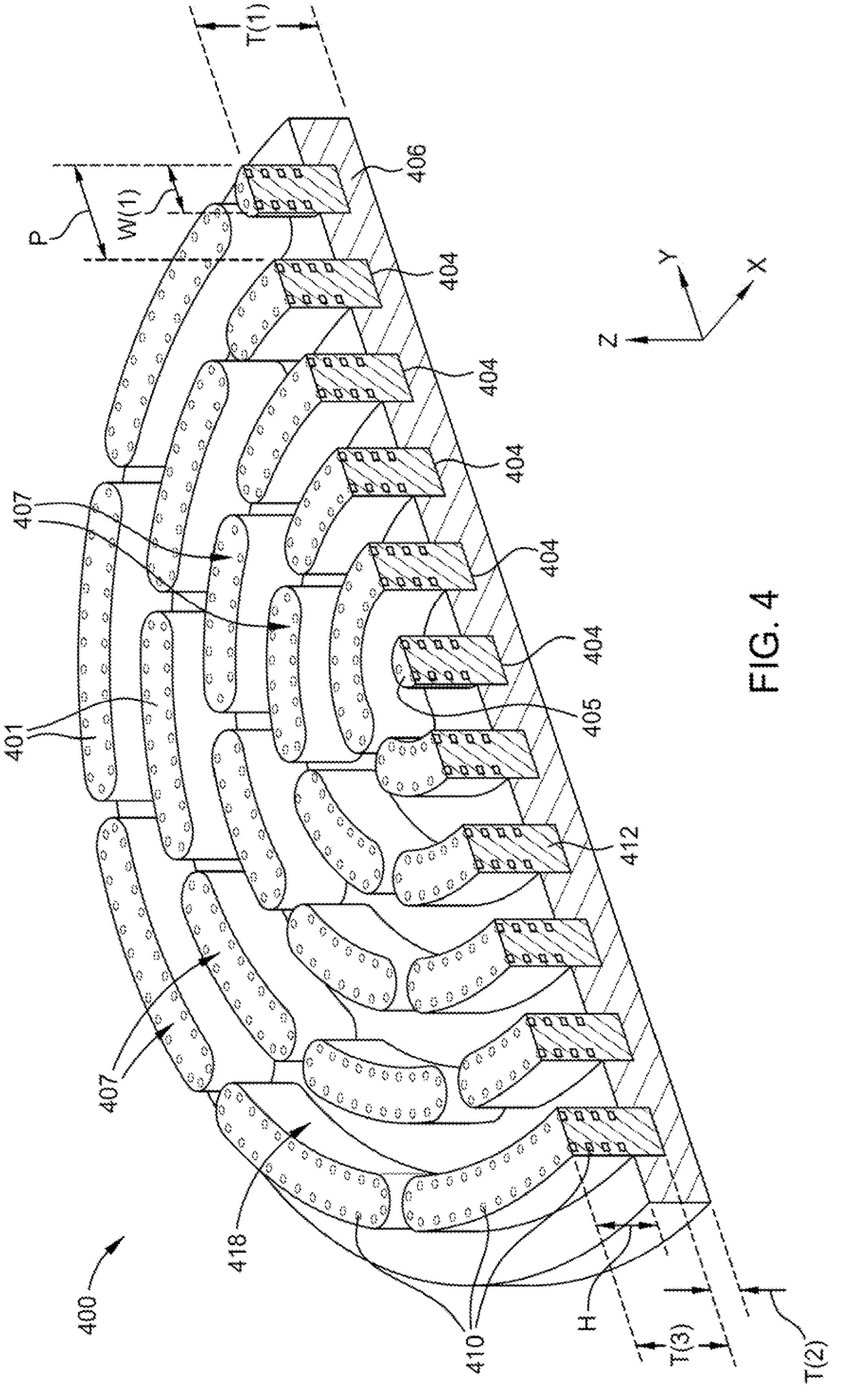

400
401
407
407
404
404
404
404
404
405
406
410
412
418
P
W(1)
T(1)
T(2)
T(3)
H
X
Y
Z

FIG. 4

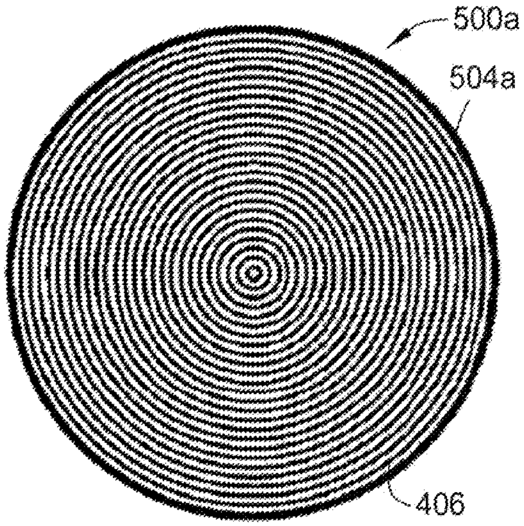


FIG. 5A

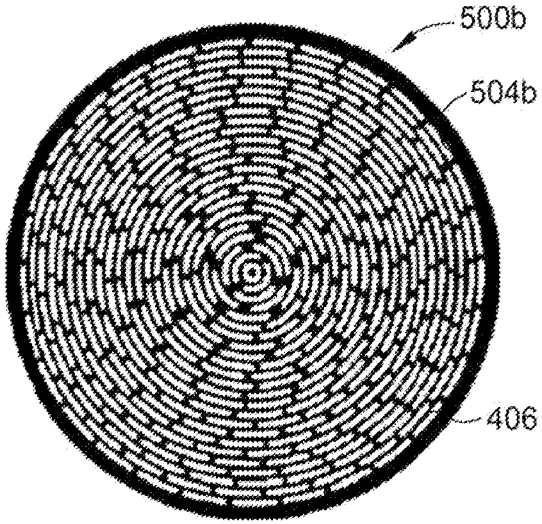


FIG. 5B

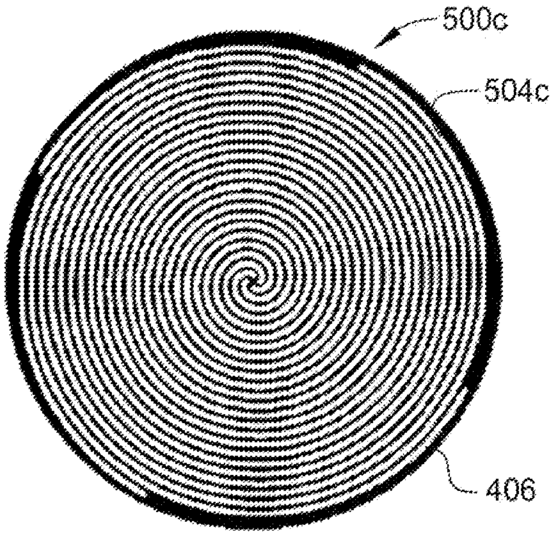


FIG. 5C

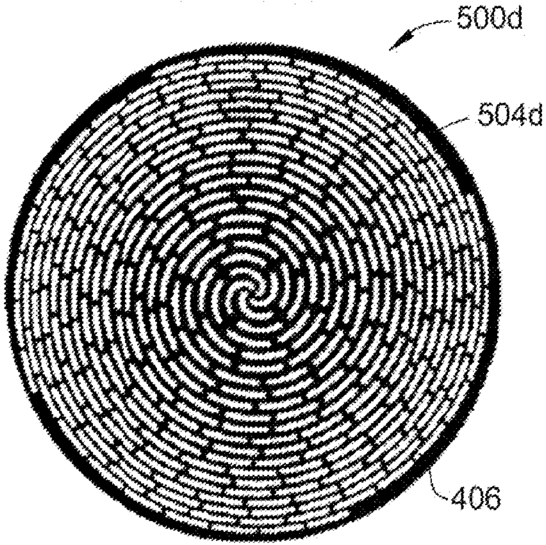


FIG. 5D

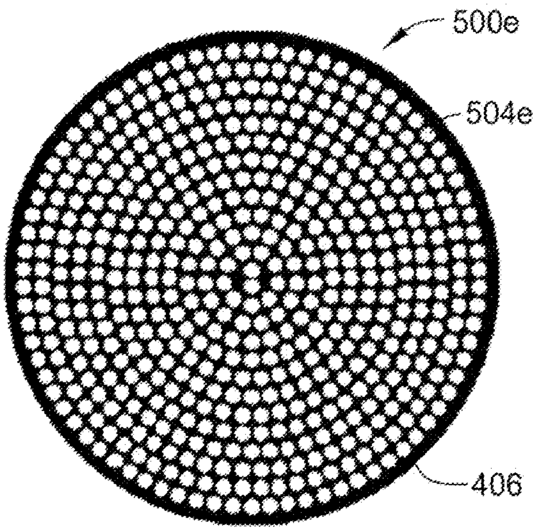


FIG. 5E

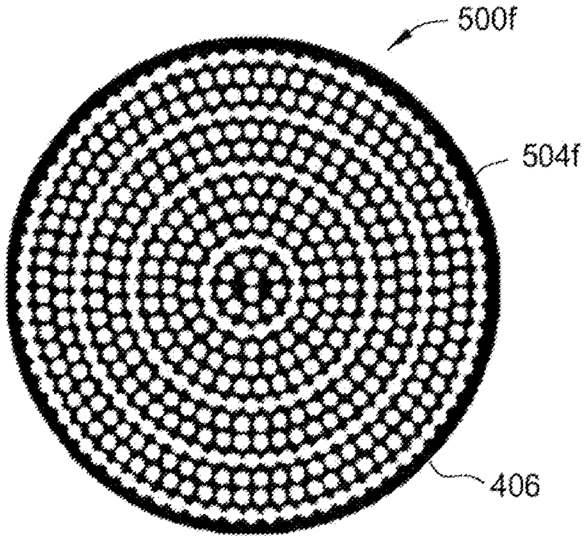


FIG. 5F

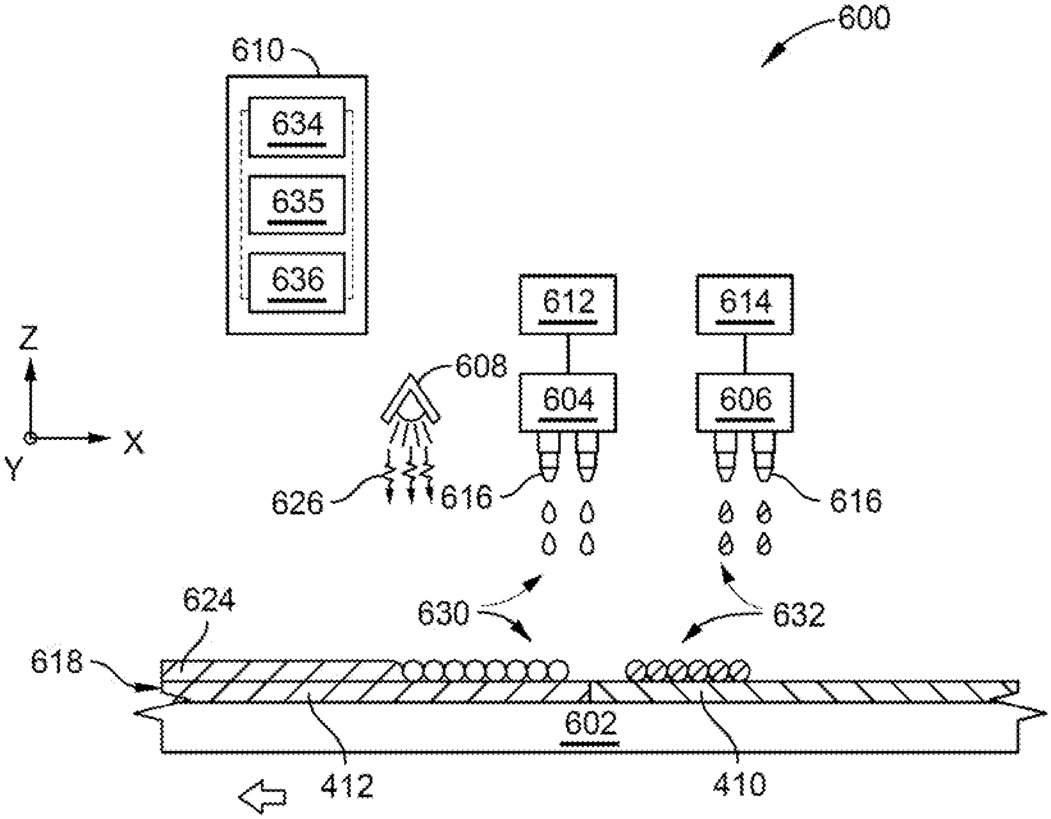

600
610
634
635
636
612
614
604
606
608
Z
X
Y
626
616
616
630
632
624
618
602
412
410

FIG. 6A

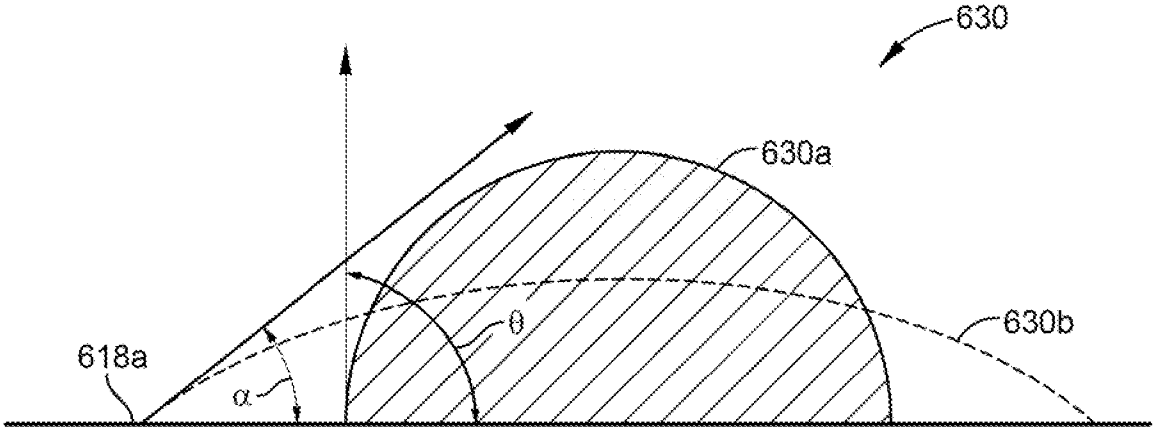

630
630a
630b
θ
α
618a

FIG. 6B

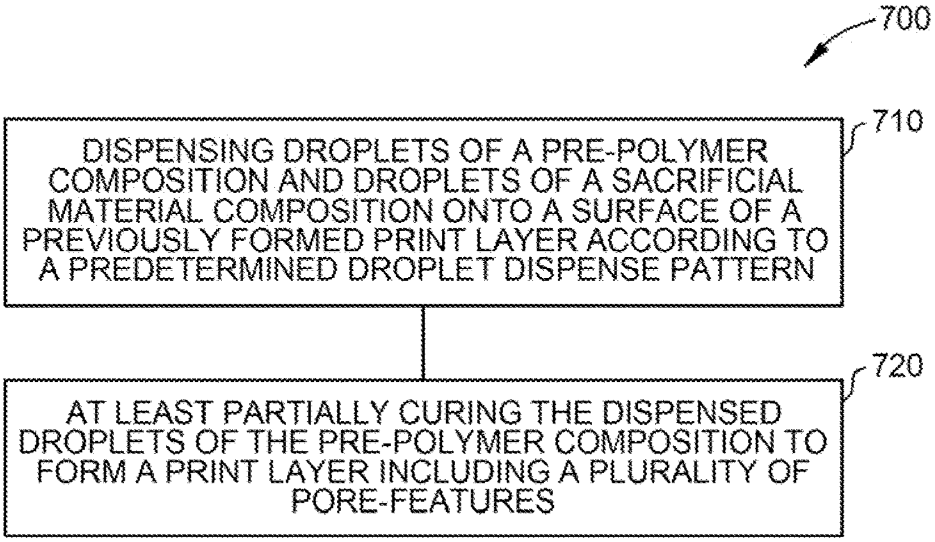

700
DISPENSING DROPLETS OF A PRE-POLYMER COMPOSITION AND DROPLETS OF A SACRIFICIAL MATERIAL COMPOSITION ONTO A SURFACE OF A PREVIOUSLY FORMED PRINT LAYER ACCORDING TO A PREDETERMINED DROPLET DISPENSE PATTERN
710
AT LEAST PARTIALLY CURING THE DISPENSED DROPLETS OF THE PRE-POLYMER COMPOSITION TO FORM A PRINT LAYER INCLUDING A PLURALITY OF PORE-FEATURES
720

FIG. 7

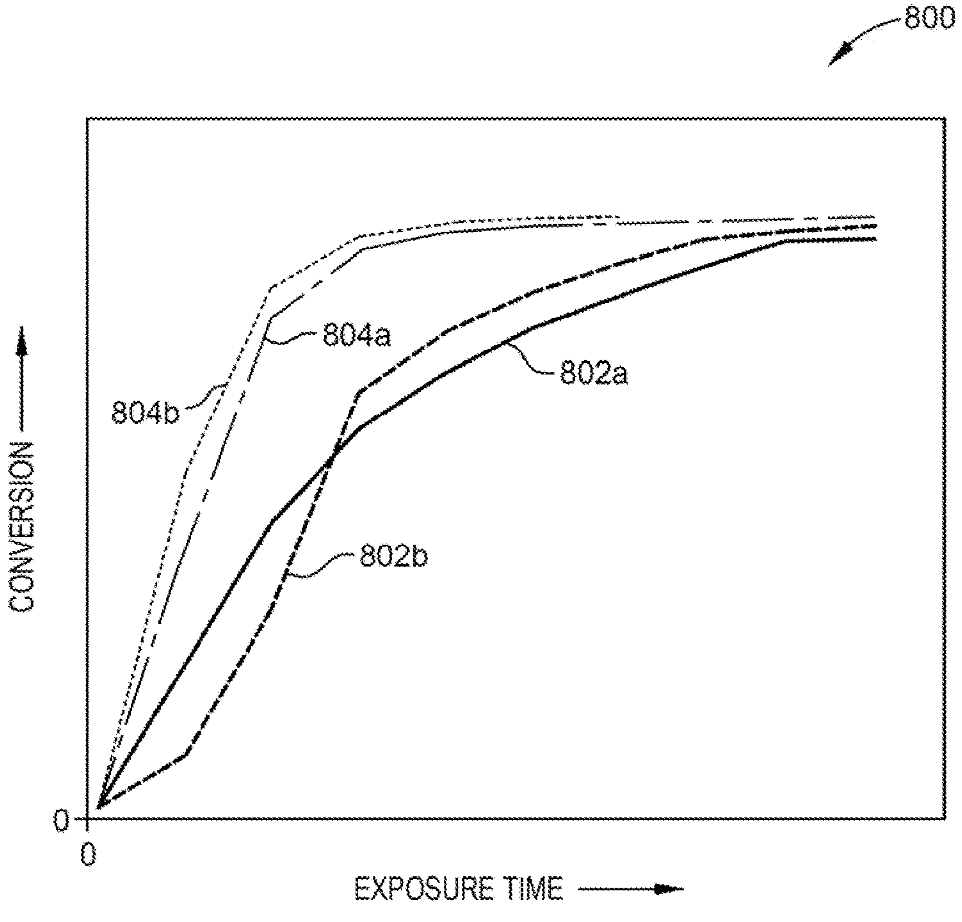

800
804a
804b
802a
802b
CONVERSION
0
0
EXPOSURE TIME

FIG. 8

POLISHING PADS HAVING IMPROVED PORE STRUCTURE

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 typical CMP process includes contacting the material layer to be planarized with a polishing pad and moving the polishing pad, the substrate, or both, and hence creating relative movement between the material layer surface and the polishing pad, in the presence of a polishing fluid including abrasive particles. One common application of CMP 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 surface of the layer to be planarized. Other common applications of CMP in semiconductor device manufacturing include shallow trench isolation (STI) and interlayer metal interconnect formation, where CMP is used to remove the via, contact or trench fill material from the exposed surface (field) of the layer having the STI or metal interconnect features disposed therein.

[0003] Often, polishing pads used in the above-described CMP processes are selected based on the material properties of the polishing pad material and the suitability of those material properties for the desired CMP application. One example of a material property that may be adjusted to tune the performance of a polishing pad for a desired CMP application is the porosity of a polymer material used to form the polishing pad and properties related thereto, such as pore size and structure, and material surface asperities. Methods of introducing porosity into the polishing pad material may include blending a pre-polymer composition with a pore-forming agent, such as a water-soluble material or air, before molding and curing the pre-polymer composition into individual polishing pads or a polymer cake and machining, e.g., skiving, individual polishing pads therefrom.

[0004] Polishing pads may also be fabricated using techniques other than molding, such as through additive manufacturing. In the production of polishing pads using additive manufacturing techniques, e.g., 3D printing, droplets of the pre-polymer composition and droplets of the pore-forming agent may be selectively spatially deposited in multiple print layers to form the polishing pads. Unfortunately, while additive manufacturing techniques may provide precision placement of pores within the formed pads, inter-mixing between adjacent droplets of the pre-polymer composition and the pore-forming agent, especially in the case of polishing pads formed of relatively softer materials, can lead to poor structure of the resulting pores, which hinders the performance-tuning opportunities that may otherwise result therefrom.

[0005] Accordingly, there is a need in the art for methods of improving pore structure within polishing pads formed by additive manufacturing techniques.

SUMMARY

[0006] 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. More particularly, embodiments herein provide for polishing pads having improved pore structure and additive manufacturing methods of forming the polishing pads.

[0007] In one embodiment, a method of forming a polishing pad includes (a) dispensing droplets of a pre-polymer composition and droplets of a sacrificial material composition onto a surface of a previously formed print layer according to a predetermined droplet dispense pattern. The method includes (b) at least partially curing the dispensed droplets of the pre-polymer composition to form a print layer. The method includes (c) sequentially repeating (a) and (b) to form a polishing layer having a plurality of pore-features formed therein. The pre-polymer composition includes a multifunctional acrylate component. A curing rate of the dispensed droplets of the pre-polymer composition including the multifunctional acrylate component when exposed to a first dose of electromagnetic radiation is greater than a curing rate of the pre-polymer composition without the multifunctional acrylate component when exposed to the same first dose of electromagnetic radiation. The plurality of pore-features include openings defined in a surface of the polishing layer, voids that are formed in the polishing layer below the surface, pore-forming features including the sacrificial material composition, or combinations thereof.

[0008] In another embodiment, a method of forming a polishing pad includes (a) dispensing droplets of a pre-polymer composition and droplets of a sacrificial material composition onto a surface of a previously formed print layer according to a predetermined droplet dispense pattern. The method includes (b) at least partially curing the dispensed droplets of the pre-polymer composition to form a print layer including a plurality of pore-features. The method includes (c) sequentially repeating (a) and (b) to form a polishing layer. The pre-polymer composition includes a surface active agent. A volume of a pore-feature space of an individual one of the plurality of pore-features comprises at least 50% of a volume of the sacrificial material composition dispensed to form the corresponding pore-features. The plurality of pore-features include openings defined in a surface of the polishing layer, voids that are formed in the polishing layer below the surface, pore-forming features including the sacrificial material composition, or combinations thereof.

[0009] In another embodiment, a polishing pad includes a plurality of polishing elements. Each polishing element includes an individual surface that forms a portion of a polishing surface of the polishing pad and one or more sidewalls extending downwardly from the individual surface to define a plurality of channels disposed between the polishing elements. Each of the polishing elements has a plurality of pore-features formed therein. Each of the polishing elements is formed of a pre-polymer composition and a sacrificial material composition. A volume of pore-feature space of an individual one of the plurality of pore-features comprises at least 50% of a volume of the sacrificial material composition dispensed to form the corresponding pore-features. The plurality of pore-features include openings defined in the polishing surface, voids that are formed in the polishing elements below the polishing surface, pore-forming features including the sacrificial material composition, or combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] 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 typical embodiments of this disclosure and are therefore not to be considered limiting of its scope, for the disclosure may admit to other equally effective embodiments.

[0011] FIG. **1**A is a schematic sectional view illustrating a portion of a polishing layer of an exemplary polishing pad.

[0012] FIG. **1**B is a schematic sectional view illustrating a design layout for a to-be-printed polishing layer of a polishing pad, for example the polishing pad of FIG. **1**A.

[0013] FIG. **2** is a schematic sectional view illustrating a portion of a polishing layer of a polishing pad according to embodiments described herein.

[0014] FIG. **3** is a schematic side view of an exemplary polishing system configured to use a polishing pad formed according to embodiments described herein.

[0015] FIG. **4** is a schematic isometric sectional view of a polishing pad featuring selectively arranged pores according to embodiments described herein.

[0016] FIGS. **5**A-**5**F are schematic plan views of various polishing pad designs which may be used in place of the pad design shown in FIG. **4** according to embodiments described herein.

[0017] FIG. **6**A is a schematic sectional view of an additive manufacturing system, which may be used to form the polishing pads described herein.

[0018] FIG. **6**B 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.

[0019] FIG. **7** is a flow diagram setting forth a method of forming a polishing pad according to embodiments described herein.

[0020] FIG. **8** is a graph illustrating conversion-exposure curves for pre-polymer compositions with and without a multifunctional acrylate component.

[0021] 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 implementation may be beneficially incorporated in other implementations without further recitation.

DETAILED DESCRIPTION

[0022] 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 feature improved pore structure compared to polishing pads formed using conventional methods.

[0023] Undesirable pore structure typically associated with polishing pads formed by conventional additive manufacturing techniques, especially those formed of relatively softer materials and/or using high-resolution printing, is schematically illustrated in FIG. **1**A. FIG. **1**A is a schematic sectional view illustrating a portion of a polishing layer **102***a* of an exemplary polishing pad. A polishing material **104***a* of the polishing layer **102***a* may include a non-soluble polymer resulting from polymerization of droplets of a pre-polymer composition. A plurality of pore-features **106***a* are formed in the polishing material **104***a* by arranging droplets of a sacrificial material composition in combination with the droplets of the pre-polymer composition. The pore-features **106***a* may include openings defined in a polishing surface **108***a* of the polishing layer **102***a*. Here, the pore-features **106***a* are poorly defined, for example having non-uniform diameter, non-uniform depth, non-uniform size distribution which varies across the pad, non-uniform shape, flattened appearance in cross-section, merging of the polishing material **104***a* across the pore-features **106***a* for example in a direction parallel or perpendicular to the X-Y plane, discontinuity within each of the pore-features **106***a*, low pore-feature space as a fraction of a volume of the sacrificial material composition dispensed to form the corresponding pore-features, and combinations thereof.

[0024] The polishing layer **102***a* may be formed according to a print design layout for a to-be-printed polishing layer **102***b* shown in FIG. **1**B. In FIG. **1**B, each to-be-printed pore-feature **106***b* extends through multiple ones of print layers **110***a-k* which are stacked one on top of the other in the Z-direction. According to FIG. **1**B, print layers **110***a*, **110***c*, **110***e*, and **110***g* include pore-feature spaces corresponding to droplets of a sacrificial material composition **112** arranged adjacent to droplets of a pre-polymer composition including a polishing material **104***b*. Other print layers (e.g., **110***b*, **110***d*, and **110***f*) without pore-feature space, i.e., including only the polishing material **104***b*, are interposed in the Z-direction between the print layers **110***a*, **110***c*, **110***e*, and **110***g* in an alternating arrangement as shown. Each pair of alternating print layers may have the same pattern such that droplets of the pre-polymer composition and sacrificial material composition are to be deposited in the same position in each layer. Additional print layers (e.g., **110***h-k*) are disposed below the print layer **110***g*. In some other embodiments, the print layers **110***a*, **110***c*, **110***e*, and **110***g* which include pore-feature spaces are stacked in direct contact with each other, and the print layers without pore-feature space (e.g., **110***b*, **110***d*, and **110***f*) are omitted. In such embodiments, droplets of the sacrificial material composition **112** are to be deposited in the same position in each layer such that the sacrificial material composition **112** is continuous within individual pore-features **106***b* in the Z-direction. The resulting pore-feature structure may be referred to as a “post.”

[0025] According to the design layout of FIG. **1**B, the pore-features **106***b* are to be distributed, with respect to one another, in one or both directions of an X-Y plane parallel to a polishing surface of the polishing pad (i.e., laterally). Thus, at least portions of the pore-features **106***b* are to be spatially separated, i.e., spaced apart from one another, by at least portions of a to-be-printed polishing material **104***b* interposed therebetween. The pore-features **106***b* may be continuous with a to-be-printed polishing surface **108***b*.

[0026] In general, the to-be-printed polishing layer **102***b* is designed to have well-defined pore-features without any of the shortcomings which are apparent in the resulting polishing layer **102***a* described above. It is believed that the poorly defined pore-features **106***a* shown in FIG. **1**A are a result of inter-mixing between adjacent droplets of the pre-polymer composition and the sacrificial material composition prior to curing. In addition, it is also believed that inter-mixing may occur more readily during fabrication of polishing pads formed of relatively softer materials and/or using high resolution printing.

[0027] Advantageously, embodiments described herein provide for reduced inter-mixing between adjacent droplets of the pre-polymer composition and the sacrificial material composition thereby resulting in better defined pore-features compared to the example shown in FIG. **1**A. In addition, reduced inter-mixing results in formation of a polishing layer **202**, for example shown in FIG. **2**, which corresponds more closely to the to-be-printed polishing layer **102***b* shown in FIG. **1**B.

[0028] FIG. **2** is a schematic sectional view illustrating a portion of a polishing layer **202** of a polishing pad according to embodiments described herein. A polishing material **204** of the polishing layer **202** may include a hard or soft formulation as described in more detail below. A plurality of pore-features **206** are formed in the polishing material **204**. The pore-features **206** may include openings defined in a polishing surface **208** of the polishing layer **202**, voids that are formed in the polishing material **204** below the polishing surface **208**, pore-forming features disposed in the polishing surface **208**, pore-forming features disposed in the polishing material **204** below the polishing surface **208**, and combinations thereof. Here, the pore-features **206** are well-defined, for example having one or more of uniform diameter, uniform depth, uniform size distribution across the pad, uniform shape, rounded appearance in cross-section, separation of the polishing material **204** interposed between adjacent pore-features **206**, continuity within each of the pore-features **206**, high pore-feature space as a fraction of a volume of the sacrificial material composition dispensed to form the corresponding pore-features, less spread in a radial plane (e.g., in the X-Y plane) compared to the pore-features **106***a*, reduced depth compared to the pore-features **106***a*, and combinations thereof.

[0029] Embodiments described herein provide a universal method to improve pore structure independent of other aspects of the formulation such as polarity of the components, relative strength (e.g., storage modulus or ultimate tensile strength) of the polishing material, additives for adjusting zeta potential, additives for tuning water uptake, or monomers for tuning mechanical properties. Embodiments described herein improve pore structure even for high resolution printing such as 300 dpi or 600 dpi. Embodiments described herein provide polishing pads with improved surface cure which may reduce surface tackiness. Embodiments described herein provide polishing pads having a reduced concentration of residual monomers which may be hazardous. Embodiments described herein provide polishing pads with a reduced internal structural stress level which may improve a flatness of the polishing pads.

[0030] Embodiments described herein provide improved pore structure even for polishing pads formed using relatively soft material formulations. It is believed that during a conventional pad fabrication process pre-polymer droplets of soft polishing material formulations suffer from increased inter-mixing with adjacent droplets of sacrificial material when compared to hard material formulations due to the greater hydrophilicity of the soft material formulations. However, embodiments described herein overcome the challenge of maintaining pore structure even with the more hydrophilic formulations.

[0031] Embodiments described herein provide a pre-polymer composition including a multifunctional acrylate component which increases a curing rate of the dispensed droplets of the pre-polymer composition when exposed to a dose of electromagnetic radiation. In other words, the curing rate of the pre-polymer composition with the multifunctional acrylate component is greater than a curing rate of the pre-polymer composition without the multifunctional acrylate component when exposed to the same dose of electromagnetic radiation. Advantageously, the accelerated curing of the pre-polymer composition in embodiments described herein provides for reduced inter-mixing between adjacent droplets of the pre-polymer composition and the sacrificial material composition when compared to the pre-polymer composition without the multifunctional acrylate component.

[0032] Advantageously, embodiments described herein provide a pre-polymer composition including a surface active agent which provides for reduced inter-mixing between adjacent droplets of the pre-polymer composition and the sacrificial material composition when compared to the pre-polymer composition without the surface active agent.

[0033] Embodiments described herein provide a sacrificial material composition including a polyethylene glycol monoacrylate component which reduces flowability of the resulting pore-forming phase after curing. Advantageously, the reduced flowability in embodiments described herein improves the structure of resulting pore-features when compared to polishing pads formed without the polyethylene glycol monoacrylate component.

[0034] 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 both chemically active and chemically inactive polishing fluids and/or 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.

Exemplary Polishing System

[0035] FIG. **3** is a schematic side view of an exemplary polishing system **300** configured to use a polishing pad **400** formed according to embodiments described herein. The polishing pad **400** is further described in FIG. **4**.

[0036] Here, the polishing system **300** features a platen **304**, having the polishing pad **400** secured thereto using a pressure sensitive adhesive, and a substrate carrier **306**. The substrate carrier **306** faces the platen **304** and the polishing pad **400** mounted thereon. The substrate carrier **306** is used to urge a material surface of a substrate **308**, disposed therein, against the polishing surface of the polishing pad **400** while simultaneously rotating about a carrier axis **310**. Typically, the platen **304** rotates about a platen axis **312** while the rotating substrate carrier **306** sweeps back and forth from an inner diameter to an outer diameter of the platen **304** to, in part, reduce uneven wear of the polishing pad **400**.

[0037] The polishing system **300** further includes a fluid delivery arm **314** and a pad conditioner assembly **316**. The fluid delivery arm **314** is positioned over the polishing pad **400** and is used to deliver a polishing fluid, such as a polishing slurry having abrasives suspended therein, to a surface of the polishing pad **400**. Typically, the polishing fluid contains a pH adjuster and other chemically active components, such as an oxidizing agent, to enable chemical mechanical polishing of the material surface of the substrate **308**. The pad conditioner assembly **316** is used to condition the polishing pad **400** by urging a fixed abrasive conditioning disk **318** against the surface of the polishing pad **400** before, after, or during polishing of the substrate **308**. Urging the conditioning disk **318** against the polishing pad **400** includes rotating the conditioning disk **318** about a conditioner axis **320** and sweeping the conditioning disk **318** from an inner diameter the platen **304** to an outer diameter of the platen **304**. The conditioning disk **318** is used to abrade and rejuvenate the polishing pad **400** polishing surface, and to remove polish byproducts or other debris from the polishing surface of the polishing pad **400**.

Polishing Pad Examples

[0038] The polishing pads described herein include a foundation layer and a polishing layer disposed on the foundation layer. The polishing layer forms the polishing surface of the polishing pad and the foundation layer provides support for the polishing layer as a to-be-polished substrate is urged thereagainst. The foundation layer and the polishing layer are formed of different pre-polymer compositions that, when cured, have different material properties. The foundation layer and the polishing layer are integrally and sequentially formed using a continuous layer-by-layer additive manufacturing process. The additive manufacturing process provides a polishing pad body having a continuous polymer phase between the polishing layer and the foundation layer thus eliminating the need for an adhesive layer or other bonding method therebetween. In some embodiments, the polishing layer is formed of a plurality of polishing elements, which are separated from one another across the polishing surface by recesses, and/or channels, disposed therebetween.

[0039] The term "pore-feature," as used herein includes openings defined in the polishing surface, voids that are formed the polishing material below the polishing surface, pore-forming features disposed in the polishing surface, pore-forming features disposed in polishing material below the polishing surface, and combinations thereof. Pore-forming features typically include a water-soluble-sacrificial material that dissolves upon exposure to a polishing fluid thus forming a corresponding opening in the polishing surface and/or void in the polishing material below the polishing surface. In some embodiments, the water-soluble-sacrificial material may swell upon exposure to a polishing fluid thus deforming the surrounding polishing material to provide asperities at the polishing pad material surface. The resulting pores and asperities desirably facilitate transporting liquid and abrasives to the interface between the polishing pad and a to-be-polished material surface of a substrate, and temporarily fixes those abrasives (abrasive capture) in relation to the substrate surface to enable chemical and mechanical material removal therefrom.

[0040] The term "pore-feature space," as used herein refers to a volume of each pore-feature. When multiple pore-features are merged together, boundary lines defining the pore-feature space of each individual pore-feature may be determined according to the corresponding design layout for the to-be-printed polishing layer. For example, when two pore-features are merged together, an average distance between the to-be-printed pore-features may be used as the boundary line between the merged pore-features.

[0041] The term "pore-feature density," as used herein refers to the cumulative area including pore-features in an X-Y plane of a given sample as a percentage of the total area of the given sample in the X-Y plane, such as the cumulative area including pore-features in a pore-feature density micro-region in the polishing surface of a polishing pad or in an X-Y plane parallel thereto. The term "porosity," as used herein refers to the volume of pore-feature space as a percentage of the total bulk volume in a given sample. In embodiments where a pore-feature, as defined herein, includes a pore-forming feature formed of a sacrificial material the pore-feature density and porosity are measured after the sacrificial material forming the feature is dissolved therefrom.

[0042] Pore-feature density, pore-feature space, pore-feature structure, porosity, and pore size may be determined using any suitable method, such as by methods using a scanning electron microscopy (SEM) or an optical microscope. Techniques and systems for characterizing pore-feature density, porosity, and pore size are well known in the art. For example, a portion of the surface can be characterized by any suitable method (e.g., by electron microscope image analysis, by atomic force microscopy, by 3D microscopy, etc.). In one implementation, the pore-feature density and pore size analysis can be performed using a VK-X Series 3D UV Laser Scanning Confocal Microscope, produced by KEYENCE Corporation of America, located in Elmwood Park, N.J., U.S.A.

[0043] In some embodiments, the polishing material of the polishing pad may be formed from different pre-polymer compositions, or different ratios of the different pre-polymer compositions, to provide unique material properties.

[0044] Generally, the methods set forth herein use an additive manufacturing system, e.g., a 2D or a 3D inkjet printer system, to form (print) at least portions of the polishing pads in a layer-by-layer process. Typically, each print layer is formed (printed) by sequentially depositing and at least partially curing droplets of desired pre-polymer compositions and/or pore-forming sacrificial material precursor compositions on a manufacturing support or a previously formed print layer. Beneficially, the additive manufacturing system and the methods set forth herein enable at least micron scale droplet placement control within each print layer (X-Y resolution) as well as micron scale (0.1 μm to 200 μm) control over the thickness (Z resolution) of each print layer. The micron scale X-Y and Z resolutions provided by the additive manufacturing systems and the methods set forth herein facilitate the formation of desirable and repeatable patterns of the pore-features described herein. Thus, in some embodiments, the additive manufacturing methods used to from the polishing pads also impart one or more distinctive structural characteristics of the polishing pads formed therefrom.

[0045] The term "high-resolution printing," as used herein refers to pore-features formed of four or less adjacent droplets of the sacrificial material composition, such as one to four adjacent droplets. The negative changes in pore structure associated with inter-mixing between droplets of the pre-polymer composition and the sacrificial material composition are more significant using high-resolution printing because the dimensions of the pore-features are reduced substantially when compared to lower-resolution printing.

[0046] FIG. **4** is a schematic isometric sectional view of a polishing pad **400** featuring selectively arranged pore-features **410** according to embodiments described herein. The polishing pad **400** may be used as the polishing pad **400** of the exemplary polishing system **300** described in FIG. **3**. Here, the polishing pad **400** includes a plurality of polishing elements **404**, which are disposed on and partially disposed within a foundation layer **406**. An additive manufacturing process allows for co-polymerization of different pre-polymer compositions used to respectively form the foundation layer **406** and a polishing layer including the polishing elements **404**, thus providing a continuous phase of polymer material across the interfacial boundary regions therebetween.

[0047] The polishing pad **400** has a first thickness T(1) of between about 5 mm and about 30 mm. The polishing elements **404** are supported in the thickness direction of the pad **400** by a portion of the foundation layer **406** that has a second thickness of T(2) of between about ⅓ to about ⅔ of the first thickness T(1). The polishing elements **404** have a third thickness T(3) that is between about ⅓ and about ⅔ of the first thickness T(1). As shown, at least portions of the polishing elements are disposed beneath a surface of the foundation layer **406** and the remaining portions extend upwardly therefrom by a height H. In some embodiments, the height H is about ½ of the first thickness T(1) or less.

[0048] Here, the plurality of polishing elements **404** include a plurality of discontinuous (segmented) concentric rings **407** disposed about a post **405** and extending radially outward therefrom. Here, the post **405** is disposed in the center of the polishing pad **400**. In other embodiments the center of the post **405**, and thus the center of the concentric rings **407**, may be offset from the center of the polishing pad **400** to provide a wiping type relative motion between a substrate and the polishing pad surface as the polishing pad **400** rotates on a polishing platen. Sidewalls of the plurality of polishing elements **404** and an upward facing surface of the foundation layer **406** define a plurality of channels **418** disposed in the polishing pad **400** between each of the polishing elements **404** and between a plane of the polishing surface **401** of the polishing pad **400** and a surface of the foundation layer **406**. The plurality of channels **418** enable the distribution of polishing fluids across the polishing pad **400** and to an interface between the polishing pad **400** and the material surface of a substrate to be polished thereon. Here, the polishing elements **404** have an upper surface that is parallel to the X-Y plane and sidewalls that are substantially vertical, such as within about 20° of vertical (orthogonal to the X-Y plane), or within about 10° of vertical. A width W(1) of the polishing element(s) **404** is between about 250 microns and about 10 millimeters, such as between about 250 microns and about 5 millimeters, or between about 1 mm and about 5 mm. A pitch P between the polishing element(s) **404** is between about 0.5 millimeters and about 5 millimeters. In some embodiments, one or both of the width W(1) and the pitch P vary across a radius of the polishing pad **400** to define zones of pad material properties.

[0049] The polishing elements **404** include a plurality of pore-features **410** disposed therein. The plurality of pore-features **410** may be disposed in any desired vertical arrangement when viewed in cross-section. For example, in FIG. **4**, the plurality of pore-features **410** are vertically disposed in columnar arrangements (two columns shown) where the pore-features **410** in each of the columns are in substantial vertical alignment. In some other examples, groups of rows or individual rows of pore-features **410** in the depth direction of the polishing elements **404** may be offset in one or both of X-Y directions to provide corresponding pore-features **410** below the polishing surface **401** that are vertically staggered with respect to the pore-features **410** disposed there above and/or there below. The orientation of the pore-features **410** can be advantageously used to adjust the compliance of the polishing material with respect to a direction of the load exerted by a substrate that is being polished thereon. Thus, in one example, the staggered pore-features **410** may be advantageously used to adjust and/or control the polishing planarization performance of a polishing pad formed therefrom.

[0050] In some embodiments, the individual pore-features **410** may have a height of about 600 μm or less, such as about 500 μm or less, about 400 μm or less, about 300 μm or less, about 200 μm or less, about 100 μm or less, about 50 μm or less, about 40 μm or less, about 30 μm or less, about 20 μm or less, or about 10 μm or less. The height of individual pore-features **410** is typically a multiple, e.g., **1**X or more, of a thickness of the each of the print layers. For example, the thickness of the pore-features within a print layer may be the same as the thickness of the continuous polymer phase of polishing material disposed adjacent thereto. Thus, if pore-features laterally disposed within at least two sequentially deposited print layers are aligned or at least partially overlap in the Z-direction, the thickness of the resulting pore-feature is at least the combined thickness of the at least two sequentially deposited print layers. In some embodiments, one or more of the pore-features do not overlap with a pore-feature in an adjacent layer disposed there above or there below and thus has a thickness of a single print layer.

[0051] In some embodiments, the individual pore-features **410** are formed to have a diameter D (measured in an X-Y plane) of about 600 μm or less, such as about 500 μm or less, about 400 μm or less, about 300 μm or less, about 200 μm or less, about 100 μm or less, about 50 μm or less, about 40 μm or less, about 30 μm or less, about 20 μm or less, or about 10 μm or less and about 5 μm or more, such as about 10 μm or more, about 25 μm or more, or about 50 μm or more. In some embodiments, the mean diameter D of the individual pore-features **410** is between about 50 μm and about 600 μm. In some embodiments, the pore-features **410** are formed to be relatively narrow in the X-Y plane compared to the height thereof, for example, in some embodiments a diameter D of the individual pore-features is about ⅔ or less than the height thereof, such as about ½ or less, or about ⅓ or less.

[0052] Here, individual ones of the plurality of pore-features **410** are spaced apart in the vertical direction by one or more printed layers of polymer material **412** formed therebetween. In some examples, spacing between pore-features **410** in a vertical direction may be about 100 μm or less, such as about 40 μm or less, such as about 10 μm or less, or about 10 μm to about 40 μm. The pore-features **410** may form a substantially closed-celled structure once the sacrificial-material used to form the pore-features is removed therefrom. In one example, spacing between pore-features **410** in the vertical direction may be about 40 μm. The 40 μm spacing can be formed by disposing four 10 μm print layers of the polymer material **412** between the printed layers that include the pore-features **410**. In another example, spacing between pore-features **410** in the vertical direction may be about 10 μm. The 10 μm spacing can be formed by disposing four 2.5 μm print layers of the polymer material **412** between the printed layers that include the pore-features **410**.

[0053] In other embodiments one or more of the pore-features **410**, or portions thereof, are not spaced apart from one or more of the pore-features **410** adjacent thereto and thus form a more open-celled structure once the sacrificial-material is removed therefrom. A thickness of the one or more printed layers may be about 5 μm or more, such as about 10 μm or more, 20 μm or more, 30 μm or more, 40 μm or more, or 50 μm or more. The individual pore-features **410** may be formed within a corresponding single print layer and thus have a height corresponding to the thickness of the print layer or may be formed within two or more adjacent print layers to provide a pore height corresponding to the cumulative thickness thereof.

[0054] The polishing elements **404** are formed of a continuous polymer phase of polymer material **412**. The polymer material **412** may have a relatively low storage modulus E', i.e., a soft pad material, a relatively high storage modulus E', i.e., a hard pad material, or a relatively medium storage modulus E' between the relatively low and relatively high storage modulus, i.e., a medium pad material. In some examples, the polymer material **412** may have a generally homogenous material composition. In some other examples, the polymer material **412** may include at least two pre-polymer compositions, and thus include a combination of low, medium, or high storage modulus E' materials with a difference from one another in one or more material properties. Characterizations of the low, medium, and high storage modulus E' materials at a temperature of about 30° C. (E'30) are summarized in Table 1.

TABLE 1

	Low Storage Modulus Compositions	Medium Storage Modulus Compositions	High Storage Modulus Compositions
E'30	<100 MPa, (e.g., 1 MPa-100 MPa)	100 MPa-500 MPa	>500 MPa (e.g., 500 MPa-3000 MPa)

[0055] FIGS. **5**A-**5**F are schematic plan views of various polishing elements **504*a-f*** shapes which may be used with or in place of the polishing elements **404** of the polishing pad **400** described in FIG. **4**. Each of the FIGS. **5**A-**5**F includes a pixel chart having white regions (regions in white pixels) that represent the polishing elements **504*a-f*** and black regions (regions in black pixels) that represent the foundation layer **406**.

[0056] In FIG. **5**A, the polishing elements **500*a*** include a plurality of concentric annular rings. In FIG. **5**B, the polishing elements **500*b*** include a plurality of segments of concentric annular rings. In FIG. **5**C, the polishing elements **504*c*** form a plurality of spirals (four shown) extending from a center of the polishing pad **500*c*** to an edge of the polishing pad **500*c*** or proximate thereto. In FIG. **5**D, a plurality of discontinuous polishing elements **504*d*** are arranged in a spiral pattern on the foundation layer **406**.

[0057] In FIG. **5**E, each of the plurality of polishing elements **504*e*** includes a cylindrical post extending upwardly from the foundation layer **406**. In other embodiments, the polishing elements **504*e*** are of any suitable cross-sectional shape, for example columns with toroidal, partial toroidal (e.g., arc), oval, square, rectangular, triangular, polygonal, irregular shapes in a section cut generally parallel to the underside surface of the pad **500*e***, or combinations thereof. FIG. **5**F illustrates a polishing pad **500*f*** having a plurality of discrete polishing elements **504*f*** extending upwardly from the foundation layer **406**. The polishing pad **500*f*** of FIG. **5**F is similar to the polishing pad **500*e*** except that some of the polishing elements **504*f*** are connected to form one or more closed circles. The one or more closed circles create damns to retain polishing fluid during a CMP process.

Additive Manufacturing System and Process Examples

[0058] FIG. **6**A 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 sacrificial material sources **614** which are used to from the polymer material **412** and the pore-features **410** described in FIG. **4** above. 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 the foundation layer **406** described above. 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.

[0059] 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 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**.

[0060] 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 FIG. **6**B. 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**.

[0061] FIG. **6**B is a close up cross-sectional view schematically illustrating a droplet **630** disposed on a surface **618***a* of a previously formed layer, such as the previously formed layer **618** described in FIG. **6**A, according to some embodiments. In a typically additive manufacturing process, a droplet of pre-polymer composition, such as the droplet **630***a* spreads and reaches an equilibrium contact angle α with the surface **618***a* of a previously formed layer within about one second from the moment in time that the droplet **630***a* contacts the surface **618***a*. 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 **618***a* (surface energy) of the previously formed layer, e.g., previously formed layer **618**. In some embodiments, it is desirable to at least the partially cure the dispensed droplet before it reaches an equilibrium size in order to fix the droplets contact angle with the surface **618***a* of the previously formed layer. In those embodiments, the fixed droplet's **630***b* contact angle θ is greater than the equilibrium contact angle α of the droplet **630***a* of the same pre-polymer composition which was allowed to spread to its equilibrium size.

[0062] Herein, at least partially curing a dispensed droplet causes the at least partial polymerization, e.g., the cross-linking, of the pre-polymer composition(s) within the droplets and with adjacently disposed droplets of the same or different pre-polymer composition 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.

Formulation and Material Examples

[0063] The pre-polymer compositions used to form the foundation layer **406** and the polymer material **412** of the polishing elements described above each includes a mixture of one or more of functional polymers, functional oligomers, functional monomers, reactive diluents, and photoinitiators.

[0064] 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.

[0065] 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.

[0066] Examples of suitable monomers which may be used to from 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), 3,3,5-trimethylcyclohexane 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 SR562, SR563, SR564 from Sartomer®.

[0067] 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 trimethylolpropane formal acrylate, caprolactone acrylate, isobornyl acrylate (IBOA), or alkoxylated lauryl methacrylate.

[0068] 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.

[0069] 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.

[0070] The sacrificial material composition(s), which may be used to form the pore-features **410** described above, include water-soluble material, 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), trimethylolethane, 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.

[0071] 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, 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.

Exemplary Pre-Polymer Compositions—Multifunctional Acrylate Component

[0072] In some examples, the pre-polymer composition **612** includes a multifunctional acrylate component, such as tripropylene glycol diacrylate, poly(propylene glycol) diacrylate (e.g., with molecular weight within a range of about 350 g/mol to about 2000 g/mol, trimethylyol triacrylate, neopentyl glycol diacrylate, ethoxylated neopentyl glycol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, or combinations thereof. In some examples, the multifunctional acrylate component may include at least one diacrylate or triacrylate having a molecular weight of about 200 g/mol or greater, about 350 g/mol, or greater or about 600 g/mol or greater, such as about 350 g/mol to about 2000 g/mol. In some examples, a concentration of the multifunctional acrylate component in the pre-polymer composition **612** may be about 20 wt % or less, such as about 10 wt % or less, or about 10 wt % to about 20 wt %. In some examples, the pre-polymer composition **612** further includes at least one of phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, butylcarbamatoethyl acrylate, isobornyl acrylate, or combinations thereof.

[0073] In some examples, a curing rate of the dispensed droplets **630** of the pre-polymer composition **612** including the multifunctional acrylate component when exposed to a first dose of electromagnetic radiation is greater than a curing rate of the pre-polymer composition **612** without the multifunctional acrylate component when exposed to the same first dose of electromagnetic radiation. In some examples, the pre-polymer composition **612** may form a polymer having a shore A hardness of less than 100, less than 90, less than 80, less than 70, less than 60, less than 50, less than 40, less than 30, less than 20, or less than 10, or 0 to about 20, about 20 to about 40, about 40 to about 60, about 60 to about 80, or about 80 to about 100, when cured.

[0074] In some examples, at least partial curing of the dispensed droplets **630** of the pre-polymer composition **612** includes exposing the dispensed droplets **630** to electromagnetic radiation for a first time period of about 2 seconds to about 4 seconds, and the curing rate of the pre-polymer composition **612** with the multifunctional acrylate component corresponds to about 50% to about 70% conversion of the multifunctional acrylate component during the first time period.

[0075] In some examples, a volume of a pore-feature space of an individual one of the plurality of pore-features **410** is at least 50%, at least 60%, at least 70% at least 80%, or at least 90%, or about 50% to about 60%, about 60% to about 70%, about 70% to about 80%, about 80% to about 90%, or about 90% to about 100% of a volume of the sacrificial material composition **614** dispensed to form the corresponding pore-features **410**.

[0076] In some examples, the curing rate of the pre-polymer composition **612** with the multifunctional acrylate component reduces inter-mixing between adjacent droplets **630**, **632** of the pre-polymer composition **612** and the sacrificial material composition **614** when compared to the curing rate of the pre-polymer composition **612** without the multifunctional acrylate component.

[0077] In some examples, the curing rate of the pre-polymer composition **612** with the multifunctional acrylate component satisfies a threshold condition for inter-mixing between adjacent droplets **630**, **632** of the pre-polymer composition **612** and the sacrificial material composition **614**. In some examples, the threshold condition for inter-mixing corresponds to a volume of pore-feature space of individual ones of the plurality pore-features **410** of at least 50%, at least 60%, at least 70% at least 80%, or at least 90%, or about 50% to about 60%, about 60% to about 70%, about 70% to about 80%, about 80% to about 90%, or about 90% to about 100% of a volume of the sacrificial material composition **614** dispensed to form the corresponding pore-features **410**.

[0078] In some examples, when the curing rate of the pre-polymer composition **612** with the multifunctional acrylate component meets or exceeds a threshold curing rate, at least 5%, at least 10%, at least 20%, at least 30%, at least

40%, or at least 50% of the plurality of pore-features are isolated from other ones of the plurality of pore-features within the polishing layer.

[0079] In some examples, the multifunctional acrylate component reduces swelling of the polishing pad **400** when exposed to an aqueous polishing fluid when compared to a polishing pad formed using the pre-polymer composition **612** without the multifunctional acrylate component.

[0080] In some examples, the multifunctional acrylate component increases a surface contact angle of a water droplet disposed on the polishing layer compared to a polishing layer formed using the pre-polymer composition **612** without the multifunctional acrylate component.

Exemplary Pre-Polymer Compositions—Surface Active Agent

[0081] In some examples, the pre-polymer composition **612** includes a surface active agent, such as polybutylated phenol, nonylphenol, 2-methyl-4-t-octylphenol, 4,6-di-t-butyl-2-methylphenol, or combinations thereof. In some examples, a concentration of the surface active agent in the pre-polymer composition **612** may be about 1 wt % or less, such as about 0.1 wt % or less, or about 0.1 wt % to about 1 wt %.

[0082] In some examples, the surface active agent increases the hydrophobicity of the dispensed droplets **630** of the pre-polymer composition **630**. In some examples, a volume of a pore-feature space of an individual one of the plurality of pore-features **410** is at least 50%, at least 60%, at least 70% at least 80%, or at least 90%, or about 50% to about 60%, about 60% to about 70%, about 70% to about 80%, about 80% to about 90%, or about 90% to about 100% of a volume of the sacrificial material composition **614** dispensed to form the corresponding pore-features **410**.

Exemplary Sacrificial Material Compositions—Polyethylene Glycol Monoacrylate Component

[0083] In some examples, the sacrificial material composition **614** includes a polyethylene glycol monoacrylate component. A concentration of the polyethylene glycol monoacrylate component in the sacrificial material composition **614** may be about 30 wt % or greater, about 40 wt % or greater, or about 50 wt % or greater. In some examples, a molecular weight of the polyethylene glycol monoacrylate component may be about 400 g/mol to about 1200 g/mol, such as about 400 g/mol to about 750 g/mol.

[0084] In some examples, the sacrificial material composition **614** may further include a polyethylene glycol diacrylate component, a polyethylene glycol component, or combinations thereof. In some examples, a concentration of the polyethylene glycol diacrylate component in the sacrificial material composition may be about 30 wt % or less, about 20 wt % or less, or about 10 wt % or less. In some examples, a concentration of the polyethylene glycol component in the sacrificial material composition may be about 40 wt % or less, about 30 wt % or less or about 20 wt % or less. In one example, a concentration of a polyethylene glycol monoacrylate component in the sacrificial material composition may be about 30 wt % or greater, a concentration of a polyethylene glycol diacrylate component in the sacrificial material composition may be about 10 wt % or less, and a concentration of a polyethylene glycol component in the sacrificial material composition may be about 40 wt % or less. In some examples, the sacrificial material composition **614** may form a polymer having a shore A hardness of greater than 1, greater than 5, or greater than 10, such as from **10** to **100**, at room temperature when cured.

[0085] In some examples, the polymer is water-soluble and exposing the polymer to an aqueous solution forms a plurality of pores in the polishing layer. In some examples, the sacrificial material composition **614** forms a linear polymer matrix when cured. In some examples, a pre-polymer composition **612** may include at least one of phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, butylcarbamatoethyl acrylate, isobornyl acrylate, or combinations thereof.

[0086] In some examples, a volume of a pore-feature space of an individual one of the plurality of pore-features **410** is at least 50%, at least 60%, at least 70% at least 80%, or at least 90%, or about 50% to about 60%, about 60% to about 70%, about 70% to about 80%, about 80% to about 90%, or about 90% to about 100% of a volume of the sacrificial material composition **614**, including the polyethylene glycol monoacrylate component, dispensed to form the corresponding pore-features **410**.

[0087] Here, the additive manufacturing system **600** shown in FIG. **6**A 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.

[0088] Typically, the memory **635** is in the form of a computer-readable storage media 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.

[0089] 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).

[0090] 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.

[0091] 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.

[0092] FIG. **7** is a flow diagram setting forth a method of forming a print 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 FIG. **6**A and the fixed droplets of FIG. **6**B. 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.

[0093] At activity **710**, the method **700** includes dispensing droplets of a pre-polymer composition and droplets of a sacrificial material composition onto a surface of a previously formed print layer according to a predetermined droplet dispense pattern.

[0094] At activity **720**, the method **700** includes at least partially curing the dispensed droplets of the pre-polymer composition to form a print layer including a plurality of pore-features.

[0095] 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. In some embodiments, the plurality of print layers include a polishing layer having a plurality of 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.

[0096] Desirably, pre-polymer composition embodiments described herein including a multifunctional acrylate component provide accelerated curing when compared to conventional pre-polymer compositions, as illustrated in the conversion-exposure curves shown in FIG. **8**.

[0097] FIG. **8** is a graph **800** illustrating conversion-exposure curves **802***a-b* for pre-polymer compositions without the multifunctional acrylate component and conversion-exposure curves **804***a-b* for corresponding pre-polymer compositions with the multifunctional acrylate component at a concentration of about 10 wt %. In the example illustrate in FIG. **8**, droplets of the pre-polymer composition and the sacrificial material composition may be dispensed and cured, for example according to the method **700**. In this example, the sacrificial material composition may form about 16% of the total volume of the dispensed droplets.

[0098] In the example of FIG. **8**, the dispensed droplets are exposed to a sequence of pulses of electromagnetic radiation (e.g., UV radiation) with each pulse having a fixed energy (dosage). Therefore, the exposure time (x-axis) corresponds to a cumulative dose of electromagnetic radiation applied to the dispensed droplets, and the conversion of the multifunctional acrylate component (y-axis) is measured as a function of the cumulative dose. In this example, conversion may refer to the extent of chemical cross-linking of a UV curable composition measured by photo differential scanning calorimetry (DSC).

[0099] As shown in FIG. **8**, the conversion-exposure curves for the pre-polymer compositions with the multifunctional acrylate component are beneficially shifted towards increased conversion at the same exposure time (cumulative dose) when compared to the corresponding conversion-exposure curves **802***a-b* for the pre-polymer compositions without the multifunctional acrylate component. In some examples, an initial curing rate (which corresponds to an initial slope of the conversion-exposure curve) is increased about 2× or more, or about 1× to about 2×, such as about 1.6× to about 1.95×. In one example, a ratio of the curing rate of the pre-polymer composition with the multifunctional acrylate component to the curing rate of the pre-polymer composition without the multifunctional acrylate component may be about 1.6 or greater, such as about 1.6 to about 1.95.

[0100] Table 2 shows hardness and pore-feature space % (i.e., a volume of a pore-feature space of an individual one of the plurality of pore-features as a fraction of a volume of the sacrificial material composition dispensed to form the corresponding pore-features) values for the polishing pads formed using the pre-polymer compositions of FIG. **8**.

TABLE 2

Pre-Polymer Composition	Hardness (shore A)	Ratio of pore feature space to volume of the sacrificial material composition dispensed to form the corresponding pore-features
802a	53	<50%
804a	70	>50%
802b	57	<50%
804b	68	>50%

[0101] 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.

1. A method of forming a polishing pad, comprising:

(a) dispensing droplets of a pre-polymer composition and droplets of a sacrificial material composition onto a surface of a previously formed print layer according to a predetermined droplet dispense pattern; and

(b) at least partially curing the dispensed droplets of the pre-polymer composition to form a print layer; and

(c) sequentially repeating (a) and (b) to form a polishing layer having a plurality of pore-features formed therein, wherein:

the pre-polymer composition comprises a multifunctional acrylate component,

a curing rate of the dispensed droplets of the pre-polymer composition comprising the multifunctional acrylate component when exposed to a first dose of electromagnetic radiation is greater than a curing rate of the pre-polymer composition without the multifunctional acrylate component when exposed to the same first dose of electromagnetic radiation, and

the plurality of pore-features comprise openings defined in a surface of the polishing layer, voids that are formed in the polishing layer below the surface, pore-forming features comprising the sacrificial material composition, or combinations thereof.

2. The method of claim **1**, wherein a concentration of the multifunctional acrylate component in the pre-polymer composition is about 20 wt % or less.

3. The method of claim **1**, wherein the multifunctional acrylate component comprises at least one diacrylate or triacrylate having a molecular weight of about 200 g/mol or greater.

4. The method of claim **1**, wherein the multifunctional acrylate component comprises at least one of tripropylene glycol diacrylate, poly(propylene glycol) diacrylate, trimethylyol triacrylate, neopentyl glycol diacrylate, ethoxylated neopentyl glycol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, or combinations thereof.

5. The method of claim **1**, wherein a ratio of the curing rate of the pre-polymer composition with the multifunctional acrylate component to the curing rate of the pre-polymer composition without the multifunctional acrylate component is about 1.6 or greater.

6. The method of claim **1**, wherein a volume of a pore-feature space of an individual one of the plurality of pore-features comprises at least 50% of a volume of the sacrificial material composition dispensed to form the corresponding pore-features.

7. The method of claim **1**, wherein the curing rate of the pre-polymer composition with the multifunctional acrylate component reduces inter-mixing between adjacent droplets of the pre-polymer composition and the sacrificial material composition when compared to the curing rate of the pre-polymer composition without the multifunctional acrylate component.

8. The method of claim **1**, wherein:

the curing rate of the pre-polymer composition with the multifunctional acrylate component satisfies a threshold condition for inter-mixing between adjacent droplets of the pre-polymer composition and the sacrificial material composition,

the threshold condition for inter-mixing corresponds to a volume of pore-feature space of individual ones of the plurality pore-features comprising at least 50% of a volume of the sacrificial material composition dispensed to form the corresponding pore-features.

9. The method of claim **1**, wherein when the curing rate of the pre-polymer composition with the multifunctional acrylate component meets or exceeds a threshold curing rate, at least 5% of the plurality of pore-features are isolated from other ones of the plurality of pore-features within the polishing layer.

10. The method of claim **1**, wherein the pre-polymer composition further comprises at least one of phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, butylcarbamatoethyl acrylate, isobornyl acrylate, or combinations thereof.

11. The method of claim **1**, wherein the multifunctional acrylate component reduces swelling of the polishing pad when exposed to an aqueous polishing fluid when compared to a polishing pad formed using the pre-polymer composition without the multifunctional acrylate component.

12. The method of claim **1**, wherein the multifunctional acrylate component increases a surface contact angle of a water droplet disposed on the polishing layer compared to a polishing layer formed using the pre-polymer composition without the multifunctional acrylate component.

13. A method of forming a polishing pad, comprising:

(a) dispensing droplets of a pre-polymer composition and droplets of a sacrificial material composition onto a surface of a previously formed print layer according to a predetermined droplet dispense pattern; and

(b) at least partially curing the dispensed droplets of the pre-polymer composition to form a print layer comprising a plurality of pore-features; and

(c) sequentially repeating (a) and (b) to form a polishing layer, wherein:

the pre-polymer composition comprises a surface active agent,

wherein a volume of a pore-feature space of an individual one of the plurality of pore-features comprises at least 50% of a volume of the sacrificial material composition dispensed to form the corresponding pore-features, and

the plurality of pore-features comprise openings defined in a surface of the polishing layer, voids that are formed in the polishing layer below the surface, pore-forming features comprising the sacrificial material composition, or combinations thereof.

14. The method of claim **13**, wherein the surface active agent comprises at least one of polybutylated phenol, nonylphenol, 2-methyl-4-t-octylphenol, 4,6-di-t-butyl-2-methylphenol, or combinations thereof.

15. The method of claim **13**, wherein a concentration of the surface active agent in the pre-polymer composition is about 1 wt % or less.

16. The method of claim **13**, wherein the surface active agent increases the hydrophobicity of the dispensed droplets of the pre-polymer composition.

17. A polishing pad, comprising:

a plurality of polishing elements, each comprising:

an individual surface that forms a portion of a polishing surface of the polishing pad; and

one or more sidewalls extending downwardly from the individual surface to define a plurality of channels disposed between the polishing elements, wherein:

each of the polishing elements has a plurality of pore-features formed therein,

each of the polishing elements is formed of a pre-polymer composition and a sacrificial material composition,

a volume of pore-feature space of an individual one of the plurality of pore-features comprises at least 50% of a volume of the sacrificial material composition dispensed to form the corresponding pore-features, and the plurality of pore-features comprise openings defined in the polishing surface, voids that are formed in the polishing elements below the polishing surface, pore-forming features comprising the sacrificial material composition, or combinations thereof.

18. The polishing pad of claim **17**, wherein the pre-polymer composition comprises a multifunctional acrylate component.

19. The polishing pad of claim **17**, wherein the pre-polymer composition comprises a surface active agent.

20. The polishing pad of claim **17**, wherein:

a concentration of a polyethylene glycol monoacrylate component in the sacrificial material composition is about 30 wt % or greater,

a concentration of a polyethylene glycol diacrylate component in the sacrificial material composition is about 10 wt % or less, and

a concentration of a polyethylene glycol component in the sacrificial material composition is about 40 wt % or less.

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