

## ULTRA HIGH VOID VOLUME POLISHING PAD WITH CLOSED PORE STRUCTURE

### BACKGROUND OF THE INVENTION

**[0001]** Chemical-mechanical polishing (“CMP”) processes are used in the manufacturing of microelectronic devices to form flat surfaces on semiconductor wafers, field emission displays, and many other microelectronic substrates. For example, the manufacture of semiconductor devices generally involves the formation of various process layers, selective removal or patterning of portions of those layers, and deposition of yet additional process layers above the surface of a semiconducting substrate to form a semiconductor wafer. The process layers can include, by way of example, insulation layers, gate oxide layers, conductive layers, and layers of metal or glass, etc. It is generally desirable in certain steps of the wafer process that the uppermost surface of the process layers be planar, i.e., flat, for the deposition of subsequent layers. CMP is used to planarize process layers wherein a deposited material, such as a conductive or insulating material, is polished to planarize the wafer for subsequent process steps.

**[0002]** In a typical CMP process, a wafer is mounted upside down on a carrier in a CMP tool. A force pushes the carrier and the wafer downward toward a polishing pad. The carrier and the wafer are rotated above the rotating polishing pad on the CMP tool’s polishing table. A polishing composition (also referred to as a polishing slurry) is introduced between the rotating wafer and the rotating polishing pad during the polishing process. The polishing composition typically contains a chemical that interacts with or dissolves portions of the uppermost wafer layer(s) and an abrasive material that physically removes portions of the layer(s). The wafer and the polishing pad can be rotated in the same direction or in opposite directions, whichever is desirable for the particular polishing process being carried out. The carrier also can oscillate across the polishing pad on the polishing table.

**[0003]** Polishing pads made of harder materials exhibit high removal rates and have long useful pad life, but tend to produce numerous scratches on substrates being polished. Polishing pads made of softer materials exhibit low scratching of substrates, but tend to exhibit lower removal rates and have shorter useful pad life. Accordingly, there remains a need in the art for polishing pads that provide effective removal rates and have extended pad life, and also produce limited scratching.

## BRIEF SUMMARY OF THE INVENTION

**[0004]** The invention provides a polishing pad for chemical-mechanical polishing comprising a porous polymeric material, wherein the polishing pad comprises closed pores and wherein the polishing pad has a void volume fraction of 70% or more.

**[0005]** The invention also provides a method of preparing a polishing pad, which method comprises (a) providing a polishing pad material comprising a polymer resin, (b) subjecting the polishing pad material to an inert gas at a first elevated pressure, (c) foaming the polishing pad material by increasing the temperature of the polishing pad material to a first temperature above the glass transition temperature of the polishing pad material and less than the melting point of the polishing pad material, (d) subjecting the polishing pad material to an inert gas at a second elevated pressure, and (e) foaming the polishing pad material by increasing the temperature of the polishing pad material to a second temperature above the glass transition temperature of the polishing pad material.

**[0006]** The invention additionally provides a method of polishing a substrate, which method comprises (a) providing a substrate to be polished, (b) contacting the substrate with a polishing system comprising the aforesaid polishing pad and a polishing composition, and (c) abrading at least a portion of the substrate with the polishing system to polish the substrate.

## BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

**[0007]** FIG. 1A is an SEM image of a cross-section of a polishing pad material comprising a thermoplastic polyurethane having a Shore D hardness of 42D that was subjected to one cycle of pressurizing/foaming. FIG. 1B is an SEM image at a lower magnification than FIG. 1A of the aforesaid workpiece after a second cycle of pressurizing/foaming. FIG. 1C is an SEM image at the same magnification as FIG. 1B of the aforesaid workpiece after a third cycle of pressurizing/foaming.

**[0008]** FIG. 2A is an SEM image of a cross-section of a polishing pad material comprising a thermoplastic polyurethane having a Shore D hardness of 25D that was subjected to one cycle of pressurizing/foaming. FIG. 2B is an SEM image at the same magnification as FIG. 2A of the aforesaid workpiece after a second cycle of pressurizing/foaming. FIG. 2C is the image shown in FIG. 2B at a higher magnification.

**[0009]** FIG. 3A is an SEM image of a cross-section of a polishing pad material comprising a thermoplastic polyurethane having a Shore D hardness of 72D that was

subjected to one cycle of pressurizing/foaming. FIG. 3B is an SEM image at a lower magnification as FIG. 3A of the aforesaid workpiece after a second cycle of pressurizing/foaming. FIG. 3C is an SEM image at a lower magnification than FIGS. 3A and 3B of the aforesaid workpiece after a third cycle of pressurizing/foaming.

**[0010]** FIG. 4 is an SEM image of a cross-section of a polishing pad material comprising a thermoplastic polyurethane having a Shore D hardness of 42D that was subjected to one cycle of pressurizing/foaming.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0011]** The invention provides a polishing pad for chemical-mechanical polishing comprising a porous polymeric material, wherein the polishing pad comprises closed pores and wherein the polishing pad has a void volume fraction of 70% or more.

**[0012]** The polishing pad can comprise, consist essentially of, or consist of any suitable material. Desirably, the polishing pad comprises, consists essentially of, or consists of a polymer resin. The polymer resin can be any suitable polymer resin. Typically, the polymer resin is selected from the group consisting of thermoplastic elastomers, thermoplastic polyurethanes, polyolefins, polycarbonates, polyvinylalcohols, nylons, elastomeric rubbers, styrenic polymers, polyaromatics, fluoropolymers, polyimides, cross-linked polyurethanes, cross-linked polyolefins, polyethers, polyesters, polyacrylates, elastomeric polyethylenes, polytetrafluoroethylenes, polyethyleneterephthalates, polyimides, polyaramides, polyarylenes, polystyrenes, polymethylmethacrylates, copolymers and block copolymers thereof, and mixtures and blends thereof. Preferably, the polymer resin is a polyurethane, more preferably, a thermoplastic polyurethane.

**[0013]** The polymer resin typically is a pre-formed polymer resin; however, the polymer resin also can be formed in situ according to any suitable method, many of which are known in the art (see, for example, Szycher's Handbook of Polyurethanes CRC Press: New York, 1999, Chapter 3). For example, thermoplastic polyurethane can be formed in situ by reaction of urethane prepolymers, such as isocyanate, di-isocyanate, and tri-isocyanate prepolymers, with a prepolymer containing an isocyanate reactive moiety. Suitable isocyanate reactive moieties include amines and polyols.

**[0014]** Typically, the void volume of the polishing pad predominantly is formed by closed cells (i.e., pores); however, the polishing pad also can comprise open cells.

Preferably, at least 75% or more, e.g., 80% or more, 85% or more, 90% or more, 95% or more, 98% or more, 99% or more, or 100%, of the void volume of the polishing pad is provided by closed cells.

**[0015]** The polymer resin can have a Shore D hardness of 15D or more, e.g., 20D or more, 25D or more, 30D or more, 35D or more, 40D or more, 42D or more, 45D or more, 50D or more, 55D or more, 60D or more, 65D or more, or 70D or more. Alternatively, or in addition, the polymer resin can have a Shore D hardness of 75D or less, e.g., 72D or less, 70D or less, 65D or less, 60D or less, 55D or less, 50D or less, or 45D or less. Thus, the polymer resin can have a Shore D hardness bounded by any two of the endpoints recited for the Shore D hardness. For example, the polymer resin can have a Shore D hardness of 15D to 75D, 20D to 75D, 25D to 75D, 25D to 72D, 30D to 72D, 35D to 72D, 40D to 72D, 42D to 72D, 15D to 72D, 15D to 70D, 15D to 65D, 15D to 60D, 15D to 55D, 15D to 50D, 15D to 45D, 20D to 45D, 25D to 45D, 50D to 75D, 55D to 75D, 60D to 75D, 65D to 75D, or 70D to 75D. All Shore D hardness values are as measured using ASTM 2240-05 (2010).

**[0016]** The polishing pad typically can have a compressibility of 5% or more, e.g., 10% or more, 15% or more, or 20% or more. Alternatively, or in addition, the polishing pad can have a compressibility of 25% or less, e.g., 20% or less, 15% or less, or 10% or less. Thus, the polishing pad can have a compressibility bounded by any two of the endpoints recited for the compressibility. For example, the polishing pad can have a compressibility of 5% to 25%, 5% to 20%, 5% to 15%, 5% to 10%, 10% to 25%, 10% to 20%, or 10% to 15%.

**[0017]** The polishing pad can have a void volume fraction of 70% or more, e.g., 72% or more, 74% or more, 76% or more, 78% or more, 80% or more, 82% or more, 84% or more, 86% or more, 88% or more, or 90% or more. Alternatively, or in addition, the polishing pad can have a void volume fraction of 90% or less, e.g., 88% or less, 86% or less, 84% or less, 82% or less, or 80% or less. Thus, the polishing pad can have a void volume fraction bounded by any two of the endpoints recited for the void volume. For example, the polishing pad can have a void volume fraction of 70% to 90%, 70% to 88%, 70% to 86%, 70% to 84%, 70% to 82%, 70% to 80%, 72% to 90%, 72% to 88%, 72% to 86%, 72% to 84%, 72% to 82%, 74% to 90%, 74% to 88%, 74% to 86%, 74% to 84%, 74% to 82%, 76% to 90%, 76% to 88%, 76% to 86%, 76% to 84%, 76% to 82%, 78% to 90%, 78% to 88%, 78% to 86%, 78% to 84%, or 78% to 82%.

**[0018]** The void volume fraction of the polishing pad can be measured using any suitable measurement method. For example, the void volume fraction of the polishing pad can be measured using a density measurement, wherein the void volume fraction can be expressed by:  $\text{void volume \%} = (1 - \rho_{\text{foamed}} / \rho_{\text{solid}}) \times 100\%$ , wherein  $\rho_{\text{foamed}}$  is the density of the polishing pad and  $\rho_{\text{solid}}$  is the density of the polymeric resin used to form the polishing pad. The terms “void volume”, “void volume fraction”, or “void volume percentage” as used herein can be synonymous with porosity.

**[0019]** The polishing pad, more specifically the closed pores of the polishing pad, can have an average pore size of 5  $\mu\text{m}$  or more, e.g., 10  $\mu\text{m}$  or more, 15  $\mu\text{m}$  or more, 20  $\mu\text{m}$  or more, 25  $\mu\text{m}$  or more, 30  $\mu\text{m}$  or more, 35  $\mu\text{m}$  or more, 40  $\mu\text{m}$  or more, 45  $\mu\text{m}$  or more, 50  $\mu\text{m}$  or more, 55  $\mu\text{m}$  or more, 60  $\mu\text{m}$  or more, 65  $\mu\text{m}$  or more, 70  $\mu\text{m}$  or more, 75  $\mu\text{m}$  or more, 100  $\mu\text{m}$  or more, 125  $\mu\text{m}$  or more, or 150  $\mu\text{m}$  or more. Alternatively, or in addition, the polishing pad can have an average pore size of 200  $\mu\text{m}$  or less, e.g., 190  $\mu\text{m}$  or less, 180  $\mu\text{m}$  or less, 175  $\mu\text{m}$  or less, 170  $\mu\text{m}$  or less, 160  $\mu\text{m}$  or less, 150  $\mu\text{m}$  or less, 140  $\mu\text{m}$  or less, 130  $\mu\text{m}$  or less, 125  $\mu\text{m}$  or less, 120  $\mu\text{m}$  or less, 110  $\mu\text{m}$  or less, 100  $\mu\text{m}$  or less, 90  $\mu\text{m}$  or less, 80  $\mu\text{m}$  or less, 70  $\mu\text{m}$  or less, 60  $\mu\text{m}$  or less, 50  $\mu\text{m}$  or less, 40  $\mu\text{m}$  or less, 30  $\mu\text{m}$  or less, or 20  $\mu\text{m}$  or less. Thus, the polishing pad can have an average pore size bounded by any two of the endpoints recited for the average pore size. For example, the polishing pad can have an average pore size of 5  $\mu\text{m}$  to 200  $\mu\text{m}$ , 5  $\mu\text{m}$  to 20  $\mu\text{m}$ , 25  $\mu\text{m}$  to 75  $\mu\text{m}$ , 50  $\mu\text{m}$  to 100  $\mu\text{m}$ , 75  $\mu\text{m}$  to 125  $\mu\text{m}$ , 100  $\mu\text{m}$  to 150  $\mu\text{m}$ , 125  $\mu\text{m}$  to 175  $\mu\text{m}$ , or 150  $\mu\text{m}$  to 200  $\mu\text{m}$ .

**[0020]** As used herein, the average pore size refers to the average of the largest diameter of a representative sample of individual pores in the polishing pad. The largest diameter is the same as the Feret diameter. The largest diameter can be obtained from an image of a sample, such as a transmission electron microscope image, either manually or by using image analysis software. Typically, the sample is obtained by sectioning a portion of a polishing pad.

**[0021]** The average pore size as used herein refers to the average pore size within the bulk portion of the polishing pad, i.e., the portion of the polishing pad between, but not including, the surface(s) of the polishing pad. The surface can be the region of the pad within 5 mm, e.g., within 4 mm, within 3 mm, within 2 mm, or within 1 mm, of the pad surface as produced and before any finishing operations, such as skiving, dressing, or the like.

**[0022]** In an embodiment, the polishing pad can have a storage modulus of elasticity of 0.01 MPa or more, e.g., 0.05 MPa or more, 0.1 MPa or more, 0.2 MPa or more, 0.3 MPa or more, 0.4 MPa or more, 0.5 MPa or more, 0.6 MPa or more, 0.8 MPa or more, or 0.9 MPa or more. Alternatively, or in addition, the polishing pad can have a storage modulus of elasticity of 1 MPa or less, e.g., 0.9 MPa or less, 0.8 MPa or less, 0.7 MPa, or less, 0.6 MPa or less, or 0.5 MPa or less. Thus, the polishing pad can have a storage modulus of elasticity bounded by any two of the endpoints recited for the storage modulus of elasticity. For example, the polishing pad can have a storage modulus of elasticity of 0.01 MPa to 1 MPa, 0.05 MPa to 1 MPa, 0.1 MPa to 1 MPa, 0.2 MPa, to 1 MPa, 0.3 MPa to 1 MPa, 0.4 MPa to 1 MPa, or 0.5 MPa to 1 MPa. The storage modulus of elasticity typically refers to the storage modulus of elasticity at a temperature that exists in the polishing zone that exists between the surface of the polishing pad and a substrate being polished during the polishing operation. Typically, the temperature is 40°C to 80°C, 40°C, 45°C, 50°C, 55°C, 60°C, 65°C, 70°C, 75°C, or 80°C.

**[0023]** The invention also provides a method of preparing a polishing pad. The method comprises (a) providing a polishing pad material comprising a polymer resin, (b) subjecting the polishing pad material to an inert gas at a first elevated pressure, (c) foaming the polishing pad material by increasing the temperature of the polishing pad material to a first temperature above the glass transition temperature of the polishing pad material and less than the melting point of the polishing pad material, and then optionally (d) subjecting the polishing pad material to an inert gas at a second elevated pressure, and (e) foaming the polishing pad material by increasing the temperature of the polishing pad material to a second temperature above the glass transition temperature of the polishing pad material and less than the melting point of the polishing pad material.

**[0024]** The polishing pad material is subjected to at least one cycle, preferably at least two cycles, of (a) subjecting the polishing pad material to an inert gas at an elevated pressure and then (b) subjecting the polishing pad material to a temperature that is above the glass transition temperature ( $T_g$ ) of the polishing pad material and less than the melting point ( $T_m$ ) of the polishing pad material. The first and second elevated pressures and the first and second elevated temperatures may be the same or may be different. The inert gas can be a hydrocarbon, chlorofluorocarbon, hydrochlorofluorocarbon (e.g., FREON™ hydrochlorofluorocarbon) nitrogen, carbon dioxide, carbon monoxide, or a combination

thereof. Preferably, the inert gas comprises, or is, nitrogen or carbon dioxide, and more preferably, the gas comprises, or is, carbon dioxide.

**[0025]** The polishing pad material is maintained at the elevated pressure(s) for a time sufficient to cause an appropriate amount of the inert gas to dissolve into the polishing pad material. The amount of gas dissolved in the polishing pad material is directly proportional to the applied pressure according to Henry's law. Increasing the temperature of the polishing pad material while at the elevated pressure(s) increases the rate of diffusion of the gas into the polishing pad material, but also decreases the amount of gas that can dissolve in the polishing pad material. Higher pressure of inert gas results in the production of smaller pore sizes, while lower pressure of inert gas results in the production of larger pore sizes. Desirably, the inert gas thoroughly saturates the polishing pad material. Thereafter, the polishing pad material is depressurized. The resulting polishing pad material typically is supersaturated with the inert gas.

**[0026]** The polishing pad material is then subjected to a temperature(s) that is above the glass transition temperature ( $T_g$ ) of the polishing pad material and less than the melting point ( $T_m$ ) of the polishing pad material. The resulting thermodynamic instability results in the formation of nucleation sites in the polishing pad material, which are the sites at which the dissolved molecules of the inert gas form clusters which grow to form voids (i.e., cells or pores, which typically are closed pores) in the polishing pad material.

**[0027]** Following production of the polishing pad, the polishing pad can be annealed by heating to a temperature above  $T_g$  for a period of time. The polishing pad can be further processed using any suitable technique. For example, the polishing pad can be skived or milled to provide a polishing surface. The thus-produced polishing surface can be further processed using techniques such as conditioning the polishing surface, for example, by diamond conditioning.

**[0028]** The polishing pad of the invention, which is produced by at least two stages of foaming, desirably has a high void volume, with the result that the pores are closely packed together. By varying the gassing and foaming conditions in each step, a variety of pore morphologies can be obtained. In many cases, the morphology resembles a close packing of roughly hexagonal pores similar to a honeycomb structure.

**[0029]** FIGS. 1A-1C depict scanning electron microscope (“SEM”) images of a cross-section of a polishing pad material comprising a thermoplastic polyurethane having a Shore D hardness of 42D that was subjected to one, two, and three cycles of pressurizing/foaming. FIG. 1A is an SEM image of the thermoplastic polyurethane after the first pressurizing/foaming step. The void volume fraction is 65%, and the average pore diameter is 5  $\mu\text{m}$ . FIG. 1B is an SEM image at a lower magnification than FIG. 1A of the thermoplastic polyurethane after the second pressurizing/foaming step. The void volume fraction is 85%, and the average pore diameter is 10  $\mu\text{m}$ . FIG. 1C is an SEM image at the same magnification as FIG. 1B of the thermoplastic polyurethane after the third pressurizing/foaming step. The void volume fraction is 87%, and the average pore diameter is 9  $\mu\text{m}$ .

**[0030]** FIGS. 2A-2C depict SEM images of a cross-section of a workpiece comprising a thermoplastic polyurethane having a Shore D hardness of 25D that was subjected to one and two cycles of pressurizing/foaming. FIG. 2A is an SEM image of the thermoplastic polyurethane after the first pressurizing/foaming step. The void volume fraction is 72%, and the average pore diameter is 40  $\mu\text{m}$ . FIG. 2B is an SEM image as the same magnification as FIG. 2A of the thermoplastic polyurethane after the second pressurizing/foaming step. The void volume fraction is 75%, and the average pore diameter is 40  $\mu\text{m}$ . FIG. 2C is the image of FIG. 2B at a higher magnification.

**[0031]** FIGS. 3A-3C depict SEM images of a cross-section of a workpiece comprising a thermoplastic polyurethane having a Shore D hardness of 72D that was subjected to one, two, and three cycles of pressurizing/foaming. FIG. 3A is an SEM image of the thermoplastic polyurethane after the first pressurizing/foaming step. The void volume fraction is 50%, and the average pore diameter is 57  $\mu\text{m}$ . FIG. 3B is an SEM image at a lower magnification as FIG. 3A of the thermoplastic polyurethane after the second pressurizing/foaming step. The void volume fraction is 80%, and the average pore diameter is 92  $\mu\text{m}$ . FIG. 3C is an SEM image at a lower magnification than FIGS. 3A and 3B of the thermoplastic polyurethane after the third pressurizing/foaming step. The void volume fraction is 89%, and the average pore diameter is 109  $\mu\text{m}$ .

**[0032]** Desirably, the combination of high void volume and the dense packing of pores is thought to create a high number of asperities at the surface of the inventive polishing pad.

The high number of asperities allows for high removal rates when the inventive polishing pad is used to polish substrates. In addition, the high void volume and high compressibility thereby confer to the inventive polishing pad high removal rates and long pad life associated with hard polishing pad materials along with low scratching associated with soft polishing pad materials.

**[0033]** Typically, the pores have a polygonal shape or morphology, in a plane coplanar with the polishing surface. The pores are separated from each other via thin cell walls. The polygonal shape permits closer packing of the pores within the polishing pad and may be correlated with the high void volume fraction of the inventive polishing pad.

**[0034]** The invention further provides a method of polishing a substrate, comprising (a) providing a substrate to be polished, (b) contacting the substrate with a polishing system comprising the polishing pad of claim 1 and a polishing composition, and (c) abrading at least a portion of the substrate with the polishing system to polish the substrate.

**[0035]** The polishing pad of the invention is particularly suited for use in conjunction with a chemical-mechanical polishing (CMP) apparatus. Typically, the apparatus comprises a platen, which, when in use, is in motion and has a velocity that results from orbital, linear, or circular motion, a polishing pad of the invention in contact with the platen and moving with the platen when in motion, and a carrier that holds a substrate to be polished by contacting and moving relative to the surface of the polishing pad intended to contact a substrate to be polished. The polishing of the substrate takes place by the substrate being placed in contact with the polishing pad and then the polishing pad moving relative to the substrate, typically with a polishing composition therebetween, so as to abrade at least a portion of the substrate to polish the substrate. The CMP apparatus can be any suitable CMP apparatus, many of which are known in the art. The polishing pad of the invention also can be used with linear polishing tools.

**[0036]** The polishing pad described herein can be used alone or optionally can be used as one layer of a multi-layer stacked polishing pad. For example, the polishing pad can be used in combination with a subpad. The subpad can be any suitable subpad. Suitable subpads include polyurethane foam subpads (e.g., PORON™ foam subpads from Rogers Corporation), impregnated felt subpads, microporous polyurethane subpads, and sintered urethane subpads. The subpad optionally comprises grooves, channels, hollow sections,

windows, apertures, and the like. When the polishing pad of the invention is used in combination with a subpad, typically there is an intermediate backing layer such as a polyethyleneterephthalate film, coextensive with and in between the polishing pad and the subpad. Alternatively, the porous foam of the invention also can be used as a subpad in conjunction with a conventional polishing pad.

**[0037]** The polishing pad described herein is suitable for use in polishing many types of substrates and substrate materials. For example, the polishing pad can be used to polish a variety of substrates including memory storage devices, semiconductor substrates, and glass substrates. Suitable substrates for polishing with the polishing pad include memory disks, rigid disks, magnetic heads, MEMS devices, semiconductor wafers, field emission displays, and other microelectronic substrates, especially substrates comprising insulating layers (e.g., silicon dioxide, silicon nitride, or low dielectric materials) and/or metal-containing layers (e.g., copper, tantalum, tungsten, aluminum, nickel, titanium, platinum, ruthenium, rhodium, iridium, or other noble metals).

**[0038]** The following example further illustrates the invention but, of course, should not be construed as in any way limiting its scope.

#### EXAMPLE 1

**[0039]** In this example, the average pore size was determined according to the following procedure: The samples were prepared by cutting a small rectangle out of each sample square using a razor blade. The samples were supported on carbon tape and are sputtered for 30 seconds with a 3.5 - 5.0 nm coating layer. An image of each sample was captured using scanning electron microscopy ("SEM"). Appropriate resolution was used to ensure that there were enough pores for measurement in the field. The image was obtained and stored.

**[0040]** For image analysis, a minimum of 30 pores were measured using PAX-IT™ image analysis software (MIS, Inc., Villa Park, IL). This is performed by manually drawing horizontal lines from one edge of the pore to the other and using the software to calculate pore size for each of the bubbles. The results were summarized in a report that provided the pore size distribution of the sample including minimum, maximum, average size and standard deviation.

**[0041]** The void volume of the polishing pad was measured by performing a density measurement on samples cut from polishing pads and employing a pycnometer with absolute

ethanol as the liquid medium. The void volume is expressed by: void volume % =  $(1 - \rho_{\text{foamed}} / \rho_{\text{solid}}) \times 100\%$ , wherein  $\rho_{\text{foamed}}$  is the density of the polishing pad and  $\rho_{\text{solid}}$  is the density of the polymeric resin used to form the polishing pad.

**[0042]** This example illustrates a method for preparing polishing pads of the invention.

**[0043]** A series of thermoplastic polyurethane (TPU) sheets were subjected to two successive cycles (cycles 1 and 2) of gassing and foaming using carbon dioxide as the inert gas. For both cycles, the gassing pressures were in the range of 2.42-3.45 MPa, the foaming temperatures were in the range of 115-155°C, and the gassing temperature was 10° C. The ratio of gassing pressures in cycle two versus cycle one ( $P_2/P_1$ ), the ratio of gassing time in cycle two versus cycle one ( $t_{\text{gas}2}/t_{\text{gas}1}$ ), the ratio of foaming temperature in cycle two versus cycle one ( $T_2/T_1$ ), the ratio of CO<sub>2</sub> concentration in cycle two versus cycle one ( $[\text{CO}_2]_2/[\text{CO}_2]_1$ ), the ratio of bulk pore size after the first cycle and after the second cycle ( $dp_2/dp_1$ ), the bulk pore size after the second cycle ( $dp_2$ ), the ratio of void volumes after the first cycle and after the second cycle ( $\varepsilon_2/\varepsilon_1$ ), and the void volume fraction after the second cycle are set forth in Table 1.

Table 1

| Sample | $P_2/P_1$<br>(MPa) | $t_{\text{gas}2}/t_{\text{gas}1}$ | $T_2/T_1$ | $([\text{CO}_2]_2/[\text{CO}_2]_1)$ | $dp_2/dp_1$ | $dp_2$ | $\varepsilon_2/\varepsilon_1$ | Final<br>void<br>volume<br>fraction |
|--------|--------------------|-----------------------------------|-----------|-------------------------------------|-------------|--------|-------------------------------|-------------------------------------|
| 1A     | 1.32               | 1.00                              | 1.00      | 3.30                                | 1.71        | 280    | 1.52                          | 88.5                                |
| 1B     | 1.25               | 1.00                              | 1.00      | 3.33                                | 2.01        | 92     | 1.54                          | 88.5                                |
| 1C     | 1.19               | 1.00                              | 1.00      | 3.14                                | 2.09        | 81     | 1.38                          | 89.6                                |
| 1D     | 1.00               | 1.00                              | 1.00      | 3.03                                | 1.96        | 39     | 1.33                          | 90.5                                |
| 1E     | 1.32               | 1.00                              | 1.00      | 3.54                                | 1.79        | 248    | 1.48                          | 89.4                                |
| 1F     | 1.25               | 1.00                              | 1.00      | 3.59                                | 1.94        | 131    | 1.49                          | 89.4                                |
| 1G     | 1.19               | 1.00                              | 1.00      | 3.32                                | 2.46        | 97     | 1.43                          | 90.3                                |
| 1H     | 1.11               | 1.00                              | 1.00      | 3.20                                | 2.08        | 44     | 1.33                          | 90.5                                |
| 1I     | 1.14               | 0.17                              | 1.00      | 2.60                                | 1.47        | 61     | 1.34                          | 87.9                                |
| 1J     | 1.00               | 0.17                              | 1.00      | 2.41                                | 1.75        | 34     | 1.29                          | 87.7                                |
| 1K     | 1.32               | 0.17                              | 0.95      | 3.14                                | 1.43        | 224    | 1.32                          | 88.4                                |
| 1L     | 1.25               | 0.17                              | 0.95      | 3.15                                | 1.55        | 86     | 1.34                          | 88.0                                |
| 1M     | 1.19               | 0.17                              | 0.95      | 2.84                                | 1.70        | 70     | 1.25                          | 88.6                                |
| 1N     | 1.14               | 0.17                              | 0.95      | 2.91                                | 1.16        | 58     | 1.24                          | 89.4                                |
| 1O     | 1.14               | 0.13                              | 0.95      | 2.45                                | 1.31        | 54     | 1.29                          | 87.0                                |
| 1P     | 1.00               | 0.13                              | 0.95      | 2.17                                | 1.63        | 35     | 1.28                          | 87.0                                |
| 1Q     | 1.32               | 0.13                              | 0.95      | 2.94                                | 1.47        | 204    | 1.29                          | 87.7                                |
| 1R     | 1.25               | 0.13                              | 0.95      | 2.91                                | 1.76        | 116    | 1.31                          | 87.5                                |
| 1S     | 1.19               | 0.13                              | 0.95      | 2.65                                | 1.65        | 65     | 1.27                          | 87.8                                |
| 1T     | 1.14               | 0.13                              | 0.95      | 2.68                                | 1.47        | 65     | 1.21                          | 88.7                                |

**[0044]** As is apparent from the data set forth in Table 1, the TPU sheets exhibited an increase in the void volume after the second cycle of pressurizing/foaming as evidenced by a void volume ratio  $\varepsilon_2/\varepsilon_1$  of approximately 1.21 to 1.52. All of the TPU sheets exhibited void volumes of greater than 87.0% after the second cycle of pressurizing/foaming. The average pore size in the bulk portion of the TPU sheets after the second cycle of pressurizing/foaming varied from 34.4  $\mu\text{m}$  to 279.9  $\mu\text{m}$ .

## EXAMPLE 2

**[0045]** This example demonstrates TEOS removal rates achievable with polishing pads in accordance with embodiments of the invention.

**[0046]** Similar substrates comprising blanket layers of TEOS were polished using the same polishing composition and four different polishing pads (Polishing Pads 2A-2D). The polishing composition comprised 12.5 wt.% fumed silica in water at a pH of 11. Polishing Pad 2A (invention) comprised a thermoplastic polyurethane having a Shore D hardness of

42D and had a void volume of 85%. Polishing Pad 2B (comparative) comprised a thermoplastic polyurethane having a Shore D hardness of 72D and had a void volume of 15%. Polishing Pad 2C (invention) comprised a thermoplastic polyurethane having a Shore D hardness of 72D and had a void volume of 85%. Polishing Pad 2D (comparative) was a IC1010™ polishing pad comprising a microporous polyurethane having a Shore D hardness of 65D and is commercially available from Dow Chemical (Midland, MI). The polishing tool was a REFLEXION™ system (Applied Materials, Santa Clara, CA).

**[0047]** Following polishing, the TEOS removal rates were determined, and the results are set forth in Table 2.

Table 2

| Polishing Pad    | Shore D hardness | Void Volume | TEOS Removal Rate (Å/min) |
|------------------|------------------|-------------|---------------------------|
| 2A (invention)   | 42D              | 85%         | 3110                      |
| 2B (comparative) | 72D              | 15%         | 2570                      |
| 2C (invention)   | 72D              | 85%         | 4780                      |
| 2D (comparative) | 65D              | 29%         | 3610                      |

**[0048]** As is apparent from the results set forth in Table 2, Polishing Pad 2C, which had a Shore D hardness of 72D and a void volume of 85%, exhibited a TEOS removal rate that was approximately 1.9 times greater than the TEOS removal rate exhibited by Polishing Pad 2B, which had a Shore D hardness of 72D and a void volume of 15%. In addition, Polishing Pad 2C exhibited a TEOS removal rate that was approximately 1.54 times greater than the TEOS removal rate exhibited by Polishing Pad 2A, which had a Shore D hardness of 42D and a void volume of 85%. Polishing Pad 2C also exhibited a TEOS removal rate that was approximately 1.32 times greater than the TEOS removal rate exhibited by Polishing Pad 2D, which has a similar Shore D hardness but a significantly lower void volume.

### EXAMPLE 3

**[0049]** This example demonstrates tungsten removal rates achievable with a polishing pad in accordance with an embodiment of the invention.

**[0050]** Similar substrates comprising blanket layers of tungsten were polished using the same polishing composition and three different polishing pads (Polishing Pads 3A-3C). The polishing composition comprised 2.5 wt.% colloidal wet-process silica, 0.0123 wt.% ferric nitrate, 0.0267 wt.% malonic acid, 0.16 wt.% glycine, and 2 wt.% hydrogen peroxide in water

at a pH of 2.3. Polishing Pad 3A (comparative) comprised a thermoplastic polyurethane having a Shore D hardness of 42D and had a void volume of 50%. Polishing Pad 3B (invention) comprised a thermoplastic polyurethane having a Shore D hardness of 42D and had a void volume of 85%. Polishing Pad 3C (comparative) was a IC1010™ polishing pad comprising a microporous polyurethane having a Shore D hardness of 65D and is commercially available from Dow Chemical (Midland, MI). The polishing tool was a REFLEXION™ system (Applied Materials, Santa Clara, CA).

**[0051]** Following polishing, the tungsten removal rates were determined, and the results are set forth in Table 3.

Table 3

| Polishing Pad    | Shore D hardness | Void Volume | TEOS Removal Rate (Å/min) |
|------------------|------------------|-------------|---------------------------|
| 3A (comparative) | 42D              | 50%         | 1530                      |
| 3B (invention)   | 42D              | 85%         | 3200                      |
| 3C (comparative) | 65D              | 29%         | 3160                      |

**[0052]** As is apparent from the results set forth in Table 3, Polishing Pad 3B, which had a Shore D hardness of 42 D and a void volume of 85%, exhibited a tungsten removal rate that was approximately 2.1 times greater than the tungsten removal rate exhibited by Polishing Pad 2A, which had a Shore D hardness of 42D and a void volume of 50%. In addition, Polishing Pad 3B exhibited a tungsten removal rate that was approximately equal to the tungsten removal rate exhibited by Polishing Pad 3C, which has a significantly higher Shore D hardness.

#### EXAMPLE 4

**[0053]** This example demonstrates reduced defectivity achievable with a polishing pad in accordance with an embodiment of the invention.

**[0054]** Four polishing runs were performed on sixty similar substrates using the same polishing composition and four different polishing pads (Polishing Pads 4A-4D). The polishing composition comprised 2.5 wt.% colloidal wet-process silica, 0.0123 wt.% ferric nitrate, 0.0267 wt.% malonic acid, and 0.16 wt.% glycine in water at a pH of 2.3. Polishing Pad 4A (invention) comprised a thermoplastic polyurethane having a Shore D hardness of 42D and had a void volume of 85%. Polishing Pad 4B (comparative) comprised a thermoplastic polyurethane having a Shore D hardness of 42D and had a void volume of

50%. Polishing Pad 4C (comparative) comprised a thermoplastic polyurethane having a Shore D hardness of 25D and had a void volume of 50%. Polishing Pad 4D (comparative) was an open-cell polyurethane pad obtained from Fujibo Ehime Co., Ltd. (Tokyo, Japan). The polishing tool was a MIRRA™ system (Applied Materials, Santa Clara, CA).

**[0055]** Following polishing, substrates 20, 40, and 60 from each polishing run with each different polishing pad were examined at four different regions on the substrates using a SURFSCAN™ SP2 tool (KLA-Tencor, Milpitas, CA). The scratch counts were normalized, and the results are set forth in Table 4.

Table 4

| Polishing Pad    | Region  | Number of Scratches (normalized) |              |              |
|------------------|---------|----------------------------------|--------------|--------------|
|                  |         | Substrate 20                     | Substrate 40 | Substrate 60 |
| 4A (invention)   | 1       | 1.0                              | 0.0          | 0.0          |
|                  | 2       | 0.0                              | 0.0          | 0.0          |
|                  | 3       | 0.0                              | 0.0          | 0.0          |
|                  | 4       | 0.0                              | 1.0          | 0.0          |
|                  | Average | 0.3                              | 0.3          | 0.3          |
| 4B (comparative) | 1       | 0.0                              | 1.0          | 0.0          |
|                  | 2       | 1.0                              | 0.0          | 1.0          |
|                  | 3       | 1.0                              | 0.0          | 2.0          |
|                  | 4       | 0.0                              | 0.0          | 0.0          |
|                  | Average | 0.5                              | 0.3          | 0.8          |
| 4C (comparative) | 1       | 0.0                              | 0.0          | 0.0          |
|                  | 2       | 0.0                              | 0.0          | 0.0          |
|                  | 3       | 2.1                              | 0.0          | 0.0          |
|                  | 4       | 3.3                              | 0.0          | 0.0          |
|                  | Average | 1.3                              | 0.0          | 0.0          |
| 4D (comparative) | 1       | 0.0                              | 1.0          | 0.0          |
|                  | 2       | 0.0                              | 0.0          | 0.0          |
|                  | 3       | 0.0                              | 1.0          | 1.0          |
|                  | 4       | 0.0                              | 2.0          | 0.0          |
|                  | Average | 0.0                              | 1.0          | 0.3          |

**[0056]** As is apparent from the data set forth in Table 4, Polishing Pad 4A, which comprised a thermoplastic polyurethane having a Shore D hardness of 42D and a void volume of 85%, exhibited significantly less scratching than Polishing Pad 4B, which comprised a thermoplastic polyurethane having a Shore D hardness of 42D and a void volume of 50%. Polishing Pad 4A exhibited comparable scratching to the scratching exhibited by Polishing Pad 4C, which comprised a thermoplastic polyurethane having a

Shore D hardness of 25D and a void volume of 50%, and exhibited comparable scratching to the scratching exhibited by Polishing Pad 4D, which is an industry standard soft polishing pad.

#### EXAMPLE 5

**[0057]** This example illustrates a method for preparing polishing pads of the invention using a single step of gassing and foaming, in accordance with an embodiment.

**[0058]** Specimens of 42D hardness TPU material were saturated with CO<sub>2</sub> at 2.41 MPa at -1°C for 24 hours. The specimens were foamed in an oil bath at 143°C for 70 seconds. The average bulk pore size of the foamed specimens was 19 microns and the void volume fraction was 85.5%. A SEM micrograph of a cross-section of a representative specimen is depicted in FIG. 4.

**[0059]** All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

**[0060]** The use of the terms “a” and “an” and “the” and “at least one” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The use of the term “at least one” followed by a list of one or more items (for example, “at least one of A and B”) is to be construed to mean one item selected from the listed items (A or B) or any combination of two or more of the listed items (A and B), unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a

limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

**[0061]** Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

## CLAIM(S):

1. A method of preparing a polishing pad, which method comprises:
  - (a) providing a polishing pad material comprising a polymer resin,
  - (b) subjecting the polishing pad material to an inert gas at a first elevated pressure,
  - (c) foaming the polishing pad material by increasing the temperature of the polishing pad material to a first temperature above the glass transition temperature of the polishing pad material and less than the melting temperature of the polishing pad material,
  - (d) subjecting the polishing pad material to an inert gas at a second elevated pressure, and
  - (e) foaming the polishing pad material by increasing the temperature of the polishing pad material to a second temperature above the glass transition temperature of the polishing pad material and less than the melting temperature of the polishing pad material,

wherein the polishing pad comprises closed pores and the pores have an average pore size of 15  $\mu\text{m}$  to 200  $\mu\text{m}$ .

2. The method of claim 1, wherein the gas comprises nitrogen, carbon dioxide, or combinations thereof.
3. The method of claim 2, wherein the gas is carbon dioxide, and the first and second pressures are 1 MPa to 20 MPa.
4. The method of claim 1, wherein the polishing pad comprises a polymer resin selected from the group consisting of thermoplastic elastomers, thermoplastic polyurethanes, polyolefins, polycarbonates, polyvinylalcohols, nylons, elastomeric rubbers, styrenic polymers, polyaromatics, fluoropolymers, polyimides, cross-linked polyurethanes, cross-linked polyolefins, polyethers, polyesters, polyacrylates, elastomeric polyethylenes, polytetrafluoroethylenes, polyethyleneteraphthalates, polyimides, polyaramides, polyarylenes, polystyrenes, polymethylmethacrylates, copolymers and block copolymers thereof, and mixtures and blends thereof.
5. The method of claim 3, wherein the polymer resin is a thermoplastic polyurethane.
6. A method of polishing a substrate, comprising:
  - (a) providing a substrate to be polished,

- (b) contacting the substrate with a polishing system comprising the polishing pad of claim 1 and a polishing composition, and
- (c) abrading at least a portion of the substrate with the polishing system to polish the substrate.