

## TRANSPARENT MICROPOROUS MATERIALS FOR CMP

## FIELD OF THE INVENTION

[0001] This invention pertains to a chemical-mechanical polishing pad substrate comprising a microporous closed-cell foam characterized by a narrow pore size distribution.

## BACKGROUND OF THE INVENTION

[0002] 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 manufacturing process that the uppermost surface of the process layers be planar, i.e., flat, for the deposition of subsequent layers. CMP is used to polish process layers of a deposited material, such as a conductive or insulating material, to planarize the wafer for subsequent process steps.

[0003] 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) generally 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.

[0004] In polishing the surface of a wafer, it is often advantageous to monitor the polishing process *in situ*. One method of monitoring the polishing process *in situ* involves the use of a polishing pad having an aperture or window. The aperture or window provides a portal through which light can pass to allow the inspection of the wafer surface during the polishing process. Polishing pads having apertures and windows are known and have been used to polish substrates, such as the surface of semiconductor devices. For example, U.S. Patent 5,605,760 provides a pad having a transparent window formed from a solid, uniform polymer, which has no intrinsic ability to absorb or transport slurry. U.S. Patent 5,433,651

discloses a polishing pad wherein a portion of the pad has been removed to provide an aperture through which light can pass. U.S. Patents 5,893,796 and 5,964,643 disclose removing a portion of a polishing pad to provide an aperture and placing a transparent polyurethane or quartz plug in the aperture to provide a transparent window, or removing a portion of the backing of a polishing pad to provide a translucency in the pad. U.S. Patents 6,171,181 and 6,387,312 disclose a polishing pad having a transparent region that is formed by solidifying a flowable material (e.g., polyurethane) at a rapid rate of cooling.

[0005] Only a few materials have been disclosed as useful for polishing pad windows. U.S. Patent 5,605,760 discloses the use of a solid piece of polyurethane. U.S. Patents 5,893,796 and 5,964,643 disclose the use of either a polyurethane plug or a quartz insert. U.S. Patent 6,146,242 discloses a polishing pad with a window comprising either polyurethane or a clear plastic such as CLARIFLEX™ tetrafluoroethylene-*co*-hexafluoropropylene-*co*-vinylidene fluoride terpolymer sold by Westlake. Polishing pad windows made of a solid polyurethane are easily scratched during chemical-mechanical polishing, resulting in a steady decrease of the optical transmittance during the lifetime of the polishing pad. This is particularly disadvantageous because the settings on the endpoint detection system must be constantly adjusted to compensate for the loss in optical transmittance. In addition, pad windows, such as solid polyurethane windows, typically have a slower wear rate than the remainder of the polishing pad, resulting in the formation of a “lump” in the polishing pad which leads to undesirable polishing defects. To address some of these problems, WO 01/683222 discloses a window having a discontinuity that increases the wear rate of the window during CMP. The discontinuity purportedly is generated in the window material by incorporating into the window either a blend of two immiscible polymers or a dispersion of solid, liquid, or gas particles.

[0006] While many of the known window materials are suitable for their intended use, there remains a need for effective polishing pads having translucent regions that can be produced using efficient and inexpensive methods and provide constant light transmissivity over the lifetime of the polishing pad.

[0007] Another problem that arises in advanced CMP polishing applications is the need for optimized consumables to achieve desired performance, such as lower defectivity, lower dishing and erosion. Available commercial pads have a wide spectrum of pore sizes ranging from a few to hundreds of microns. It is believed that abrasive and metal particles fill these pores during polishing and are difficult to wash away. Such contaminants are known to cause wafer scratches and are especially problematic for 65 nanometer or lower nodes.

[0008] Polishing pads having microporous open or closed structures, non-porous structures, and porous open-celled interconnected structures are commonly known in the art.

See *e.g.*, U.S. Patents 4,138,228, 4,239,567, 5,489,233, 6,017,265, 6,062,968, 6,022,268, 6,106,754, 6,120,353, 6,126,532, 6,203,407, 6,217,434, 6,231,434, and 6,287,185. The disadvantage of these prior art pads is that the pores are randomly distributed with extremely broad pore or cell size distributions and with no good control on interconnected pore morphology. Higher defectivity and poor control of dishing and erosion has been attributed to such morphological features of the commercial pads.

[0009] A pad with small and narrowly distributed pore sizes and a closed-cell morphology would make it difficult for residues to deposit in the pores and would facilitate removal of any residue left on the pad. A narrow size distribution of small pores in such a CMP polishing pad would have a significant advantage in reducing defectivity in 65 nanometer or lower nodes.

[0010] The present invention provides such a polishing pad, as well as methods of its manufacture and use. These and other advantages of the present invention, as well as additional inventive features, will be apparent from the description of the invention provided herein.

#### BRIEF SUMMARY OF THE INVENTION

[0011] The invention provides a chemical-mechanical polishing pad substrate comprising a porous material having an average pore size of 0.01 microns to 1 micron, wherein the polishing pad substrate has a light transmittance of at least 10% for at least one wavelength of light in the range of 200 nm to 35,000 nm. The invention also provides a chemical-mechanical polishing apparatus and method of polishing a workpiece. The CMP apparatus comprises (a) a platen that rotates, (b) a polishing pad comprising the polishing pad substrate of the invention, and (c) a carrier that holds a workpiece to be polished by contacting the rotating polishing pad. The method of polishing comprises the steps of (i) contacting a workpiece with the polishing pad comprising the polishing pad substrate of the invention and (ii) moving the polishing pad relative to the workpiece to abrade the workpiece and thereby polish the workpiece.

[0012] A particularly preferred aspect of the invention provides a chemical-mechanical polishing pad substrate comprising a microporous closed-cell foam characterized by a narrow pore size distribution in the range of 0.01 microns to 10 microns. The polishing pad substrate is produced by extruding a polymer resin into a solid polymer sheet, combining the solid polymer sheet with a supercritical gas under elected temperature and pressure until the polymer sheet has been saturated, and forming a polishing pad substrate from the gas saturated polymer sheet. The invention further provides a chemical-mechanical polishing apparatus for using the polishing pad substrate. The CMP apparatus comprises a platen that rotates, the polishing pad substrate of the invention, and a carrier that holds a workpiece to be polished by contacting the rotating polishing pad.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0013] In the drawings:

[0014] FIG. 1 shows the Cu removal rate comparison of a commercial Freudenberg FX-9 pad with the pad of this invention; and

[0015] FIG. 2 shows the within wafer nonuniformity data for the Cu polishing of FIG. 1.

## DETAILED DESCRIPTION OF THE INVENTION

[0016] The invention is directed to a chemical-mechanical polishing pad substrate comprising a closed-cell and porous polymeric material. The polishing pad substrate can be a portion within a polishing pad, or the polishing pad substrate can be an entire polishing pad (e.g., the entire polishing pad or polishing top pad is transparent). In some embodiments, the polishing pad substrate consists of, or consists essentially of, the porous polymeric material. The polishing pad substrate comprises a volume of the polishing pad that is at least  $0.5 \text{ cm}^3$  (e.g., at least  $1 \text{ cm}^3$ ).

[0017] The porous polymeric material of the polishing pad substrate has an average pore size of 0.01 microns to 10 microns. Preferably, the average cell size distribution ranges from 0.05 microns to 5 microns. While not wishing to be bound to any particular theory, it is believed that pore sizes greater than 1 micron will scatter incident radiation, while a pore size less than 1 micron will scatter less incident radiation, or will not scatter the incident radiation at all, thereby providing the polishing pad substrate with a desirable degree of transparency.

[0018] The porous polymeric material of the polishing pad substrate has a highly uniform distribution of pore sizes (i.e., cell sizes). Typically, 75% or more (e.g., 80% or more, or 85% or more) of the pores (e.g., cells) in the porous material have a pore size distribution of  $\pm 0.5 \text{ }\mu\text{m}$  or less (e.g.,  $\pm 0.3 \text{ }\mu\text{m}$  or less, or  $\pm 0.2 \text{ }\mu\text{m}$  or less). In other words, 75% or more (e.g., 80% or more, or 85% or more) of the pores in the porous material have a pore size within  $0.5 \text{ }\mu\text{m}$  or less (e.g.,  $0.3 \text{ }\mu\text{m}$  or less, or  $0.2 \text{ }\mu\text{m}$  or less) of the average pore size. Preferably, 90% or more (e.g., 93% or more, or 95% or more) of the pores (e.g., cells) in the porous material have a pore size distribution of  $\pm 0.5 \text{ }\mu\text{m}$  or less (e.g.,  $\pm 0.3 \text{ }\mu\text{m}$  or less, or  $\pm 0.2 \text{ }\mu\text{m}$  or less).

[0019] Typically, the porous polymeric material of the polishing pad substrate comprises of predominantly closed cells (i.e., pores). The porous material of the present invention preferably comprises at least 70% or more closed cells. The polishing pad ideally has a hardness of 75 Shore A to 75 Shore D.

[0020] The porous material of the polishing pad substrate can have any suitable density or void volume. Typically, the porous material has a density of  $0.2 \text{ g/cm}^3$  or greater (e.g.,  $0.3 \text{ g/cm}^3$  or greater, or even  $0.4 \text{ g/cm}^3$  or greater), preferably a density of  $0.5 \text{ g/cm}^3$  or

greater (e.g., 0.7 g/cm<sup>3</sup> or greater, or even 0.9 g/cm<sup>3</sup> or greater). The void volume typically is 95% or less (e.g., 75% or less, or even 50% or less), preferably 25% or less (e.g., 15% or less, 10% or less, or even 5% or less). Typically the porous material has a cell density of 10<sup>5</sup> cells/cm<sup>3</sup> or greater (e.g., 10<sup>6</sup> cells/cm<sup>3</sup> or greater). The cell density is determined by analyzing a cross-sectional image (e.g., an SEM image) of a porous material with an image analysis software program such as OPTIMAS® imaging software and IMAGEPRO® imaging software, both by Media Cybernetics, or CLEMEX VISION® imaging software by Clemex Technologies.

[0021] The porous material of the polishing pad substrate can comprise any suitable polymer resin. The porous material preferably comprises a polymer resin selected from the group consisting of a thermoplastic elastomer, a thermoplastic polyurethane, a polyolefin, a polycarbonate, a polyvinylalcohol, a nylon, an elastomeric rubber, a styrenic polymer, a polyaromatic polymer, a fluoropolymer, a polyimide, a cross-linked polyurethane, a cross-linked polyolefin, a polyether, a polyester, a polyacrylate, an elastomeric polyethylene, a polytetrafluoroethylene, a polyethyleneterephthalate, a polyimide, a polyaramide, a polyarylene, a polystyrene, a polymethylmethacrylate, copolymers and block copolymers thereof, and mixtures and blends thereof. Preferably, the polymer resin is thermoplastic polyurethane.

[0022] 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.

[0023] The selection of the polymer resin will depend, in part, on the rheology of the polymer resin. Rheology is the flow behavior of a polymer melt. For Newtonian fluids, the viscosity is a constant defined by the ratio between the shear stress (i.e., tangential stress,  $\sigma$ ) and the shear rate (i.e., velocity gradient,  $dy/dt$ ). However, for non-Newtonian fluids, shear rate thickening (dilatant) or shear rate thinning (pseudo-plastic) may occur. In shear rate thinning cases, the viscosity decreases with increasing shear rate. It is this property that allows a polymer resin to be used in melt fabrication (e.g., extrusion, injection molding) processes. In order to identify the critical region of shear rate thinning, the rheology of the polymer resins must be determined. The rheology can be determined by a capillary technique in which the molten polymer resin is forced under a fixed pressure through a capillary of a particular length. By plotting the apparent shear rate versus viscosity at different temperatures, the relationship between the viscosity and temperature can be

determined. The Rheology Processing Index (RPI) is a parameter that identifies the critical range of the polymer resin. The RPI is the ratio of the viscosity at a reference temperature to the viscosity after a change in temperature equal to 20 °C for a fixed shear rate. When the polymer resin is thermoplastic polyurethane, the RPI preferably is 2 to 10 (e.g., 3 to 8) when measured at a shear rate of 150 l/s and a temperature of 205 °C.

**[0024]** Another polymer viscosity measurement is the Melt Flow Index (MFI) which records the amount of molten polymer (in grams) that is extruded from a capillary at a given temperature and pressure over a fixed amount of time. For example, when the polymer resin is thermoplastic polyurethane or polyurethane copolymer (e.g., a polycarbonate silicone-based copolymer, a polyurethane fluorine-based copolymers, or a polyurethane siloxane-segmented copolymer), the MFI preferably is 20 or less (e.g., 15 or less) over 10 minutes at a temperature of 210 °C and a load of 2160 g. When the polymer resin is an elastomeric polyolefin or a polyolefin copolymer (e.g., a copolymer comprising an ethylene  $\alpha$ -olefin such as elastomeric or normal ethylene-propylene, ethylene-hexene, ethylene-octene, and the like, an elastomeric ethylene copolymer made from metallocene based catalysts, or a polypropylene-styrene copolymer), the MFI preferably is 5 or less (e.g., 4 or less) over 10 minutes at a temperature of 210 °C and a load of 2160 g. When the polymer resin is a nylon or polycarbonate, the MFI preferably is 8 or less (e.g., 5 or less) over 10 minutes at a temperature of 210 °C and a load of 2160 g.

**[0025]** The rheology of the polymer resin can depend on the molecular weight, polydispersity index (PDI), the degree of long-chain branching or cross-linking, the glass transition temperature ( $T_g$ ), and the melt temperature ( $T_m$ ) of the polymer resin. When the polymer resin is thermoplastic polyurethane or polyurethane copolymer (such as the copolymers described above), the weight average molecular weight ( $M_w$ ) is typically 50,000 g/mol to 300,000 g/mol, preferably 70,000 g/mol to 150,000 g/mol, with a PDI of 1.1 to 6, preferably 2 to 4. Typically, the thermoplastic polyurethane has a glass transition temperature of 20 °C to 110 °C and a melt transition temperature of 120 °C to 250 °C. When the polymer resin is an elastomeric polyolefin or a polyolefin copolymer (such as the copolymers described above), the weight average molecular weight ( $M_w$ ) typically is 50,000 g/mol to 400,000 g/mol, preferably 70,000 g/mol to 300,000 g/mol, with a PDI of 1.1 to 12, preferably 2 to 10. When the polymer resin is nylon or polycarbonate, the weight average molecular weight ( $M_w$ ) typically is 50,000 g/mol to 150,000 g/mol, preferably 70,000 g/mol to 100,000 g/mol, with a PDI of 1.1 to 5, preferably 2 to 4.

**[0026]** The polymer resin selected for the porous material preferably has certain mechanical properties. For example, when the polymer resin is a thermoplastic polyurethane, the Flexural Modulus (ASTM D790) preferably is 130 MPa (~20,000 psi) to 1200 MPa (~170,000 psi), the average % compressibility is 8 or less, the average %

rebound is 30 or greater, and the Shore D hardness (ASTM D2240-95) is 40 to 90 (e.g., 50 to 80).

[0027] The polishing pad substrate of the present invention has a light transmittance of 10% or more (e.g., 20% or more) for at least one wavelength of light in the range of 200 nm to 35,000 nm. Preferably, the porous material has a light transmittance of 30% or more (e.g., 40% or more, or even 50% or more) for at least one wavelength of light in the range of 200 nm to 35,000 nm (e.g., 200 nm to 10,000 nm, or 200 nm to 1,000 nm, or even 200 nm to 800 nm). The light transmittance of the polishing pad substrate is at least in part determined by controlling properties of the porous material selected from the group consisting of density, void volume, Flexural Modulus, and any combination thereof.

[0028] The polishing pad substrate of the invention offers improved consistency of the light transmittance over the lifetime of the polishing pad substrate. This feature arises from the fact that the pores are present throughout the thickness of the polishing pad substrate. Thus, when the surface of the pad is removed during polishing, the material beneath the surface has substantially similar porosity and roughness, and thus substantially similar polishing properties and light transmittance properties to the original top surface of the pad. In addition, the transmissivity of the polishing pad substrate is on average lower than the transmissivity of a pad made from the same material without pores, because of the roughness. Accordingly, the percentage change in light scattering due to any change resulting from abrasion of the polishing pad substrate during polishing is lessened. Desirably, the light transmittance of the polishing pad substrate decreases by less than 20% (e.g., less than 10%, or even less than 5%) over the lifetime of the polishing pad substrate. These changes, taken together, lessen or even obviate the need to adjust the gain of the endpoint detection system over the lifetime of the polishing pad substrate. For example, the consistency in light transmittance of the polishing pad substrate of the invention can be compared to a solid, or nearly solid, polyurethane window of the prior art. Before polishing, solid polyurethane windows have consistent surface properties; however, during polishing the window becomes abraded and scratched giving rise to inconsistent surface properties. Therefore, an endpoint detection system must be constantly adjusted in response to each new pattern of scratches that arises during polishing. In contrast, the polishing pad substrate of the invention begins with a roughened surface that remains substantially unchanged during and after abrasion during polishing, such that the endpoint detection settings can remain substantially unchanged over the lifetime of the polishing pad substrate.

[0029] The presence of pores in the polishing pad substrate of the invention can have a significant beneficial effect on the polishing properties. For example, in some cases, the pores are capable of absorbing and transporting polishing slurry. Thus, the transmissive region can have polishing properties that are substantially the same as the remaining

portions of the polishing pad. In some embodiments, the surface texture of the transmissive polishing pad substrate is sufficient to make the polishing pad substrate useful as a polishing surface without the need for a second, opaque portion of the polishing pad that is used exclusively for polishing.

**[0030]** The polishing pad substrate of the invention optionally further comprises a dye, which enables the substrate to selectively transmit light of a particular wavelength(s). The dye acts to filter out undesired wavelengths of light (e.g., background light) and thus improve the signal to noise ratio of detection. The polishing pad substrate can comprise any suitable dye or can comprise a combination of dyes. Suitable dyes include polymethine dyes, di- and tri-arylmethine dyes, aza analogues of diarylmethine dyes, aza (18) annulene dyes, natural dyes, nitro dyes, nitroso dyes, azo dyes, anthraquinone dyes, sulfur dyes, and the like. Desirably, the dye is selected so that it substantially transmits the wavelength of light used for *in situ* endpoint detection with minimal or no absorption of light at the detection wavelength. For example, when the light source for the endpoint detection (EPD) system is a HeNe laser, which produces visible light having a wavelength of 540 to 570 nm, the dye preferably is a red dye.

**[0031]** The polishing pad substrate of the invention can be produced using any suitable technique, many of which are known in the art. For example, the polishing pad substrate can be produced by (a) a mucell process, (b) a sol-gel process, (c) a phase inversion process, (d) a spinodal or bimodal decomposition process, or (e) a pressurized gas injection process. Preferably, the polishing pad substrate is produced by a pressurized gas injection process.

**[0032]** The mucell process involves (a) combining a polymer resin with a supercritical gas to produce a single-phase solution and (b) forming a polishing pad substrate of the invention from the single-phase solution. The polymer resin can be any of the polymer resins described above. A supercritical gas is generated by subjecting a gas to an elevated temperature (e.g., 100 °C to 300 °C) and pressure (e.g., 5 MPa (~800 psi) to 40 MPa (~6000 psi)) sufficient to create a supercritical state in which the gas behaves like a fluid (i.e., a supercritical fluid, SCF). The gas can be a hydrocarbon, chlorofluorocarbon, hydrochlorofluorocarbon (e.g., freon), nitrogen, carbon dioxide, carbon monoxide, or a combination thereof. Preferably, the gas is a non-flammable gas, for example a gas that does not contain C-H bonds. The single-phase solution of the polymer resin and the supercritical gas typically is prepared by blending the supercritical gas with molten polymer resin in a machine barrel. The single-phase solution then can be injected into a mold, where the gas expands to form a pore structure with high uniformity of pore size within the molten polymer resin. The concentration of the supercritical gas in the single-phase solution typically is 0.01% to 5% (e.g., 0.1% to 3%) of the total volume of the single-phase solution. These and additional process features are described in further detail in U.S. Patent

6,284,810. The microcellular structure is formed by creating a thermodynamic instability in the single-phase solution (e.g., by rapidly changing the temperature and/or pressure) sufficient to produce greater than  $10^5$  nucleation sites per  $\text{cm}^3$  of the solution. Nucleation sites are the sites at which the dissolved molecules of the supercritical gas form clusters from which the cells in the porous material grow. The number of nucleation sites is estimated by assuming that the number of nucleation sites is approximately equal to the number of cells formed in the polymer material. Typically, the thermodynamic instability is induced at the exit of the mold or die that contains the single-phase solution. The porous material can be formed from the single-phase solution by any suitable technique including extrusion into a polymer sheet, co-extrusion of multilayer sheets, injection molding, compression molding, blow molding, blown film, multilayer blown film, cast film, thermoforming, and lamination. Preferably, the polishing pad substrate (e.g., the porous material) is formed by extrusion or injection molding. The pore size of the porous material is at least in part controlled by the temperature, pressure, and concentration of the supercritical gas, and combinations thereof.

**[0033]** The sol-gel process involves the preparation of a three-dimensional metal oxide network (e.g., siloxane network) having a controllable pore size, surface area, and pore size distribution. Such three-dimensional networks (i.e., sol-gels) can be prepared using a variety of methods, many of which are known in the art. Suitable methods include single-step (e.g., "one-pot") methods and two-step methods. In one method, a dilute, aqueous solution of silica (e.g., sodium silicate) is prepared which spontaneously condenses under appropriate pH and salt concentration conditions, to form the silicon-based network. Another typical method involves the use of metal alkoxide precursors (e.g.,  $\text{M(OR)}_4$ , wherein M is Si, Al, Ti, Zr, or a combination thereof, and R is an alkyl, aryl, or a combination thereof) which when placed in a solvent containing water and an alcohol, undergo hydrolysis of the alkoxide ligands and condensation (e.g., polycondensation) resulting in the formation of M-O-M linkages (e.g., Si-O-Si siloxane linkages). Optionally, catalysts such as protic acids (e.g., HCl) and bases (e.g., ammonia) can be used to improve the kinetics of the hydrolysis and condensation reactions. Two-step methods typically involve the use of pre-polymerized precursors such as pre-polymerized tetraethyl orthosilicate (TEOS). As the number of M-O-M linkages increases, a three-dimensional network is formed which contains pores that are filled with solvent (e.g., water). The solvent can be exchanged with alcohol to form a structure referred to as an alcogel. Simple evaporation of the solvent typically leads to considerable destruction of the solid three-dimensional network resulting in the formation of a xerogel. A more preferred drying technique, which does not result in substantial destruction of the solid three-dimensional network, is supercritical extraction. Supercritical extraction typically involves combining

the solid three-dimensional network with a suitable low molecular weight expanding agent (such as an alcohol, in particular methanol, as is present in an alcogel, or CO<sub>2</sub> gas which is accomplished by gas/solvent exchange) and applying a temperature and pressure to the mixture that is above the critical point of the expanding agent. Under these conditions, vitrification, cross-linking, or polymerization of the solid material can occur. The pressure is then slowly lowered to allow the expanding agent to diffuse out of the vitrified structure. The resulting sol-gel material, referred to as an aerogel, has a microcellular pore structure in which the average pore size and pore size distribution can be controlled. Such aerogel materials can be transparent to visible or ultraviolet light having a wavelength above 250 nm. Hybrid organic-inorganic sol-gel materials also can be transparent, or at least partially transparent. Hybrid sol-gel materials typically are prepared using chemical precursors containing both inorganic and organic groups. When a three-dimensional M-O-M network is formed from such precursors, the organic groups can become trapped inside the pore structure. The pore size can be controlled through the selection of an appropriate organic group. Examples of hybrid sol-gel materials include clay-polyamide hybrid materials and metal oxide-polymer hybrid materials.

**[0034]** The phase inversion process involves the dispersion of extremely fine particles of a polymer resin that have been heated above the  $T_m$  or  $T_g$  of the polymer in a highly agitated non-solvent. The polymer resin can be any of the polymer resins described above. The non-solvent can be any suitable solvent having a high Flory-Huggins polymer-solvent interaction parameter (e.g., a Flory-Huggins interaction parameter greater than 0.5). Such polymer-solvent interactions are discussed in more detail in Ramanathan et al. in the following references: *Polymer Data Handbook*, Ed. James E. Mark, Oxford University Press, New York, p. 874, c. 1999; Oberth *Rubber Chem. and Technol.* **1984**, 63, 56; Barton in *CRC Handbook of Solubility Parameters and Other Cohesion Parameters* CRC Press, Boca Raton, FL, 1983, p. 256; and Prasad et al. *Macromolecules* **1989**, 22, 914. For example, when the polymer resin is a thermoplastic polyurethane, an aromatic ether-based polyurethane, strongly polar solvents such as ethers, ketones, chloroform, dimethylformamide, and the like have interaction parameters less than 0.3 and will act as "good solvents" for the polymer. On the other hand, hydrocarbon solvents such as cyclohexane, cyclobutane, and n-alkanes have an interaction parameter greater than 0.5 and function as poor solvents or "non-solvents." The Flory-Huggins interaction parameter is sensitive to temperature so a solvent that is a good solvent at high temperatures may become a non-solvent at lower temperatures. As the number of fine polymer resin particles added to the non-solvent increases, the fine polymer resin particles connect to form initially as tendrils and ultimately as a three-dimensional polymer network. The non-solvent mixture is then cooled causing the non-solvent to form into discrete droplets within the three-

dimensional polymer network. The resulting material is a polymer material having sub-micron pore sizes.

[0035] The spinodal or binodal decomposition process involves controlling the temperature and/or volume fraction of a polymer-polymer mixture, or a polymer-solvent mixture, so as to move the mixture from a single-phase region into a two-phase region. Within the two-phase region, either spinodal decomposition or binodal decomposition of the polymer mixture can occur. Decomposition refers to the process by which a polymer-polymer mixture changes from a nonequilibrium phase to an equilibrium phase. In the spinodal region, the free energy of mixing curve is negative, such that phase separation of the polymers (i.e., formation of a two-phase material), or phase separation of the polymer and the solvent, is spontaneous in response to small fluctuations in the volume fraction. In the binodal region, the polymer mixture is stable with respect to small fluctuations in volume fraction, and thus requires nucleation and growth to achieve a phase-separated material. Precipitation of the polymer mixture at a temperature and volume fraction within a two-phase region (i.e., the binodal or spinodal region) results in the formation of a polymer material having two phases. If the polymer mixture is laden with a solvent or a gas, the biphasic polymer material will contain sub-micron pores at the interface of the phase-separation. The polymers preferably comprise the polymer resins described above.

[0036] The pressurized gas injection process involves the use of high temperatures and pressures to force a gas into a solid polymer sheet comprising a polymer resin. The polymer resin can be any of the polymer resins described above. Solid extruded sheets are placed at room temperature into a pressure vessel. A gas (e.g.,  $N_2$  or  $CO_2$ ) is added to the vessel, and the vessel is pressurized to a level sufficient to force an appropriate amount of the gas, as a supercritical fluid, into the free volume of the polymer sheet. The amount of gas dissolved in the polymer is directly proportional to the applied pressure according to Henry's law. Increasing the temperature of the polymer sheet increases the rate of diffusion of the gas into the polymer, but also decreases the amount of gas that can dissolve in the polymer sheet. Once the pressurized gas has thoroughly saturated the polymer, the sheet is removed from the pressurized vessel. The release of pressure causes the polymer sheet to form a foam. The resulting polymeric foam typically has an average cell size ranging from 0.5 microns to 1 micron. If desired, the polymer sheet can be quickly heated to a softened or molten state. As with the mucell process, the pore size of the porous material is at least in part controlled by the temperature, pressure, and concentration of the supercritical gas, and combinations thereof.

[0037] The preferred polymeric material for a successful pressurized gas injection process is a thermoplastic polyurethane (TPU) with a hardness in the range of 40 Shore D to 80 Shore D, a  $M_w$  of 20,000 to 600,000, and a PDI of 1 to 6. The polymer resin preferably

also has a MFI of 0.1 to 30 when measured at 210 °C under a 2160 g load, a Flexural Modulus of 25 psi to 200,000 psi, a RPI of 2 to 10, and a glass transition temperature of 20 °C to 120 °C.

#### EXAMPLE 1.

**[0038]** Typical properties of pad samples given in Table 1 were produced from extruded TPU sheets with a solid sheet density of 1.2 g/cc with resin hardness of 72 Shore D, sheet thickness of 58 mils, saturation CO<sub>2</sub> pressure of 5 MPa, saturation time of 40 hours, CO<sub>2</sub> desorption time of 3 minutes and foaming time of 2 minutes. Foaming temperatures of 106 °C and 111 °C were used for sample A and B, respectively. The amount of CO<sub>2</sub> used to foam each sheet was 43 mg CO<sub>2</sub>/g of polymer for sample A and 53 mg CO<sub>2</sub>/g of polymer for sample B.

Table 1: Pad Properties

| Sample | Shore A | $\rho_p$ (g/cc) | $\rho_p/\rho_s$ | Cell Size ( $\mu\text{m}$ )            | %R/%C | $T_g$ (°C) |
|--------|---------|-----------------|-----------------|----------------------------------------|-------|------------|
| A      | 96.5    | 0.988           | 83%             | $0.5 \mu\text{m} \pm 0.28 \mu\text{m}$ | 0.06  | 44         |
| B      | 95.5    | 0.850           | 71%             | $1.4 \mu\text{m} \pm 1.2 \mu\text{m}$  | 0.08  | 46         |

**[0039]** A copper polishing comparison test between a commercially available pad (Freudenberg FX-9) with the sample A pad of the present invention was performed using a 20 inch (508 cm) diameter pad with subpad and x-y grooves on a Mirra polisher. As shown in FIG.S 1 and 2, the sample A pad of the present invention (labeled Nanocell) afforded a higher Cu removal rate compared to the commercial FX-9 pads, while providing a comparable within wafer nonuniformity (WIWNU).

**[0040]** When the polishing pad substrate of the invention constitutes only a portion of a polishing pad, the polishing pad substrate can be mounted into a polishing pad using any suitable technique. For example, the polishing pad substrate can be mounted into a polishing pad through the use of adhesives. The polishing pad substrate can be mounted into the top portion of the polishing pad (e.g., the polishing surface), or can be mounted into the bottom portion of the polishing pad (e.g., the subpad). The polishing pad substrate can have any suitable dimensions and shape, e.g., round, oval, square, rectangular, triangular, and so on. The polishing pad substrate can be positioned so as to be flush with the polishing surface of the polishing pad, or can be recessed from the polishing surface of the polishing pad. The polishing pad can comprise one or more of the polishing pad substrates of the invention. The polishing pad substrate(s) can be placed in any suitable position on the polishing pad relative to the center and/or periphery of the polishing pad.

**[0041]** The polishing pad into which the polishing pad substrate is placed can be made of any suitable polishing pad material, many of which are known in the art. The polishing

pad typically is opaque or only partially translucent. The polishing pad can comprise any suitable polymer resin. For example, the polishing pad typically comprises a polymer resin selected from the group consisting of a thermoplastic elastomer, a thermoplastic polyurethane, a thermoplastic polyolefin, a polycarbonate, a polyvinylalcohol, a nylon, an elastomeric rubber, an elastomeric polyethylene, a polytetrafluoroethylene, a polyethyleneterephthalate, a polyimide, a polyaramide, a polyarylene, a polystyrene, a polymethylmethacrylate, copolymers thereof, and mixtures thereof. The polishing pad can be produced by any suitable method including sintering, injection molding, blow molding, extrusion, and the like. The polishing pad can be solid and non-porous, can contain microporous closed cells, can contain open cells, or can contain a fibrous web onto which a polymer has been molded.

**[0042]** Polishing pads comprising the polishing pad substrate of the invention have a polishing surface that optionally further comprises grooves, channels, and/or perforations which facilitate the lateral transport of polishing compositions across the surface of the polishing pad. Such grooves, channels, or perforations can be in any suitable pattern and can have any suitable depth and width. The polishing pad can have two or more different groove patterns, for example a combination of large grooves and small grooves as described in U.S. Patent 5,489,233. The grooves can be in the form of slanted grooves, concentric grooves, spiral or circular grooves, XY crosshatch pattern, and can be continuous or non-continuous in connectivity. Preferably, the polishing pad comprises at least small grooves produced by standard pad conditioning methods.

**[0043]** Polishing pads comprising the polishing pad substrate of the invention can comprise, in addition to the polishing pad substrate, one or more other features or components. For example, the polishing pad optionally can comprise regions of differing density, hardness, porosity, and chemical compositions. The polishing pad optionally can comprise solid particles including abrasive particles (e.g., metal oxide particles), polymer particles, water-soluble particles, water-absorbent particles, hollow particles, and the like.

**[0044]** Polishing pads comprising the polishing pad substrate of the invention are 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 comprising the polishing pad substrate of the invention in contact with the platen and moving with the platen when in motion, and a carrier that holds a workpiece to be polished by contacting and moving relative to the surface of the polishing pad. The polishing of the workpiece takes place by placing the workpiece in contact with the polishing pad and then moving the polishing pad relative to the workpiece, typically with a polishing composition therebetween, so as to abrade at least a portion of the workpiece thereby polishing the

workpiece. The polishing composition typically comprises a liquid carrier (e.g., an aqueous carrier), a pH adjustor, and optionally an abrasive. Depending on the type of workpiece being polished, the polishing composition optionally can further comprise oxidizing agents, organic acids, complexing agents, pH buffers, surfactants, corrosion inhibitors, anti-foaming agents, and the like. The CMP apparatus can be any suitable CMP apparatus, many of which are known in the art. The polishing pad comprising the polishing pad substrate of the invention also can be used with linear polishing tools.

[0045] Desirably, the CMP apparatus further comprises an *in situ* polishing endpoint detection system, many of which are known in the art. Techniques for inspecting and monitoring the polishing process by analyzing light or other radiation reflected from a surface of the workpiece are known in the art. Such methods are described, for example, in U.S. Patent 5,196,353, U.S. Patent 5,433,651, U.S. Patent 5,609,511, U.S. Patent 5,643,046, U.S. Patent 5,658,183, U.S. Patent 5,730,642, U.S. Patent 5,838,447, U.S. Patent 5,872,633, U.S. Patent 5,893,796, U.S. Patent 5,949,927, and U.S. Patent 5,964,643. Desirably, the inspection or monitoring of the progress of the polishing process with respect to a workpiece being polished enables the determination of the polishing end-point, i.e., the determination of when to terminate the polishing process with respect to a particular workpiece.

[0046] A polishing pad comprising the polishing pad substrate of the invention 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, or sintered urethane subpads. The subpad typically is softer than the polishing pad comprising the polishing pad substrate of the invention and therefore is more compressible and has a lower Shore hardness value than the polishing pad. For example, the subpad can have a Shore A hardness of 35 to 50. In some embodiments, the subpad is harder, is less compressible, and has a higher Shore hardness than the polishing pad. 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 between the polishing pad and the subpad.

[0047] Polishing pads comprising the polishing pad substrates of the invention are suitable for use in polishing many types of workpieces (e.g., substrates or wafers) and workpiece materials. For example, the polishing pads can be used to polish workpieces including memory storage devices, semiconductor substrates, and glass substrates. Suitable workpieces for polishing with the polishing pads include memory or rigid disks, magnetic

heads, MEMS devices, semiconductor wafers, field emission displays, and other microelectronic substrates, especially microelectronic 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).

## CLAIMS

1. A chemical-mechanical polishing pad substrate comprising a microporous polymeric foam wherein at least 70% of the pores of the microporous polymeric foam are closed-celled and have an average pore size in the range of 0.01 $\mu$ m to 10 $\mu$ m.
2. The polishing pad substrate of claim 1, wherein the pores of the microporous polymeric foam have an average cell size in the range of 0.05 $\mu$ m to 5 $\mu$ m.
3. The polishing pad substrate of claim 1, wherein the microporous polymeric foam has an average cell density of at least 10<sup>5</sup> cells/cm<sup>3</sup>.
4. The polishing pad substrate of claim 1, wherein the microporous polymeric foam has a pore volume of 95% or less.
5. The polishing pad substrate of claim 1, wherein the microporous polymeric foam has a pad density is at least 0.5 g/cm<sup>3</sup> and a relative density in the range of 40% to 93%.
6. The polishing pad substrate of claim 1, wherein the microporous polymeric foam has a hardness in the range of 75 Shore A to 75 Shore D.
7. The polishing pad substrate of claim 1, wherein the pad has a ratio of % compressibility to pad % rebound in the range of 0.01 to 1.0, measured at 5 psi by an Ames method.
8. The polishing pad substrate of claim 1, wherein the polymeric foam comprises thermoplastic polyurethane.
9. The polishing pad substrate of claim 8, wherein the thermoplastic polyurethane has a weight average molecular weight in the range of 20,000 g/mol to 600,000 g/mol.
10. The polishing pad substrate of claim 9, wherein the thermoplastic polyurethane has a polydispersity index in the range of 1 to 10.
11. The polishing pad substrate of claim 9, wherein the thermoplastic polyurethane has a melt flow index in the range of 0.1 to 30 over ten minutes at a temperature of 210 °C and a load of 2160 g.
12. The polishing pad substrate of claim 9, wherein the thermoplastic polyurethane has a flexural modulus in the range of 25 psi to 200,000 psi.
13. The polishing pad substrate of claim 9, wherein the thermoplastic polyurethane has a rheology processing index in the range of 2 to 10.
14. The polishing pad substrate of claim 9, wherein the thermoplastic polyurethane has a glass transition temperature in the range of 20 °C to 120 °C.
15. A chemical-mechanical polishing apparatus comprising:
  - (a) a platen that rotates,
  - (b) a polishing pad comprising the polishing pad substrate of claim 1, and
  - (c) a carrier that holds a workpiece to be polished by contacting workpiece with the rotating polishing pad.

16. The apparatus of claim 15, wherein the polishing pad substrate comprises thermoplastic polyurethane.
17. A method for producing the polishing pad substrate of claim 1 comprising:
  - (a) combining a solid polymer sheet with a supercritical gas in a vessel under elevated temperature and pressure until the gas has saturated the polymer sheet,
  - (b) releasing the pressure to afford a microporous polymeric foam from the gas saturated polymer sheet, and
  - (c) forming a polishing pad from the microporous polymeric foam.
18. The method of claim 17 wherein the gas comprises nitrogen, carbon dioxide, or any combination thereof.
19. The method of claim 17 wherein the polishing pad substrate comprises thermoplastic polyurethane.
20. The polishing pad substrate of claim 19, wherein the thermoplastic polyurethane has a weight average molecular weight in the range of 20,000 g/mol to 600,000 g/mol.