

POLISHING PAD HAVING EDGE SURFACE TREATMENT

[0001] This application is a conversion of United States Provisional Patent Application having Serial No. 60/493,292, filed on August 7, 2003.

[0002] The present invention is directed to a polishing pad having a sublayer and a polishing layer. The surface of the outer peripheral edge of the sublayer can be at least partially treated to reduce the absorption or permeation of polishing fluid into the sublayer through the outer peripheral edge. The application of the surface treatment at least reduces the amount of polishing fluid absorbed by the sublayer of the polishing pad during the polishing process. The polishing pad of the present invention is useful in polishing microelectronic substrates and especially useful in chemical mechanical planarization of semiconductor wafers.

[0003] It is typical to use polishing fluid, such as polishing slurry, in conjunction with a polishing pad to polish a microelectronic substrate. The polishing pad can comprise a stacked pad construction including a sublayer. During the polishing process, it is advantageous to at least reduce or minimize the adsorption of slurry into the sublayer. Absorption of slurry into the sublayer can alter or change the compressibility of the sublayer. For example, if the sublayer is made less compressible, the work surface of the pad construction may not adequately conform to the microelectronic substrate being polished, which can result in polishing performance which is not uniform across the substrate. Furthermore, if the sublayer compressibility decreases during the process of polishing a series of wafers, the wafer-to-wafer polish consistency can be compromised.

[0004] There is a need in the art to develop a polishing pad that at least reduces the absorption of polishing fluid into the sublayer of the pad. It is still further contemplated that it would be desirable to develop such a polishing pad and means without significantly impacting the compressibility of the sublayer.

[0005] It is noted that, as used in this specification,

the singular forms "a," "an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

[0006] For the purposes of this specification, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0007] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0008] The present invention is directed to a polishing pad for use in polishing a microelectronic substrate. Various pad constructions suitable for use in the present invention are known in the art. The polishing pad can include a polishing layer and a sublayer. The polishing layer can be at least partially connected to the sublayer. The sublayer can have an outer peripheral edge. At least a portion of the outer peripheral edge can be surface treated with a material that reduces the ability of the outer peripheral edge of the sublayer to absorb polishing fluid, such that permeation of polishing liquid into the sublayer is reduced. In a non-limiting embodiment, the material can be selected such that at least a portion of the surface of the outer peripheral edge of the sublayer is made substantially hydrophobic. In a further non-limiting embodiment, the material can be selected such that the

wettability or at least a portion of the surface of the outer peripheral edge of the sublayer is at least reduced.

[0009] A polishing pad can generally comprise a stacked layer construction including at least a polishing layer and a sublayer. The polishing layer can function as the working surface of the pad such that the polishing layer can at least partially interact with the microelectronic substrate to be polished and the polishing fluid. In alternate non-limiting embodiments, the material of the polishing layer can be selected such that the polishing layer is substantially impermeable to polishing fluid or substantially permeable to polishing fluid. In further non-limiting embodiments, the material of the polishing layer can be selected such that the polishing layer is substantially non-porous or substantially porous.

[0010] The polishing layer of the pad can be at least partially connected to a sublayer. In a non-limiting embodiment, the sublayer of the pad can function as the bottom layer of the pad which can be attached to the platen of a polishing apparatus. The material of the sublayer can be selected such that the sublayer is substantially permeable to polishing fluid. Further, the material of the sublayer can be selected such that the sublayer is substantially porous.

[0011] Non-limiting examples of suitable materials for the polishing layer can include but are not limited to particulate polymer and crosslinked polymer binder such as described in International Publication No. WO 02/22309; particulate polymer and an organic polymer binder; sintered particles of thermoplastic resin as described in United States Patents 6,062,968; 6,117,000; and 6,126,532 describe; and pressure sintered powder compacts of thermoplastic polymer as described in United States Patents 6,231,434 B1, 6,325,703 B2, 6,106,754 and 6,017,265. Additional non-limiting examples of suitable materials for the polishing layer can include polymeric matrices impregnated with a plurality of polymeric microelements, wherein each polymeric microelement can have a void space within, as described in United States Patents 5,900,164 and 5,578,362. The relevant portions of the above-mentioned patents are incorporated herein by reference.

[0012] In a non-limiting embodiment, the thickness of the polishing layer can vary widely depending on its composition. In alternate non-limiting embodiments, the polishing layer can have a thickness of at least 0.020 inches, or at least 0.040 inches; or 0.150 inches or less, or 0.080 inches or less.

[0013] In another non-limiting embodiment, the polishing layer can include pores such that polishing fluid can be at least partially absorbed by the polishing layer. The number of pores can vary widely. In a further non-limiting embodiment, the number of pores can be such that the polishing layer can be substantially non-porous and substantially impermeable to polishing fluid. In alternate non-limiting embodiments, the polishing layer can have a porosity, expressed as percent pore volume, of at least two (2) percent by volume based on the total volume of the polishing layer, or 50 percent or less by volume based on the total volume of the polishing layer. The percent pore volume of the polishing pad can be determined using a variety of techniques known in the art. In a non-limiting embodiment, the following expression can be used to calculate percent pore volume:

$$100 \times (\text{density of the pad}) \times (\text{pore volume of the pad}).$$

[0014] The density can be expressed in units of grams per cubic centimeter, and can be determined by a variety of conventional methods known in the art. In a non-limiting embodiment, the density can be determined in accordance with ASTM D 1622-88. The pore volume can be expressed in units of cubic centimeters per gram, and can be determined using conventional methods and equipment known in the art. In a non-limiting embodiment, pore volume can be measured in accordance with the mercury porosimetry method in ASTM D 4284-88, using an Autopore III mercury porosimeter from Micromeritics. In a further non-limiting embodiment, the pore volume measurements can be made under the following conditions: a contact angle of 140°; a mercury surface tension of 480 dynes/cm; and degassing of the polishing pad sample under a vacuum of 50 micrometers of mercury.

[0015] In a non-limiting embodiment, the polishing layer

can have at least a partially open cell structure such that it can absorb slurry. In a further non-limiting embodiment, the cell structure can be such that the polishing layer can be substantially non-absorbent. In alternate non-limiting embodiments, the polishing layer can absorb at least 2 percent by weight of polishing fluid based on the total weight of the polishing layer, or not more than 50 percent by weight, or from 2 percent by weight to 50 percent by weight.

[0016] The sublayer to which the polishing layer can be at least partially connected, can increase the uniformity of contact between the polishing pad and the surface of the substrate being polishing. A consideration in selecting the material for the sublayer can be the ability of a material to provide compliant support to the work surface of the polishing pad such that the polishing layer can substantially conform to the macroscopic contour or long-term surface of the device being polished. Such material can be desirable for use as the sublayer in the polishing pad of the present invention.

[0017] The surface of a microelectronic substrate, such as a semiconductor wafer, can have a "wave" contour as a result of the manufacturing process. It is contemplated that if the polishing pad cannot adequately conform to the "wave" contour of the substrate surface, the uniformity of the polishing performance can be degraded. For example, if the pad can substantially conform to the ends of the "wave", but cannot substantially conform to and contact the middle portion of the "wave", only the ends of the "wave" can be substantially polished or planarized and the middle portion can remain substantially unpolished or unplanarized.

[0018] In a non-limiting embodiment, the flexibility of the sublayer can be such that the polishing layer can conform to the macroscopic or long-term surface of the substrate being polished. The flexibility of the sublayer can vary widely. In a further non-limiting embodiment, the sublayer can be more flexible than the polishing layer. The flexibility of the sublayer can be determined using various methods known to the skilled artisan. In a non-limiting embodiment, "flexibility" (F) can be determined by the inverse relationship of sublayer thickness cubed (t^3) and the

flexural modulus of the sublayer material (E), i.e. $F = 1/t^3E$. In alternate non-limiting embodiments, the flexibility of the sublayer can be greater than $1.0 \times 10^{-8} \text{ in}^{-1}\text{lb}^{-1}$, or greater than $1.0 \times 10^{-4} \text{ in}^{-1}\text{lb}^{-1}$.

[0019] In a non-limiting embodiment, the sublayer can be softer than the polishing layer. As used herein, "softness" refers to the Shore A Hardness of the material. In general, the softer the material, the lower the Shore A Hardness value. Thus, in the present invention the Shore A Hardness value of the sublayer can be lower than the Shore A Hardness value of the polishing layer. In alternate non-limiting embodiments, the sublayer can have a Shore A Hardness of at least 15, or at least 45, or 75 or less, or from 45 to 75. In further alternate non-limiting embodiments, the Shore A Hardness of the polishing layer can be at least 85, or 99 or less, or from 85 to 99. The Shore A Hardness value can be determined using various methods and equipment known in the art. In a non-limiting embodiment, Shore A Hardness can be determined in accordance with the procedure recited in ASTM D 2240, using a Shore "Type A" Durometer having a maximum indicator (available from PCT Instruments, Los Angeles, CA). In a non-limiting embodiment, the test method for Shore A Hardness can include the penetration of a specific type of indenter being forced into the test material under specified conditions. In this embodiment, the Hardness can be inversely related to the penetration depth and can be dependent on the elastic modulus and viscoelastic behavior of the test material.

[0020] In another non-limiting embodiment of the present invention, the sublayer of the polishing pad can be more compressible than the polishing layer. As used herein, "compressibility" refers to the percent volume compressibility measurement. In a non-limiting embodiment, the percent volume compressibility of the sublayer can be greater than the percent volume compressibility of the polishing layer. In alternate non-limiting embodiments, the percent volume compressibility of the sublayer can be less than 20 percent when a load of 20 psi is applied, or less than 10 percent when a load of 20 psi is applied, or less than 5 percent when a load of 20 psi is applied. In another non-limiting embodiment, the percent volume compressibility of the polishing layer can be less than the percent volume compressibility

of the sublayer. In a further non-limiting embodiment, the percent volume compressibility of the polishing layer can be from 0.3 to 3 percent when a load of 20 psi is applied.

[0021] The percent volume compressibility of the sublayer can be determined using various methods known in the art. In a non-limiting embodiment, the percent volume compressibility of the sublayer can be determined using the following expression.

$$100 \times \frac{(\text{pad volume without load} - \text{pad volume under load})}{(\text{pad volume without load})}$$

[0022] In a non-limiting embodiment, if the area of the pad does not change when the load is placed on it, then the preceding equation for volume compressibility can be expressed in terms of pad thickness by the following expression.

$$100 \times \frac{(\text{pad thickness without load} - \text{pad thickness under load})}{(\text{pad thickness without load})}$$

[0023] The pad thickness can be determined using a variety of known methods. In a non-limiting embodiment, the pad thickness can be determined by placing a load (such as, but not limited to, calibrated weights) on the pad sample and measuring the change in thickness of the pad as a result of the load. In a further non-limiting embodiment, a Mitutoyo Electronic Indicator, Model ID-C112EB can be used. The indicator has a spindle or threaded rod which can be fitted at one end with a flat contact under which the pad is placed. The spindle can be fitted at the other end with a device for applying specified loads to the contact area, such as but not limited to a balance pan which accepts calibrated weights. The Indicator displays the displacement of the pad resulting from applying the load. The Indicator display is typically representative of inches or millimeters. The Electronic Indicator can be mounted on a Mitutoyo Precision Granite Stand to provide stability while taking the measurements. The lateral dimensions of the pad can be sufficient to permit measurements at least 0.5" from any edge. The surface of the pad can be flat and parallel over a sufficient area to permit uniform contact between

the test pad and the flat contact. The pad to be tested can be placed under the flat contact. The thickness of the pad can be measured prior to applying the load. Calibrated balance weights can be added to the balance pan for a specific resultant load. The pad then can be compressed under the specified load. The Indicator can display the thickness/height of the pad under the specified load. The thickness of the pad prior to applying the load minus the thickness of the pad under the specified load can be used to determine the displacement of the pad. In a non-limiting embodiment, a load of 20 psi can be applied to the pad. Measurements can be made at a standardized temperature such as room temperature. In a non-limiting embodiment, measurements can be taken at a temperature of 22°C +/-2°C. This method of measuring thickness can be applicable to a stacked pad construction or layer(s) comprising the stacked pad construction.

[0024] The sublayer can comprise a wide variety of materials known in the art. Suitable materials can include natural rubber, synthetic rubbers, thermoplastic elastomer, foam sheet and combinations thereof. The material of the sublayer can be foamed or blown to produce a porous structure. The porous structure can be open cell, closed cell, or combinations thereof. Non-limiting examples of synthetic rubbers can include neoprene rubber, silicone rubber, chloroprene rubber, ethylene-propylene rubber, butyl rubber, polybutadiene rubber, polyisoprene rubber, EPDM polymers, styrene-butadiene copolymers, copolymers of ethylene and ethyl vinyl acetate, neoprene/vinyl nitrile rubber, neoprene/EPDM/SBR rubber, and combinations thereof. Non-limiting examples of thermoplastic elastomers can include polyolefins, polyesters, polyamides, polyurethanes such as those based on polyethers and polyesters, and copolymers thereof. Non-limiting examples of foam sheet can include ethylene vinyl acetate sheets and polyethylene foam sheets; polyurethane foam sheets and polyolefin foam sheets, such as but not limited to those which are available from Rogers Corporation, Woodstock, CT.

[0025] In a further non-limiting embodiment, the sublayer can include non-woven or woven fiber mat, and combinations thereof; such as but not limited to polyolefin, polyester, polyamide, or

acrylic fibers, which have been impregnated with a resin. The fibers can be staple or substantially continuous in the fiber mat. Non-limiting examples can include but are not limited to non-woven fabric impregnated with polyurethane as describe in United States Patent 4,728,552, such as polyurethane impregnated felt, which relevant portions of this Patent are incorporated herein by reference. A non-limiting example of a commercially available non-woven subpad can be Suba™ IV, from Rodel, Inc. Newark DE.

[0026] The thickness of the sublayer can vary widely. In general, the pad thickness can be such that the pad can be placed on and taken off of the planarizing equipment with ease. If the pad is too thick, it can be difficult to place on and take off of the planarizing equipment. In alternate non-limiting embodiments, the sublayer can be at least 0.020 inches thick, or at least 0.040 inches thick, or at least 0.045 inches thick; or 0.100 or less inches thick, or 0.080 inches thick, or 0.065 inches thick. In alternate non-limiting embodiments, the thickness of the polishing layer can be at least 0.040 inches, or at least 0.045 inches, or 0.100 inches or less, or 0.080 inches or less, or 0.065 inches or less.

[0027] In a non-limiting embodiment, the polishing pad construction can include a middle layer. In another non-limiting embodiment, the middle layer can function as a barrier to fluid transport between the polishing layer and the sublayer. In a further non-limiting embodiment, the middle layer can be essentially impermeable to the polishing fluid such that the sublayer cannot become substantially saturated with polishing fluid.

[0028] In another non-limiting embodiment, the middle layer can function to distribute the compressive forces experienced by the polishing layer over a larger area of the sublayer. In a further non-limiting embodiment, the middle layer can be substantially non-volume compressible.

[0029] In a non-limiting embodiment, the material for the middle layer can be selected such that the middle layer has the ability to substantially reduce or essentially prevent the transport of polishing fluid from the polishing layer to the sublayer.

[0030] The middle layer can include a wide variety of

materials known in the art. Suitable materials for the middle layer can include a wide variety of substantially non-compressible polymers, and metallic films and foils. Non-limiting examples of such polymers can include polyolefins, such as but not limited to low density polyethylene, high density polyethylene, ultra-high molecular weight polyethylene and polypropylene; polyvinylchloride; cellulose-based polymers, such as but not limited to cellulose acetate and cellulose butyrate; acrylic; polyesters and co-polyesters, such as but not limited to PET and PETG; polycarbonate; polyamide, such as nylon 6/6 and nylon 6/12; and high performance plastics, such as polyetheretherketone, polyphenylene oxide, polysulfone, polyimide, and polyetherimide. Non-limiting examples of metallic films can include aluminum, copper, brass, nickel and stainless steel.

[0031] The thickness of the middle layer can vary widely. In alternate non-limiting embodiments, the middle layer can have a thickness of at least 0.0005 inches, or 0.0030 inches or less; or from 0.0010 to 0.0020 inches.

[0032] In a non-limiting embodiment, the polishing layer and the sublayer of the present invention can be at least partially connected. In another embodiment, the polishing layer of the polishing pad can be at least partially connected to at least a portion of a middle layer and the middle layer can be at least partially connected to at least a portion of the sublayer. The layers can be at least partially connected using various means known in the art. In a further non-limiting embodiment, the connecting means can include an adhesive material.

[0033] Suitable adhesives for use in the present invention can be selected from a wide variety known in the art. In general, the adhesive should provide sufficient peel resistance such that the pad layers essentially remain in place during use. Further, the adhesive should generally be able to withstand shear stresses which are present during the polishing or planarization process and moreover, the adhesive should be able to resist chemical and moisture degradation during use. Non-limiting examples of suitable adhesives can include contact adhesives, pressure sensitive adhesives, structural adhesives, hot melt adhesives, thermoplastic

adhesives, curable adhesives such as but not limited to thermosetting adhesives, and combinations thereof. Non-limiting examples of structural adhesives can include polyurethane adhesives and epoxy resin adhesives such as but not limited to those based on the diglycidyl ether of bisphenol A. Non-limiting examples of pressure sensitive adhesives can include an elastomeric polymer and a tackifying resin. Non-limiting examples of elastomeric polymers can include natural rubber, butyl rubber, chlorinated rubber, polyisobutylene, poly(vinyl alkyl ethers), alkyd adhesives, acrylics such as but not limited to those based on copolymers of 2-ethylhexyl acrylate and acrylic acid, block copolymers such as but not limited to styrene-butadiene-styrene, and mixtures thereof. In alternate non-limiting embodiments, a pressure sensitive adhesive can be applied to a substrate using an organic solvent such as toluene or hexane, or from a water-based emulsion or from a melt. As used herein, the term "hot melt adhesive" refers to an adhesive comprised of a nonvolatile thermoplastic material that can be heated to a melt, then applied to a substrate as a liquid. Non-limiting examples of hot melt adhesives can include ethylene-vinyl acetate copolymers, styrene-butadiene copolymers, ethylene-ethyl acrylate copolymers, polyesters, polyamides such as but not limited to those formed from the reaction of diamine and dimer acid, and polyurethanes.

[0034] In a non-limiting embodiment, the middle layer can include an adhesive assembly. The adhesive assembly can include a middle layer interposed between an upper adhesive layer and a lower adhesive layer. In a non-limiting embodiment, the upper adhesive layer can be at least partially connected to the lower surface of the polishing layer, and the lower adhesive layer can be at least partially connected to the upper surface of the sublayer. The upper, middle, and lower layers of the adhesive assembly can be selected from the aforementioned suitable materials for the middle layer of the polishing pad. In a non-limiting embodiment, the upper and lower adhesive layers each can be contact adhesives. The adhesive assembly can be referred to in the art as two-sided or double-coated tape. Non-limiting examples of commercially available

adhesive assemblies include those from 3M, Industrial Tape and Specialties Division.

[0035] In a non-limiting embodiment, the polishing pad of the present invention can include a polishing layer, a middle layer, and a sublayer wherein a portion of the polishing layer and sublayer includes an opening, and at least a portion of the middle layer contains a window which can be at least partially transparent to wavelengths used by the metrology instrumentation of polishing equipment. The polishing layer and sublayer can comprise an opening of suitable size, shape, and positioning such that it can be substantially aligned with the at least partially transparent window in the middle layer. The window of the middle layer can be recessed below the polishing surface by a distance substantially equal to the thickness of the polishing layer. The middle layer containing the window can be at least partially coated on at least one, or two, of its surfaces with contact adhesive. The coating can provide any one of the following properties, for example: improved transparency, improved abrasion resistance, improved puncture resistance. In a further non-limiting embodiment, the openings of the polishing layer and sublayer can be at least partially aligned with the window; the lower surface of the polishing layer can be pressed against one adhesive surface, and the upper surface of the sublayer can be pressed against the other adhesive surface to form a pad construction. Any adhesive adhering to the window surfaces can be at least partially removed with the use of a solvent.

[0036] In alternate non-limiting embodiments, the opening can be produced by any suitable means known in the art, such as punching, die cutting, laser cutting or water jet cutting. In a further non-limiting embodiment, the opening can be formed by molding the polishing layer and/or sublayer such that an opening can be formed. In alternate non-limiting embodiments, the opening in the polishing layer and sublayer can be produced prior to stacking the layers, or following stacking of the layers. In a further non-limiting embodiment, the opening can be die cut into the polishing layer and/or sublayer, using an NAEF Model B die press fitted with dies of suitable size and shape, which is commercially available from MS Instruments Company, Stony Brook, NY.

[0037] The size, shape, and location of the opening in the polishing layer and sublayer can vary widely and can depend upon the equipment being used for polishing. In a non-limiting embodiment, a Mirra polisher produced by Applied Materials Inc, Santa Clara CA, can be used wherein the shape of the opening is a rectangle, having a size 0.5" x 2", being positioned with the long axis radially oriented and centered 4" from the center of the pad. The platen for the Mirra polisher is 20" in diameter. A pad for use with this polisher can comprise a circle of a 20-inch diameter having a window area located in the area as described.

[0038] In another non-limiting embodiment, a Teres polisher commercially available from Lam Research Corporation, Fremont, CA, can be employed. This polisher uses a continuous belt instead of a circular platen. The pad for this polisher can be a continuous belt of 12" width and 93.25" circumference, which has a window suitably sized and positioned to align with the metrology window of the Teres polisher.

[0039] In the present invention, the sublayer of the polishing pad can be substantially permeable and/or porous such that it can absorb polishing fluid used during the polishing process. The sublayer can have an outer peripheral edge that is at least partially surface treated to reduce absorption of polishing fluid through the outer peripheral edge. In a non-limiting embodiment, the surface treatment can minimize or essentially prevent absorption or permeation of polishing fluid into the sublayer through the outer peripheral edge. In a further non-limiting embodiment, the surface treatment can make at least a portion of the surface of the outer peripheral edge of the sublayer substantially hydrophobic. In another non-limiting embodiment, the wettability of the outer peripheral edge of the sublayer can be reduced as a result of the surface treatment.

[0040] In a non-limiting embodiment, the outer peripheral edge of the sublayer having surface treatment can at least partially absorb liquids other than polishing fluid such as but not limited to organic liquids. It is believed that such liquids can be absorbed because they generally have lower surface tension than polishing fluid. It is contemplated that the surface-treated outer peripheral

edge of the sublayer can absorb certain liquids because the pores in the sublayer are not substantially closed as a result of applying the surface treatment. Thus, it is further contemplated that if the pad were immersed in water, compressed and then released, the pad could absorb water in a manner similar to a sponge. Thus, in a non-limiting embodiment, the physical properties of the sublayer such as but not limited to porosity, permeability, and compressibility can be retained following surface treatment.

[0041] In a non-limiting embodiment, the surface treatment of the present invention can include applying to at least a portion of the surface of the outer peripheral edge of the sublayer, a material having the ability to reduce the absorption or permeation of the polishing fluid by the sublayer through the outer peripheral edge. In a non-limiting embodiment, the surface treatment can render at least a portion of the outer peripheral edge of the sublayer hydrophobic. In another non-limiting embodiment, the surface treatment can reduce the wettability of the outer peripheral edge of the sublayer. It can be understood that in applying the material to at least a portion of the surface of the outer peripheral edge of the sublayer, the material can extend onto at least a portion of a polishing layer or a middle layer of the polishing pad. Thus, in alternate non-limiting embodiments, the surface of the peripheral edge of the polishing layer and/or middle layer of the polishing pad can be at least partially coated with the material used in the surface treatment.

[0042] The material for use in the present invention can include a wide variety of compounds known in the art. In a non-limiting embodiment, the material can include those compounds known in the art to render a substrate substantially hydrophobic upon application of the material to at least a portion of the surface of the substrate. Suitable materials can include silanes, organic polymers, silane-treated silicas, and mixtures thereof. Non-limiting examples of suitable silanes can include organo silanes such as but not limited to alkyl silanes, such as but not limited to perfluoro silanes, octyl silanes, chloro alkyl silanes, and mixtures thereof. Non-limiting examples of perfluoro silanes can include but are not limited to (tridecafluoro-1,1,2,2-

tetrahydrooctyl)trichlorosilane; trichloro(1H,1H,2H,2H-perfluorooctyl)silane; (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane; (3,3,3-trifluoropropyl)trichlorosilane; (3,3,3-trifluoropropyl)trimethoxysilane; (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane; (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane; (3-heptafluoroisopropoxy)propyltrichlorosilane; and mixtures thereof. Non-limiting examples of suitable organic polymers can include but are not limited to polyolefins such as but not limited to polyethylene and polypropylene; fluoropolymers; and mixtures thereof. Non-limiting examples of suitable silane-treated silica can include those commercially available under the trade name Aerosil R202 and Aerosil R805.

[0043] In a non-limiting embodiment, the material used in surface treating the sublayer can include at least one perfluoroalkylalkyl silane as disclosed in United States Patent Numbers 4,997,684; 5,328,768 and 5,523,162; the relevant portions which are incorporated herein by reference. In a further non-limiting embodiment, the material can include at least one perfluoroalkylalkyl silane represented by the following formula $R_m R'_n Si X_{4-m-n}$, wherein R can be a perfluoroalkylalkyl radical; m can be 1, 2 or 3; n can be 0, 1, or 2; and m+n can be less than 4; R' can be a vinyl or an alkyl radical, such as but not limited to methyl, ethyl, vinyl or propyl; and X can be a radical such as but not limited to halogen, acyloxy, or alkoxy. In alternate non-limiting embodiments, perfluoroalkyl moieties in the perfluoroalkylalkyl radicals can range from CF_3 to $C_{30}F_{61}$, or C_6F_{13} to $C_{18}F_{37}$, or C_8F_{17} to $C_{12}F_{25}$. In further alternate non-limiting embodiments, the second alkyl moiety of the perfluoroalkylalkyl can be a substituted ethyl; R' can be methyl or ethyl; X can include hydrolyzable chloro, bromo, iodo, methoxy, ethoxy and acetoxy radicals. In another non-limiting embodiment, perfluoroalkylalkyl silanes can include perfluoroalkylethyltrichlorosilane, perfluoroalkylethyltrimethoxysilane, perfluoroalkylethyltriacetoxysilane,

perfluoroalkylethyldichloro(methyl)silane and perfluoroalkylethyldiethoxy(methyl)silane.

[0044] The material for use in surface treating the sublayer of the polishing pad of the present invention can include an integral primer which can be selected from a wide variety known in the art. In a non-limiting embodiment, the integral primer can be selected from the integral primers disclosed in United States Patent 5,523,161; and which relevant portions are incorporated herein by reference. In alternate non-limiting embodiments, the integral primer can be a hydrolyzable silane or siloxane capable of hydrolytic condensation to form silica gel which can function as the integral primer.

[0045] Non-limiting examples of suitable silanes capable of hydrolysis to silica gel can have the general formula SiX_4 , wherein X can be a hydrolysable radical selected from halogens, alkoxy or acyloxy radicals. In alternate non-limiting embodiments, X can be chloro, bromo, iodo, methoxy, ethoxy and acetoxy. In another non-limiting embodiment, hydrolyzable silanes can include tetrachlorosilane, tetramethoxysilane, tetraacetoxysilane, and mixtures thereof.

[0046] Non-limiting examples of suitable siloxanes can include those represented by the general formula $\text{Si}_y\text{O}_z\text{X}_{4y-2z}$, wherein X can be selected from halogen, alkoxy and acyloxy radicals, y can be two or more, z can be one or more, and $4y-2z$ can be greater than zero. In alternate non-limiting embodiments, hydrolysable siloxanes can include hexachlorodisiloxane, octachlorotrisiloxane, higher oligomer chlorosiloxanes, and mixtures thereof.

[0047] The surface treating material of the present invention can be at least partially applied to at least a portion of the surface of the outer peripheral edge of the sublayer using a variety of conventional techniques known to the skilled artisan. In alternate non-limiting embodiments, the material can be applied as a solution in solvent, or the composition can be applied solvent-free. In alternate non-limiting embodiments, solvent can be present with the material in a surface treating composition in an amount of from 0 to 75 percent by weight of the composition, or from 0 to 50 percent by weight of the composition. Suitable solvents can include

a wide variety known to the skilled artisan. In general, the solvent can be selected such that it is compatible with the surface treating material being used. In a non-limiting embodiment, the solvent is an aprotic solvent such as but not limited to an alkane or mixture of alkanes, or a fluorinated solvent. Further non-limiting examples of suitable solvents can include but are not limited to isopropanol, ethanol, hexane, heptane, methylene chloride, acetone, toluene, naphtha, and mixtures thereof. In alternate non-limiting embodiments, the solvent can include fluorinated hydrocarbon solvents such as trichlorotrifluoroethane, perfluorinated organic compounds such as perfluorocarbons, and mixtures thereof. In another non-limiting embodiment, the solvent can be evaporated by drying in air at ambient temperature. In a further non-limiting embodiment, the composition then can be cured by heating the treated surface.

[0048] In further alternate non-limiting embodiments, the surface treatment material can be applied by dipping, flowing or wiping. Following the application of the surface treatment, the pad can be protected against physical contact or abrading forces that could degrade the treatment for a period of time that can be referred to as a holding period. The holding period can vary widely depending on the reactivity of the polishing pad layers and the material used for the surface treatment. In a non-limiting embodiment, the holding period can be at least 24 hours or up to 96 hours. In a further non-limiting embodiment, the surface treatment can be applied under controlled relative humidity and temperature conditions. These conditions can vary widely depending upon the particular materials employed in the pad and the surface treatment. In alternate non-limiting embodiments, the relative humidity can be from 30 to 80%, or from 35 to 55%. In other alternate non-limiting embodiments, the temperature can be from 50°F to 85°F, or from 60°F to 80°F.

[0049] The amount of surface treatment material applied to the surface of the outer peripheral edge of the sublayer can vary widely. In general, the amount of the material can be such that the absorption of polishing fluid through the outer peripheral edge of the sublayer can be reduced such that permeation of polishing fluid

into the sublayer of the pad is reduced. In a non-limiting embodiment, the amount can be such that the outer peripheral edge of the sublayer is made substantially hydrophobic. Further, in another non-limiting embodiment, the amount can be such that the pores of the sublayer are not substantially closed.

[0050] The polishing pads of the present invention can be used in combination with a variety of polishing fluids, such as polishing slurries, which are known in the art. Non-limiting examples of suitable slurries for use with the pad of the present invention, include but are not limited to the slurries disclosed in United States Patent 6,656,241B1 issued December 2, 2003, and United States Patent Applications having Serial Numbers 09/882,549 and 10/627,776, filed on June 14, 2001 and July 28, 2003, respectively, and are pending. The relevant portions of this patent and these applications are herein incorporated by reference. In a non-limiting embodiment, the polishing fluid can be interposed between the polishing layer of the pad and the substrate to be polished. The polishing or planarizing process can include moving the polishing pad relative to the substrate being polished. A variety of polishing fluids or slurries are known in the art. Non-limiting examples of suitable slurries for use in the present invention include slurries comprising abrasive particles. Abrasives that can be used in the slurries include particulate cerium oxide, particulate alumina, particulate silica and the like. Examples of commercial slurries for use in the polishing of semiconductor substrates include but are not limited to ILD1200 and ILD1300 available from Rodel, Inc. Newark DE and Semi-Sperse AM100 and Semi-Sperse 12 available from Cabot Microelectronics Materials Division, Aurora, IL.

[0051] In a non-limiting embodiment, the polishing pad of the present invention can be utilized with an apparatus for planarizing an article having a non-planar surface. The planarizing apparatus can include a retaining means for holding the article; and a motive power means for moving the pad and the retaining means with respect to the other such that movement of the pad and the retaining means causes the slurry and the planarizing surface of the pad to contact and planarize the non-planar surface of the article. In a

further non-limiting embodiment, the planarizing apparatus can include a means of renewing the polishing or planarizing surface of the pad, such as but not limited to a mechanical arm equipped with an abrasive disk which abrades the work surface of the pad.

[0052] In a non-limiting embodiment, the planarizing apparatus can include an apparatus for conducting in-situ metrology of the article being polished or planarized. In general, in-situ metrology can include directing a beam of light through an at least partially transparent window located in the platen of the tool; the beam of light can be reflected off the surface of the wafer, back through the platen window, and into a detector. The polishing pad used with such apparatus can include a window that is at least partially transparent to the wavelengths used in the metrology system, and substantially aligned with the platen window. Commercial polishing or planarizing apparatuses are available from equipment manufacturers such as Applied Materials, LAM Research, SpeedFam-IPEC, and Ebara Corp.

[0053] In a non-limiting embodiment, the pad of the present invention can be placed on a cylindrical metal base; and can be connected to at least a portion of the base with a layer of adhesive. Suitable adhesives can include a wide variety of known adhesives. In a further non-limiting example, the pad can be placed on the cylindrical metal base or platen of a polishing or planarizing apparatus that includes a means of conducting in-situ metrology of the article being polished. The pad can be placed such that its window area can be aligned with the metrology window of the platen.

EXAMPLES

Example 1

[0054] Using a small sponge, micronized polypropylene in powder form was wiped onto the subpad outer peripheral edge of a stacked polishing pad commercially obtained from Rodel, Inc., Newark, DE, under the trade name IC1400. The micronized polypropylene was commercially obtained from Lubrizol Corporation, Wickliffe, OH under the trade name Lanco PP1362D. Following

application of the micronized polypropylene, the stacked pad was immersed in slurry for one hour. The slurry was commercially obtained from Rodel, Inc., Newark, DE under the trade name ILD 1300 Planarization Slurry. The pad was removed from the slurry and the outer peripheral edge was visually inspected. The outer peripheral edge of the subpad appeared dry.

Example 2

[0055] The process as described in Example 1 was carried out with the exception that the micronized polypropylene was replaced with hydrophobic fumed silica obtained from Degussa Corporation, Parsippany, NJ, under the trade name Aerosil R805.

The outer peripheral edge of the subpad appeared dry.

Example 3

[0056] Hydrophobic fumed silica commercially obtained from Degussa Corporation, Parsippany, NJ, under the trade name Aerosil R202, was dispersed in acetone at a concentration of one (1) weight percent. Using a Texwipe clean room swab, No. TX761, commercially obtained from Fisher Scientific, Pittsburgh, PA, the solution was applied to the subpad outer peripheral edge of a 22.5-inch stacked polishing pad commercially obtained from Thomas West, Incorporated, under the trade name WESTPADS, Model No. STT 711-C561-22.5. The subpad edge was treated using 0.8 grams of the 1% solution. Following application of treatment solution, the pad stack was held at ambient conditions for 2 hours then immersed in ILD 1300 slurry for one hour. The pad was then removed from the slurry and the subpad outer peripheral edge was visually inspected. The outer peripheral edge of the subpad appeared dry.

Example 4

[0057] Using a small sponge, hydrophobic fumed silica commercially obtained from Degussa Corporation, Parsippany, NJ, under the trade name Aerosil R805, in powder form was wiped onto the surface of the outer peripheral edge of the subpad layer of a IC1000/SubaIV stacked polishing pad commercially obtained from Rodel, Inc., Newark, DE. The powder was deposited in the pores

exposed at the surface and did not extend beyond the surface of the outer peripheral edge. The stacked pad was then immersed in ILD 1300 slurry for one hour. The pad was removed from the slurry and the outer peripheral edge was visibly inspected. The outer peripheral edge of the subpad appeared dry.

Example 5

[0058] Using a Texwipe clean room swab, 0.3 grams of trichloro(1H,1H,2H,2H-perfluorooctyl)silane in liquid form commercially obtained from Aldrich Chemical Company, Inc., Milwaukee, WI under the catalog number 44,893-1, was wiped onto the subpad outer peripheral edge of a 22.5-inch diameter IC1400 stacked polishing pad. Following the application, the pad stack was held at ambient conditions for two (2) hours then immersed in ILD 1300 slurry for one (1) hour. The pad was removed from the slurry and the outer peripheral edge was visually inspected. The outer peripheral edge of the subpad appeared dry.

Control 1 (untreated IC1400 subpad)

[0059] The process as described in Example 1 was carried out with the exception that the micronized polypropylene was not applied.

[0060] The outer peripheral edge of the subpad appeared wet.

Control 2 (untreated WESTPADS subpad)

[0061] The process as described in Example 3 was carried out with the exception that the hydrophobic fumed silica was not applied.

[0062] The outer peripheral edge of the subpad appeared wet.

Control 3 (untreated IC1000/SubaIV subpad)

[0063] The process as described in Example 4 was carried out with the exception that the hydrophobic fumed silica was not applied.

[0064] The outer peripheral edge of the subpad appeared wet.

IN THE CLAIMS:

1. A polishing pad for use in polishing a microelectronic substrate comprising: a polishing layer adapted to polish said substrate; a sublayer of substantially liquid permeable material, wherein said polishing layer and said sublayer are at least partially connected; and an outer peripheral edge of said sublayer wherein at least a portion of said outer peripheral edge has a surface treatment, said surface treatment being effective to reduce absorption of polishing liquid through said outer peripheral edge.
2. The polishing pad of claim 1 wherein said polishing layer is substantially impermeable to polishing fluid.
3. The polishing pad of claim 1 wherein said polishing layer is substantially permeable to polishing fluid.
4. The polishing pad of claim 1 wherein said sublayer is more compressible than said polishing layer.
5. The polishing pad of claim 1 wherein said sublayer comprises material chosen from natural rubber, synthetic rubbers, thermoplastic elastomer, foam sheet and combinations thereof.
6. The polishing pad of claim 1 wherein said sublayer is connected to said polishing layer by means of a middle layer.
7. The polishing pad of claim 6 wherein at least a portion of said middle layer comprises a transparent material.
8. The polishing pad of claim 7 wherein said sublayer and said polishing layer contain an opening substantially aligned with said transparent portion of said middle layer.
9. The polishing pad of claim 1 wherein said outer peripheral edge can absorb organic liquids.

10. The polishing pad of claim 1 wherein said surface treatment comprises treatment of said sublayer with at least one material chosen from silanes, organic polymers, silane-treated silicas, and mixtures thereof.

11. The polishing pad of claim 10 wherein said surface treatment comprises treatment of said sublayer with at least one material chosen from alkyl silanes, polyolefins and mixtures thereof.

12. A polishing pad for use in polishing a microelectronic substrate comprising: a polishing layer adapted to polish said substrate; a sublayer of substantially liquid permeable material, wherein said polishing layer and said sublayer are at least partially connected; and an outer peripheral edge of said sublayer wherein at least a portion of said outer peripheral edge has a surface treatment, said surface treatment being effective to render said outer peripheral edge substantially hydrophobic.

13. A polishing pad for use in polishing a microelectronic substrate comprising: a polishing layer adapted to polish said substrate; a sublayer of substantially liquid permeable material, wherein said polishing layer and said sublayer are at least partially connected; and an outer peripheral edge of said sublayer wherein at least a portion of said outer peripheral edge has a surface treatment, said surface treatment being effective to reduce the wettability of said outer peripheral edge.

14. A method of polishing a microelectronic substrate comprising: surface treating an outer peripheral edge of a sublayer of a polishing pad, said pad being useful for polishing a microelectronic substrate and said sublayer comprising substantially liquid permeable material, wherein said surface treatment is effect to reduce the absorption of polishing fluid through said outer peripheral edge.

15. A method of polishing a microelectronic substrate comprising: at least partially applying to an outer peripheral edge of a sublayer of a polishing pad a surface treatment material, said material being effective to render said outer peripheral edge hydrophobic, said pad being useful for polishing a microelectronic substrate and said sublayer comprising substantially liquid permeable material.

16. A method for reducing the absorption of polishing fluid through the outer peripheral edge of a sublayer of a polishing pad, comprising: surface treating at least a portion of said outer peripheral edge wherein said surface treating comprises applying to said outer peripheral edge of said sublayer at least one material chosen from silanes, organic polymers, silane-treated silicas, and mixtures thereof.