(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 November 2011 (17.11.2011)

PCT

(10) International Publication Number
WO 2011/142986 A1

(51) International Patent Classification:
B24D 3/34 (2006.01) *B24B 37/04* (2006.01)

(21) International Application Number:
PCT/US2011/034439

(22) International Filing Date:
29 April 2011 (29.04.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/333,351 11 May 2010 (11.05.2010) US

(71) **Applicant** *(for all designated States except US)*: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **QIAN, Julie Y.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **BARAN, Jimmie R., Jr.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(74) **Agents**: **WOLF, Stephen F.** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

[Continued on next page]

(54) **Title**: FIXED ABRASIVE PAD WITH SURFACTANT FOR CHEMICAL MECHANICAL PLANARIZATION

(57) **Abstract**: A fixed abrasive pad (100) in the form of a structured abrasive article is provided that has a structured abrasive layer (120) disposed on a backing (110). The structured abrasive layer (120) includes a polymeric binder, abrasive particles dipersed in the binder and a nonionic polyether surfactant dispersed in the binder. The abrasive particles have a mean particle size of less than 200 nm and the surfactant is in the binder in an amount of from 0.75 to 2.2 weight percent based upon the total weight of the structured abrasive layer. A method of abrading a workpiece using the provided fixed abrasive pad is also provided.

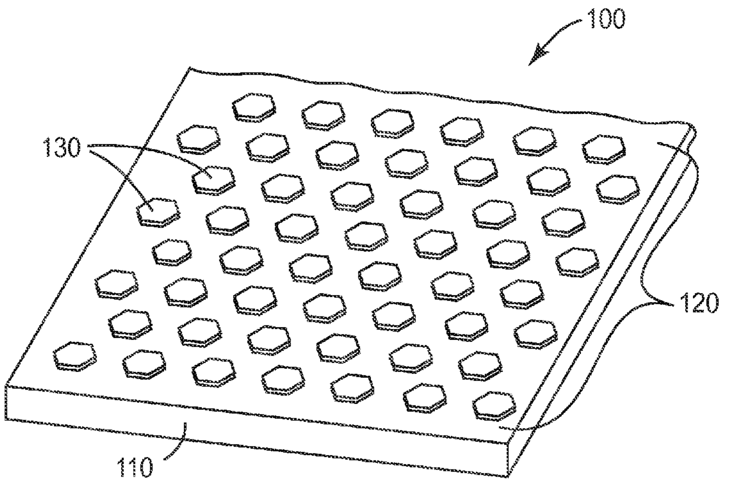

FIG. 1

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*

FIXED ABRASIVE PAD WITH SURFACTANT FOR CHEMICAL MECHANICAL PLANARIZATION

Field

The present disclosure broadly relates to abrasive articles, methods of their manufacture, and their use in wafer planarization.

Background

Abrasive articles are frequently used in microfinishing applications such as semiconductor wafer polishing, microelectromechanical (MEMS) device fabrication, finishing of substrates for hard disk drives, polishing of optical fibers and connectors, and the like. For example, during integrated circuit manufacture, semiconductor wafers typically undergo numerous processing steps including deposition of metal and dielectric layers, patterning of the layers, and etching. In each processing step, it may be necessary or desirable to modify or refine an exposed surface of the wafer to prepare it for subsequent fabrication or manufacturing steps. The surface modification process is often used to modify deposited conductors (e.g., metals, semiconductors, and/or dielectric materials). The surface modification process is also typically used to create a planar outer exposed surface on a wafer having an exposed area of a conductive material, a dielectric material, or a combination.

One method of modifying or refining exposed surfaces of structured wafers treats a wafer surface with a fixed abrasive article. In use, the fixed abrasive article is typically contacted with a semiconductor wafer surface, often in the presence of a working fluid, with a motion adapted to modify a layer of material on the wafer and provide a planar, uniform wafer surface. The working fluid may be applied to the surface of the wafer to chemically modify or otherwise facilitate the removal of material from the surface of the wafer under the action of the abrasive article.

Fixed abrasive articles generally have an abrasive layer of abrasive particles bonded together by a binder and secured to a backing. In one type of fixed abrasive article, the abrasive layer is composed of discrete raised structural elements (e.g., posts, ridges, pyramids, or truncated pyramids) termed "shaped abrasive composites". This type of fixed abrasive article is known in the art variously by the terms "textured, fixed abrasive article" or "structured abrasive article" (this latter term shall be used hereinafter). The abrasive articles can include abrasive particles and at least one nonionic polyether surfactant dispersed in a crosslinked polymer binder as disclosed in U.S.S.N. 12/560,797 (Woo et al.).

In order to assess progress during the planarization process it is common practice to use various detection methods. Optical detection methods (e.g., laser interferometry) are among the most widely used. In such techniques, a laser is typically directed through windows in a platen and a subpad in contact with the structured abrasive article. A hole or transparent (uncoated with abrasive layer) portion of the structured abrasive article is aligned with the beam.

Summary

Chemical mechanical planarization (CMP) processes can cause non-uniformity of polished wafers. There is a need for fixed abrasive articles that provide excellent wafer uniformity and high polish rates. There is a need for fixed abrasive articles that are useful for the fabrication of electronic components that have very small nodes. For example, dynamic random access memory (DRAM) and flash memory devices can have nodes of 32 nm or even 28 nm. There is a need for fixed abrasive articles that can rapidly polish semiconductor wafers having small nodes without causing defects that can produce channel-to-channel short-circuits.

It has been found that by using very small abrasive particles and a surfactant included in the structured adhesive layer that excellent wafer uniformity and high polish rates of wafers can be achieved. In one aspect, a structured abrasive article is provided that includes a backing having first and second opposed major surfaces, a structured abrasive layer disposed on and secured to the first major surface wherein the structured abrasive layer comprises a polymeric binder, abrasive particles dispersed in the binder, and a nonionic polyether surfactant dispersed in the binder, wherein the abrasive particles have a mean particle size of less than about 200 nm, wherein the nonionic polyether surfactant is not covalently bound to the crosslinked polymeric binder, and wherein the nonionic polyether surfactant is present in an amount of from 0.75 to 2.2 percent by weight based on a total weight of the structured adhesive layer. The shaped abrasive composites can be precisely-shaped. The binder can include an acrylic polymer. The surfactant can include a polyethylene oxide or a polypropylene oxide segment. The backing can be an elastomeric polyurethane film or a polymer foam.

In another aspect, a method of abrading a workpiece is provided that includes frictionally contacting at least a portion of a structured abrasive article with a surface of a workpiece while in the presence of an aqueous fluid and moving at least one of the workpiece or the structured abrasive layer relative to the other to abrade at least a portion of the surface of the workpiece, wherein the structured abrasive article includes a backing having first and second opposed major surfaces and a structured abrasive layer disposed on and secured to the first major surface wherein the structured abrasive layer includes a polymeric binder, abrasive particles dispersed in the binder, and a nonionic polyether surfactant dispersed in the binder,
wherein the abrasive particles have a mean particle size of less than about 200 nm, wherein the nonionic polyether surfactant is not covalently bound to the crosslinked polymeric binder, and wherein the nonionic polyether surfactant is present in an amount of from 0.75 to 2.2 percent by weight based on a total weight of the structured adhesive layer. The aqueous fluid can include tap water.

As used herein:

the term "abrasive particle" refers to any particle having a hardness equal or greater to that of ceria;

the term "fixed abrasive pad" and “structured abrasive article" are used interchangeably;

the term "at least translucent" means translucent or transparent;

the term "carboxylic (meth)acrylate" means a compound having a (meth)acrylate group covalently linked to a carboxyl (-CO_2H) or carboxylate (-CO_2-) group;

the term "visible light" refers to light having a wavelength in a range of from 400 nanometers to 700 nanometers, inclusive;

the term "(meth)acryl" includes acryl and/or methacryl;

the term "optical transmission" means the fraction of incident light transmitted through an object;

the term "poly(meth)acrylate" means a compound having at least two (meth)acrylate groups;

the term "transparent" means capable of transmitting visible light so that objects or images can be seen substantially as if there were no intervening material; and

the terms "cerium oxide" and "ceria" refer to $Ce(IV)O_2$.

The above summary is not intended to describe each disclosed embodiment of every implementation of the present invention. The brief description of the drawings and the detailed description which follows more particularly exemplify illustrative embodiments.

Brief Description of the Drawings

Fig. 1 is a perspective view of an exemplary structured abrasive article according to one embodiment according to the present disclosure.

Fig. 2 is a schematic side view of an exemplary method of conditioning a surface of a wafer according to the present disclosure.

Fig. 3 is a graph of the removal rate of oxide as a function of cross-sectional wafer diameter using provided articles and methods.

Detailed Description

In the following description, reference is made to the accompanying set of drawings that form a part of the description hereof and in which are shown by way of illustration several specific embodiments. It is to be understood that other embodiments are contemplated and may be made without departing from the scope or spirit of the present invention. The following detailed description, therefore, is not to be taken in a limiting sense.

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties 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 foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein. The use of numerical ranges by endpoints includes all numbers within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

Referring now to Fig. 1, structured abrasive article 100 comprises at least translucent film backing 110. Abrasive layer 120 is disposed on at least translucent film backing 110 and comprises a plurality of shaped abrasive composites 130. Shaped abrasive composites 130 comprise abrasive particles (not shown) dispersed in a binder (not shown). The abrasive particles consist essentially of ceria particles having an average primary particle size of less than 100 nanometers. The binder comprises a polyether acid and a reaction product of components comprising a carboxylic (meth)acrylate and a poly(meth)acrylate, and wherein based on a total weight of the abrasive layer, the abrasive particles are present in an amount of at least 70 percent by weight.

The translucent film backing may be flexible, rigid, or in between. A variety of backing materials are suitable for this purpose, including both flexible backings and backings that are more rigid. Useful translucent film backings include backing films selected from polymer films, treated versions thereof, and combinations thereof. Exemplary translucent backing films include films made from polyester (e.g., polyethylene terephthalate or polycaprolactone), co-polyester, polycarbonate, polyimide, polyamide, polypropylene, polyurethane, polyethylene, cellulosic polymers, and blends and combinations thereof. In some embodiments, the backing can include an elastomeric urethane or a foam.

The thickness of the translucent film backing is typically in a range of from about 20 to about 1000 micrometers, more typically, from about 50 micrometers to about 500 micrometers, and more typically from about 60 micrometers to about 200 micrometers. At least one surface of the backing may be coated with the abrasive layer. In general, the backing is of substantially uniform in thickness. If the backing is not sufficiently uniform in thickness, greater variability in wafer polishing uniformity may occur during wafer planarization.

The abrasive layer includes a plurality of shaped abrasive composites. As used herein, the term "shaped abrasive composite" refers to one of a plurality of shaped bodies comprising abrasive particles dispersed in a binder, the shaped bodies collectively providing a textured, three-dimensional abrasive layer. In some embodiments, the shaped abrasive composites are "precisely-shaped". The term "precisely-shaped abrasive composite" refers to an abrasive composite having a molded shape that is substantially the inverse of a mold cavity used to make it. Typically, precisely-shaped abrasive composites are substantially free of abrasive particles protruding beyond the exposed surface of the abrasive composite before the structured abrasive article has been used.

Provided structured abrasive articles can have a high weight content of shaped abrasive particles in the abrasive layer. For example the shaped abrasive composites comprise, on a weight basis, at least 70 percent of the abrasive layer; and may comprise at least 75, 80, or even 90 percent by weight of the abrasive layer, or more. Typically, a higher weight percentage of the abrasive particles in the shaped abrasive composites results in higher cut.

The abrasive particles can include ceria (i.e., cerium oxide) particles having an average particle size, on a volume basis, of less than 250 nanometers, less than 150 nanometers, less than 100 nanometers, or even less than 50 nanometers. The abrasive particles can consist essentially of ceria particles. The phrase "consist essentially of" used in this context is intended to exclude other (i.e., non-ceria) abrasive particles in amounts that materially affect abrading properties of the structured abrasive article, if used in wafer planarization of silicon-containing wafers. It will be recognized that that the ceria particles may comprise agglomerates and/or aggregates of smaller primary ceria particles. For example, the ceria particles (whether present as primary particle, agglomerates, aggregates, or a combination thereof) may have an average particle size, on a volume basis, in a range of from 1, 5, 10, 20, 30, or 40 nanometers up to 50, 60, 70, 80, 90, 95 nanometers, or more.

The ceria particles can be supplied, for example, in the form of a powder, dispersion, or sol; typically, as a dispersion or sol. Methods and sources for obtaining ceria sols having an average particle size less than 250 nanometers are well known in the art. Ceria dispersions and sols suitable for use in the present disclosure include, for example, ceria sols and dispersions commercially available for suppliers such as Evonik Degussa Corp. of Parsippany, NJ; Rhodia, Inc. of Cranberry, NJ; Ferro Corporation of Independence, OH; and Umicore SA, Brussels, Belgium.

The abrasive particles may be homogeneously or heterogeneously dispersed in the polymeric binder. The term "dispersed" refers to the abrasive particles being distributed throughout the polymeric binder. Dispersing the ceria particles substantially homogeneously in the binder typically increases performance of the structured abrasive article. Accordingly, it is typically useful to treat the ceria particles with carboxylic (meth)acrylates to facilitate their dispersibility and/or reduce aggregation, and enhance subsequent coupling to the binder. Exemplary carboxylic (meth)acrylates include (meth)acrylic acid, monoalkyl esters of maleic acid, fumaric acid, monoalkyl esters of fumaric acid, maleic acid, itaconic acid, isocrotonic acid, crotonic acid, citraconic acid, and β-carboxyethyl (meth)acrylate.

In one exemplary method for treating the ceria particles with a carboxylic (meth)acrylate, a dispersion (e.g., a sol) of the ceria particles in an aqueous medium (e.g., water) is combined with a polyether acid and carboxylic (meth)acrylate (in amounts of each that are sufficient to surface treat and thereby stabilize the ceria particles) and a water-miscible organic solvent having a higher boiling point than water. Typically, the proportion of polyether acid to carboxylic (meth)acrylate is in a range of from about 3:5 to 5:3, although other proportions may be used. Examples of useful solvents include 1-methoxy-2-propanol, dimethylformamide, and diglyme. Once combined, the water is substantially removed by evaporation under reduced pressure resulting in a ceria dispersion in which the ceria particles are stabilized against aggregation by associated carboxylic (meth)acrylate molecules. The resultant ceria dispersion can typically be readily combined with the poly(meth)acrylate and optional mono(meth)acrylate monomers, and any additional carboxylic (meth)acrylate that may be included in the binder precursor.

While the carboxylic (meth)acrylate typically serves to facilitate bonding of the ceria particles to the binder, the polyether acid is included primarily to facilitate dispersion stability of the ceria particles in the binder (or its precursor components) and/or solvent. As used herein, the term "polyether acid" refers to a compound having a polyether segment covalently to an acidic group or salt thereof. Exemplary polyether segments include polyethylene glycol segments, polyethylene glycol segments, and mixed poly(ethylene glycol/propylene glycol) segments. Exemplary acidic groups include $-CO_2H$, $-PO_2H$, $-PO_3H$, $-SO_3H$, and salts thereof. In certain embodiments, the polyether acids can have up to 12 carbon atoms, inclusive, and are represented by the formula:

$$R^1\text{-}(R^2\text{-}O)_n\text{-}X\text{-}A$$

wherein R^1 represents H, an alkyl group having from 1 to 6 carbon atoms (e.g., methyl ethyl, or propyl), or an alkoxy group having from 1 to 6 carbon atoms (e.g., methoxy, ethoxyl, or propoxy); each R^2 independently represents a divalent alkylene group having from 1 to 6 carbon atoms (e.g., ethylene, propylene, or butylene); n represents a positive integer (e.g., 1, 2, or 3; and X represents a divalent organic linking group or a covalent bond; and A represents an acidic group (e.g., as described hereinabove). Exemplary such polyether acids include 2'-(2"-methoxyethoxy)ethyl succinate (monoester), methoxyethoxyethoxyacetic acid, and methoxyethoxyacetic acid. The binder can further include a reaction product of components comprising a carboxylic (meth)acrylate and a poly(meth)acrylate. As discussed above, at least a portion of the carboxylic (meth)acrylate is typically combined with the abrasive particles prior to combining the resultant dispersion with the remaining binder components, although this is not a requirement.

A nonionic polyether surfactant is dispersed in the binder. Typically, there is no covalent chemical bond between the surfactant and the binder. The binder can be crosslinked as described further on to help contain the surfactant and regulate its release. The amount of polyether nonionic surfactant present in the shaped abrasive composites can be in a range of from 0.75 to 2.2, from 1.0 to 2.2, from 1.3 to 2.2 percent by weight, typically from 1.5 to 2.0 percent by weight, based on a total weight of the shaped abrasive composites. As used herein, the term "polyether nonionic surfactant" refers to one or more nonionic (i.e., not having a permanent charge) surfactant(s) that has/have a polyether segment, typically forming at least a portion of the backbone of the surfactant, although this is not a requirement. As is generally the case for surfactants, the polyether nonionic surfactant should not be covalently bound to the crosslinked polymeric binder. To facilitate dissolution into the aqueous fluid, the polyether nonionic surfactant typically has a molecular weight in a range of from 300 -1200 grams per mole, although higher and lower molecular weights may be used.

Examples of polyether nonionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkyl-phenyl ethers, polyoxyethylene acyl esters, polyoxyethylene alkylamines, polyoxyethylene alkylamides, polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyethylene glycol laurate, polyethylene glycol stearate, polyethylene glycol distearate, polyethylene glycol oleate, oxyethylene-oxypropylene block copolymer, polyoxyethylene sorbitan laurate, polyoxyethylene sorbitan stearate, polyoxyethylene sorbitan oleate, and polyoxyethylene laurylamide.

Useful polyether nonionic surfactants also include, for example, condensation products of a higher aliphatic alcohol with about 3 equivalents to about 100 equivalents of ethylene oxide (e.g., those marketed by Dow Chemical Co. under the trade designation TERGITOL 15-S such as, for example, TERGITOL 15-S-20; and those marketed by ICI Americas of Bridgewater, NJ under the trade designation BRIJ such as, for example, BRIJ 58, BRIJ 76, and BRIJ 97). BRIJ 97 surfactant is polyoxyethylene (10) oleyl ether; BRIJ 58 surfactant is polyoxyethylene (20) cetyl ether; and BRIJ 76 surfactant is polyoxyethylene (10) stearyl ether.

Useful polyether nonionic surfactants also include, for example, polyethylene oxide condensates of an alkyl phenol with about 3 equivalents to about 100 equivalents of ethylene oxide (e.g., those marketed by Rhodia of Cranbury, NJ under the trade designations IGEPAL CO and IGEPAL CA). IGEPAL CO surfactants include nonylphenoxy poly(ethyleneoxy)ethanols. IGEPAL CA surfactants include octylphenoxy poly(ethyleneoxy)ethanols. Useful polyether nonionic surfactants also include, for example, block copolymers of ethylene oxide and propylene oxide or butylene oxide (e.g., those marketed by BASF Corp. of Mount Olive, NJ under the trade designations PLURONIC (e.g., PLURONIC L10) and TETRONIC). PLURONIC surfactants may include propylene oxide polymers, ethylene oxide polymers, and ethylene oxide-propylene oxide block copolymers. TETRONIC surfactants include ethylene oxide-propylene oxide block copolymers.

In some embodiments, polyether nonionic surfactants can include polyoxyethylene sorbitan fatty acid esters (e.g., polyoxyethylene sorbitan monooleates), which may have differing degrees of ethoxylation such as, for example, 20 ethylene oxide units per molecule (e.g., marketed as TWEEN 60) or 20 ethylene oxide units per molecule (e.g., marketed as TWEEN 80)) and polyoxyethylene stearates (e.g., those marketed under the trade designations TWEEN and MYRJ by Uniqema of New Castle, DE). TWEEN surfactants include poly(ethylene oxide) C_{12}-C_{18} sorbitan monoesters. MYRJ surfactants include poly(ethylene oxide) stearates.

In some embodiments, the polyether nonionic surfactant is the only surfactant present in the shaped abrasive composites or in the aqueous fluid during abrading. In some cases, it may be desirable to add lesser quantities of anionic surfactants such as an anionic phosphate polyether ester available as TRITON H55 from Dow Chemical Co.

The abrasive layer includes abrasive particles dispersed in a binder. Suitable binder precursors are typically, in an uncured or uncrosslinked state, flowable at or near ambient conditions. The binder precursor is then typically exposed to conditions (typically an energy source) that at least partially cure or crosslink (i.e., free-radical polymerization) the binder precursor, thereby converting it into a binder capable of retaining the dispersed abrasive particles. Exemplary energy sources include: e-beam, ultraviolet radiation, visible radiation, infrared radiation, gamma radiation, heat, and combinations thereof.

Useful poly(meth)acrylates include monomers and/or oligomers that have at least two (meth)acrylate groups; for example, tri(meth)acrylates, and tetra(methacrylates). Exemplary poly(methacrylates) include: di(meth)acrylates such as, for example, 1,3-butylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,6-hexanediol mono(meth)acrylate mono(meth)acrylate, ethylene glycol di(meth)acrylate, alkoxylated aliphatic di(meth)acrylate, alkoxylated cyclohexanedimethanol di(meth)acrylate, alkoxylated hexanediol di(meth)acrylate, alkoxylated neopentyl glycol di(meth)acrylate, caprolactone modified neopentyl glycol hydroxypivalate di(meth)acrylate, caprolactone modified neopentyl glycol hydroxypivalate di(meth)acrylate, cyclohexanedimethanol di(meth)acrylate, diethylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, ethoxylated (10) bisphenol A di(meth)acrylate, ethoxylated (3) bisphenol A di(meth)acrylate, ethoxylated (30) bisphenol

A di(meth)acrylate, ethoxylated (4) bisphenol A di(meth)acrylate, hydroxypivalaldehyde modified trimethylolpropane di(meth)acrylate, neopentyl glycol di(meth)acrylate, polyethylene glycol (200) di(meth)acrylate, polyethylene glycol (400) di(meth)acrylate, polyethylene glycol (600) di(meth)acrylate, propoxylated neopentyl glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, triethylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate; tri(meth)(meth)acrylates such as glycerol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ethoxylated tri(meth)acrylates (e.g., ethoxylated (3) trimethylolpropane tri(meth)acrylate, ethoxylated (6) trimethylolpropane tri(meth)acrylate, ethoxylated (9) trimethylolpropane tri(meth)acrylate, ethoxylated (20) trimethylolpropane tri(meth)acrylate), pentaerythritol tri(meth)acrylate, propoxylated tri(meth)acrylates (e.g., propoxylated (3) glyceryl tri(meth)acrylate, propoxylated (5.5) glyceryl tri(meth)acrylate, propoxylated (3) trimethylolpropane tri(meth)acrylate, propoxylated (6) trimethylolpropane tri(meth)acrylate), trimethylolpropane tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate; and higher functionality (meth)acryl containing compounds such as ditrimethylolpropane tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, ethoxylated (4) pentaerythritol tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, caprolactone modified dipentaerythritol hexa(meth)acrylate; oligomeric (meth)acryl compounds such as, for example, polyester (meth)acrylates, epoxy (meth)acrylates; and combinations thereof. Such compounds are widely available from vendors such as, for example, Sartomer Co. of Exton, PA; UCB Chemicals Corporation of Smyrna, GA; and Aldrich Chemical Company of Milwaukee, WI.

The binder precursor may comprise an effective amount of at least one photoinitiator; for example, in an amount of from 0.1, 1, or 3 percent by weight, up to 5, 7, or even 10 percent by weight, or more. Useful photoinitiators include those known as useful for free-radically photocuring (meth)acrylates. Exemplary photoinitiators include benzoin and its derivatives such as alpha-methylbenzoin; alpha-phenylbenzoin; alpha-allylbenzoin; alpha-benzylbenzoin; benzoin ethers such as benzil dimethyl ketal (available as IRGACURE 651 from Ciba Specialty Chemicals, Tarrytown, NY), benzoin methyl ether, benzoin ethyl ether, benzoin n-butyl ether; acetophenone and its derivatives such as 2-hydroxy-2-methyl-1-phenyl-1-propanone (available as DAROCUR 1173 from Ciba

Specialty Chemicals) and 1-hydroxycyclohexyl phenyl ketone (available as IRGACURE 184 from Ciba Specialty Chemicals); 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone (available as IRGACURE 907 from Ciba Specialty Chemicals); 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone (available as IRGACURE 369 from Ciba Specialty Chemicals); and (phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (available as IRGACURE 819 from Ciba Specialty Chemicals, NY. Other useful photoinitiators include mono- and bis-acylphosphines (available, for example, from Ciba Specialty Chemicals as IRGACURE 1700, IRGACURE 1800, IRGACURE 1850, and DAROCUR 4265).

The binder precursor may comprise an effective amount of at least one thermal initiator; for example, in an amount of from 0.1, 1, or 3 percent by weight, up to 5, 7, or even 10 percent by weight, or more. Exemplary thermal free-radical initiators include: azo compounds such as, for example, 2,2-azo-bisisobutyronitrile, dimethyl 2,2'-azobis(isobutyrate), azobis(diphenyl methane), 4,4'-azobis-(4-cyanopentanoic acid), (2,2'-azobis(2,4-dimethylvaleronitrile (available as VAZO 52 from E. I. du Pont de Nemours and Co. of Wilmington, DE); peroxides such as, for example, benzoyl peroxide, cumyl peroxide, tert-butyl peroxide, cyclohexanone peroxide, glutaric acid peroxide, and dilauryl peroxide; hydrogen peroxide; hydroperoxides such as, for example, tert butyl hydroperoxide and cumene hydroperoxide; peracids such as, for example, peracetic acid and perbenzoic acid; potassium persulfate; and peresters such as, for example, diisopropyl percarbonate.

In some embodiments, it may be desirable to include one or more monoethylenically unsaturated free-radically polymerizable compounds in the binder precursor; for example, to reduce viscosity and/or or reduce crosslink density in the resultant binder. Exemplary monoethylenically unsaturated free-radically polymerizable compounds include: mono(meth)acrylates include hexyl (meth)acrylate, 2-ethylhexyl acrylate, isononyl (meth)acrylate, isobornyl (meth)acrylate, phenoxyethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, dodecyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, n-butyl (meth)acrylate, n-octyl (meth)acrylate, isobutyl (meth)acrylate, cyclohexyl (meth)acrylate, or octadecyl (meth)acrylate; N-vinyl compounds such as, for example, N-vinylformamide, N-vinylpyrrolidinone, or N-vinylcaprolactam; and combinations thereof.

In some embodiments, the abrasive layer may also include one additives. The additives can include one or more of an antioxidant, a colorant, a heat and light stabilizer, or a filler (the filler having substantially no impact on abrading performance). Accordingly, the binder is typically prepared from a binder precursor comprising the abrasive particles, the surfactant, and additives in which the abrasive particles are dispersed (e.g., as a slurry).

Provided structured abrasive articles, that include shaped abrasive composites, can be made by general methods well-known in the art. For example, in one embodied method a binder precursor and abrasive particles, in the form of a slurry, can be urged into complementary cavities in a production tool that have the dimensions of the desired shaped abrasive composites. Then, the translucent film backing can brought into contact with the production tool and slurry precursor and the binder precursor can be at least sufficiently cured to remove the shaped abrasive composites from the production tool. Alternatively, the production tool, at least translucent film backing, and slurry can be simultaneously fed through a nip. Optionally, further curing (e.g., thermal post curing) can be carried out at this stage to further advance the degree of cure and thereby improve the binder properties. Further details concerning methods for forming shaped abrasive composites can be found in, for example, U. S. Pat. No. 5,152,917 (Pieper et al.).

Individual shaped abrasive composites can have the form of any of a variety of geometric solids or be irregularly shaped. Typically, the shaped abrasive composites are precisely-shaped (as defined above). Typically, the shaped abrasive composite is formed such that the base of the shaped abrasive composite, for example, that portion of the shaped abrasive composite is in contact with, and secured to, the at least translucent film backing. The proximal portion of the shaped abrasive composite typically has the same or larger a larger surface area than that portion of the shaped abrasive composite distal from the base or backing. Precisely-shaped abrasive composites may be selected from among a number of geometric solids such as a cubic, cylindrical, prismatic (e.g., hexagonal prisms), rectangular pyramidal, truncated pyramidal, conical, hemispherical, truncated conical, cross, or post-like cross sections with a distal end. Composite pyramids may have four sides, five sides or six sides. The shaped abrasive composites may also have a mixture of different shapes. The shaped abrasive composites may be arranged in rows, in concentric circles, in helices, or in lattice fashion, or may be randomly placed.

The sides forming the shaped abrasive composites may be perpendicular relative to the backing, tilted relative to the backing or tapered with diminishing width toward the distal end. However, if the sides are tapered, it may be easier to remove the shaped abrasive composite from the cavities of a mold or production tool. The substantially perpendicular angles are preferred because this results in a consistent nominal contact area as the composite wears.

The height of each shaped abrasive composite is typically substantially the same, but it is envisaged to have composites of varying heights in a single structured abrasive article. The height of the composites with respect to the backing or to the land between the composites generally may be less than about 2,000 micrometers; for example, in a range of from about 10 micrometers to about 250 micrometers. The base dimension of an individual shaped abrasive composite may be about 5,000 micrometers or less, typically about 1,000 micrometers or less, more typically less than 500 micrometers. The base dimension of an individual shaped abrasive composite is typically greater than about 50 micrometers, more typically greater than about 100 micrometers. The base of the shaped abrasive composites may abut one another, or may be separated from one another by some specified distance.

Adjacent shaped composites may share a common shaped abrasive composite land or bridge-like structure which contacts and extends between facing sidewalls of the composites. Typically, the land structure has a height of no greater than about 33 percent of the vertical height dimension of each adjacent composite. The shaped abrasive composite land may be formed from the same slurry used to form the shaped abrasive composites. The composites are "adjacent" in the sense that no intervening composite may be located on a direct imaginary line drawn between the centers of the composites. At least portions of the shaped abrasive composites may be separated from one another so as to provide the recessed areas between the raised portions of the composites.

The linear spacing of the shaped abrasive composites may range from about 1 shaped abrasive composite per linear cm to about 200 shaped abrasive composites per linear cm. The linear spacing may be varied such that the concentration of composites may be greater in one location than in another. For example, the concentration may be greatest in the center of the abrasive article. The areal density of the composite may range, in some embodiments, from about 1 to about 40,000 composites per square centimeter. One or more areas of the backing may be exposed, i.e., have no abrasive coating contacting the at least translucent film backing.

The shaped abrasive composites are typically set out on a backing in a predetermined pattern or set out on a backing at a predetermined location. For example, in the abrasive article made by providing slurry between the backing and a production tool having cavities therein, the predetermined pattern of the composites will correspond to the pattern of the cavities on the production tool. The pattern may be thus reproducible from article to article. In one embodiment, the shaped abrasive composites may form an array or arrangement, by which may be meant that the composites are in a regular array such as aligned rows and columns, or alternating offset rows and columns. If desired, one row of shaped abrasive composites may be directly aligned in front of a second row of shaped abrasive composites. Typically, one row of shaped abrasive composites may be offset from a second row of shaped abrasive composites.

In another embodiment, the shaped abrasive composites may be set out in a "random" array or pattern. By this it may be meant that the composites are not in a regular array of rows and columns as described above. For example, the shaped abrasive composites may be set out in a manner as disclosed in U. S. Pat. Nos. 5,672,097 and 5,681,217 (both Hoopman et al.). It will be understood, however, that this "random" array may be a predetermined pattern in that the location of the composites on the abrasive article may be predetermined and corresponds to the location of the cavities in the production tool used to make the abrasive article.

Exemplary production tools include rolls, endless belts, and webs, and may be made of an suitable material such as for example, metal (e.g., in the case of rolls) or polymer films (e.g., in the cases of endless belts and webs).

Provided structured abrasive articles may be generally circular in shape, e.g., in the form of an abrasive disc. Outer edges of the abrasive disc are typically smooth, or may be scalloped. The structured abrasive articles may also be in the form of an oval or of any polygonal shape such as triangular, square, rectangular, and the like. Alternatively, the abrasive articles may be in the form of a belt. The abrasive articles may be provided in the form of a roll, typically referred to in the abrasive art as abrasive tape rolls. In general, the abrasive tape rolls may be indexed or moved continuously during the wafer planarization process. The abrasive article may be perforated to provide openings through the abrasive coating and/or the backing to permit the passage of the working fluid before, during and/or after use; although, in advantageous embodiments the structured abrasive articles are substantially free of, or even completely free of, such perforations.

Precisely-shaped abrasive composites may be of any three-dimensional shape that results in at least one of a raised feature or recess on the exposed surface of the abrasive layer. Useful shapes include, for example, cubic, prismatic, pyramidal (e.g., square pyramidal or hexagonal pyramidal), truncated pyramidal, conical, frustoconical. Combinations of differently shaped and/or sized abrasive composites may also be used. The abrasive layer of the structured abrasive may be continuous or discontinuous. Further details concerning structured abrasive articles having precisely-shaped abrasive composites, and methods for their manufacture may be found, for example, in U.S. Pat. Nos. 5,435,816 (Spurgeon et al.); 5,454,844 (Hibbard et al.); 5,851,247 (Stoetzel et al.); and 6,139,594 (Kincaid et al.).

Typically, the shaped abrasive composites are arranged on the backing according to a predetermined pattern or array, although this is not a requirement. The shaped abrasive composites may be arranged such that some of their work surfaces are recessed from the polishing surface of the abrasive layer.

The translucent film backing of the structured abrasive articles can typically be contacted with a subpad during use. In some cases, the structured abrasive article can be secured to the subpad. The abrasive layer can be applied to a front surface of the at least translucent film backing and an adhesive, for example a pressure-sensitive adhesive (or mechanical fastening device) can be applied to the opposing surface of the at least translucent film backing. Suitable subpads are disclosed, for example, in U.S. Pat. Nos. 5,692,950 and 6,007,407 (both to Rutherford et al.). If using optical detection methods, the subpad, and any platen on which it rests, should have at least one appropriately sized window (e.g., an opening or transparent insert) to permit a continuous optical path from a light source (e.g., a laser) through the platen and subpad.

Provided structured abrasive articles can be fabricated such that they have sufficient optical transmittance to be suitable for use with optical detection methods such as, for example, laser interferometry. For example, the structured abrasive article may have an optical transmission of at least 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, or even 5.0 percent, or more, over any wavelength range; for example, corresponding to the output wavelength of a laser. Exemplary laser wavelengths include: 694 nm (ruby), 676.4 nm (Kr-ion), 647.1 nm (Kr-ion), 635-660 nm (InGaAlP semiconductor), 633 nm (HeNe), 628 nm (ruby), 612 nm (HeNe), 578 (Cu vapor), 568.2 nm (Kr-ion), 543 nm (HeNe), 532 nm (DPSS semiconductor), 530.9 nm (Kr-ion), 514.5 nm (Ar-ion), 511 nm (Cu vapor), 501.7 nm (Ar), 496.5 nm (Ar), 488.0 nm (Ar), 476.5 nm (Ar), 457.9 nm (Ar), 442 nm (HeCd), or 428 nm (N_2^+).

Provided structured abrasive articles may be used for abrading and/or polishing workpieces such as wafers containing silicon (e.g., silicon wafers, glass wafers, etc.) or other metals and including those wafers having an oxide layer on an outer surface thereof. For example, the structured abrasive articles may be useful in abrading and/or polishing a dielectric material deposited on the wafer and/or the wafer itself. Additionally, it is contemplated that the provided abrasive article can be useful in abrading or polishing other materials such as sapphire or other minerals. Variables that affect the wafer polishing rate and characteristics include, for example, the selection of the appropriate contact pressure between the wafer surface and abrasive article, type of working fluid, relative speed and relative motion between the wafer surface and the abrasive article, and the flow rate of the working fluid. These variables are interdependent, and are typically selected based upon the individual wafer surface being processed.

Structured abrasive articles according to the present disclosure may be conditioned, for example, by abrading the surface using a pad conditioner (e.g., with diamond grits held in a metal matrix) prior to and/or intermittently during the wafer planarization process. One useful conditioner is a CMP pad conditioner (typically mounted on a rigid backing plate), part no. CMP-20000TS, available from Morgan Advanced Ceramics of Hayward, CA.

In general, since there can be numerous process steps for a single semiconductor wafer, the semiconductor fabrication industry expects that the process will provide a relatively high removal rate of material. The material removal rate obtained with a particular abrasive article will typically vary depending upon the machine conditions and the type of wafer surface being processed. However, although it is typically desirable to have a high conductor or dielectric material removal rate, the conductor or dielectric material removal rate may be selected such that it does not compromise the desired surface finish and/or topography of the wafer surface.

Referring now to Fig. 2, in an exemplary method of conditioning a surface of a wafer, structured abrasive article 100 contacts and is secured to subpad 210, which is in turn secured to platen 220. Subpad 210, which may comprise a foam (e.g., a polyurethane foam) or other compressible material, has first window 212 therein, and platen 220 has second window 222 therein. Wafer holder 233 is mounted to a head unit 231 that is connected to a motor (not shown). Gimbal chuck 232 extends from head unit 231 to wafer holder 233. Wafer holder 233 helps secure wafer 240 to head unit 231 and also prevent the semiconductor wafer from becoming dislodged during planarization. Wafer holder 233 extends alongside of wafer 240 at ring portion 233a. Ring portion 233a (which is optional) may be a separate piece or may be integral with wafer holder 233. Wafer 240 is brought into contact with the abrasive layer 120 of structured abrasive article 100, and the wafer 240 and abrasive layer 120 are moved relative to one another. The progress of polishing/abrading is monitored using laser beam 250 which passes through second window 222, first window 212, and structured abrasive article 100 and is reflected off oxide surface 242 wafer 240 and then retraces its path. Optional working fluid 260 may be used to facilitate the abrading process. Reservoir 237 holds optional working fluid 260 which is pumped through tubing 238 into the interface between semiconductor wafer and the abrasive layer. Useful working fluids include, for example, those listed in U.S. Pat. No. 5,958,794 (Bruxvoort et al.).

In general, wafer surface finishes that are substantially free of scratches and defects are desired. The surface finish of the wafer may be evaluated by known methods. One method is to measure the Rt value, which provides a measure of roughness, and may indicate scratches or other surface defects. The wafer surface is typically modified to yield an Rt value of no greater than about 0.4 nanometers, more typically no greater than about 0.2 nanometers, and even more typically no greater than about 0.05 nanometers. Rt is typically measured using a laser interferometer such as a Wyko RST PLUS interferometer (Wyko Corp., Tucson, AZ), or a Tencor profilometer (KLA-Tencor Corp., San Jose, CA). Scratch detection may also be measured by dark field microscopy. Scratch depths may be measured by atomic force microscopy.

Wafer surface processing may be conducted in the presence of a working fluid, which may be selected based upon the composition of the wafer surface. In some applications, the working fluid typically comprises water. The working fluid may aid processing in combination with the abrasive article through a chemical mechanical polishing process. During the chemical portion of polishing, the working fluid may react with the outer or exposed wafer surface. Then during the mechanical portion of processing, the abrasive article may remove this reaction product.

The current trend in memory storage devices and other electronics is miniaturization. There is a need for abrasive articles that can polish wafers that have very small nodes without producing defects. Some exemplary devices have nodes as small as 32 nm or even 28 nm. To polish these wafers it is important that the abrasive article be able to create a smooth surface with very few defects at a relatively high rate. In addition, the wafer, which can be There is a need for abrasive articles that can polish wafers that have very small nodes without producing defects. Some exemplary devices have nodes as small as 32 nm or even 28 nm. To polish these wafers it is important that the abrasive article be able to create a smooth surface with very few defects at a relatively high rate. In addition after polishing, the wafer, which can be 100 mm or more in diameter, needs to have a uniform profile with minimal dishing (more wear at the edges than at the center). It has been surprisingly found that structured abrasive articles that include a polymeric binder which has abrasive particles and a nonionic polyether surfactant dispersed therein can remove material from thermal oxide wafers at rates exceeding 1500 Å/min when the abrasive particles have a mean particle size of less than about 200 nm, less than about 150 nm, less than 140 nm, or even less than 130 nm and when the nonionic polyether surfactant is present in an amount of from 0.75 to 2.2, from 1.0 to 2.2, from 1.3 to 2.2 or even from 1.5 to 2.0 percent by weight of the structured adhesive. Table 1 in the Example section illustrates this result. The provided abrasive articles have a special combination of abrasive particle size, amount of nonionic polyether surfactant, and construction such that the surfactant is dispersed in a crosslinked binder in the proper amount to allow for high wafer removal rates with low defects and excellent cross-wafer uniformity.

Objects and advantages of this disclosure are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and, details, should not be construed to unduly limit this disclosure.

Examples

Example 1 – Fixed Abrasive Web with 1% Surfactant

Preparation of Ceria Dispersion 1

A ceria dispersion (11.4045 kg, 51.06% solids in water, 132 nm average particle size, available from Ferro Corporation of Independence, OH) was poured into a mixing vessel and then 703 grams of 2-(2-methoxyethoxy)ethoxyacetic acid, 568 grams of β-carboxyethyl acrylate (acid #5.9-6.0), and 2.7907 kg of 1-methoxy-2-propanol were slowly added while mixing using a polytetrafluoroethylene-coated blade. The mixture was heated to 50°C and mixed overnight. The mixture was then transferred into a rotary evaporator and excess water was removed under reduced pressure. The resultant dispersion had a solids content of 49.32 percent.

Preparation of Slurry 1

Into a mixing vessel were mixed 45.000 kg Ceria Dispersion 1, 665.8 grams of DISPERBYK-111 wetting and dispersing additive (available from BYK-Chemie USA, Inc. of Wallingford, CT). To this mixture was added 125.9 grams of 2-hydroxyethyl methacrylate (available from Rohm and Haas Co. of Philadelphia, PA), 318.7 grams of 2-phenoxyethyl acrylate (available as SR 339, from Sartomer Co. or Exton, PA)), 2.445 kg of trimethylolpropane triacrylate (available as SR 351 from Sartomer Co.), 137.1 grams of β-carboxyethyl acrylate (available from Bimax Inc. of Cockeysville, MD), 252.2 grams

TERGITAL 15-7-S (available from Sigma Aldrich Inc.,) and 15.13 grams of phenothiazine dissolved in 466.1 grams of 1-methoxy-2-propanol. The mixture was mixed using a polytetrafluoroethylene-coated blade for 30 minutes, then transferred to a rotary evaporator to remove the 1-methoxy-2-propanol. The slurry was cooled to room temperature, and then 26.16 grams of free-radical photoinitiator (phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide, available as IRGACURE 819 from Ciba Specialty Chemicals of Tarrytown, NY), 26.16 grams of thermal free-radical initiator (2,2'-azobis(2,4-dimethylvaleronitrile, available as VAZO 52 from E. I. du Pont de Nemours and Co. of Wilmington, DE) and 6.54 grams of hydroquinone monomethyl ether were added, followed by mixing for two hours.

Example 1

A roll of polypropylene production tool, 30 inches (76 cm) in width, was provided. The polypropylene production tool was polypropylene film that had a hexagonal array (350 micrometers on center) of hexagonal columnar cavities (125 μm wide and 30 μm deep), corresponding to a 10 percent cavitation area. The production tool was essentially the inverse of the desired shape, dimensions, and arrangement for the abrasive composites in the ultimate structured abrasive article. Method 4 disclosed in U. S. Pat. No. 7,497,885 (Kollodge) provides a further description of the tool and its use. Slurry 1 was coated between the cavities of production tool and roll of translucent polycarbonate/PBT based film backing material (7 mils (0.18 mm) thickness available as BAYFOL CR6-2 from Bayer Corp., Pittsburgh, PA) using a casting roll and a nip roll (nip force of 1300 pounds (5.78 kN)) and then passed through UV light source (V Bulb, Model EPIQ available from Fusion Systems), at a line speed of 10 feet/min (3.0 m/min) and a total exposure of 6.0 kilowatts/inch (2.36 kJ/hr-cm). The resultant structured abrasive article (SA1) was removed from the production tool after being UV cured.

SA1 was used to polish thermal oxide blanket wafers (200 mm in diameter with a micrometer film thickness of silicon oxide on its surface) using CMP polisher available under the trade designation REFLEXION polisher from Applied Materials, Inc. of Santa Clara, CA using a wafer pressure of 3.0 lb/in^2 (20.7 kPa), a platen speed of 30 revolutions per minute, and a web index speed of 8 millimeters for 1 minute. The measured removal rate averaged 1625 Å/min for thermal oxide wafers, with an unexpected center fast wafer profile, as shown in the graph above, which provides an option to fine tone the wafer profile to its optimal uniformity by adjusting pressures applying to the wafers.

Example 2 – Fixed Abrasive Web with 2% Surfactant

Preparation of Ceria Dispersion 2

A ceria dispersion (102.195 kg, 51.56% solids in water, 135 nm average particle size, available from Ferro Corporation of Independence, OH) was poured into a mixing vessel and then 622 grams of 2-(2-methoxyethoxy)ethoxyacetic acid, 503 grams of β-carboxyethyl acrylate acid, and 2.4752 kg of 1-methoxy-2-propanol were slowly added while mixing using a polytetrafluoroethylene-coated blade. The mixture was heated to 50°C and mixed overnight. The mixture was then transferred into a rotary evaporator and excess water was removed under reduced pressure. The resultant dispersion had a solids content of 49.13 percent.

Preparation of Slurry 2

Into a mixing vessel were mixed 45.000 kg Ceria Dispersion 2, 733.8 grams of DISPERBYK-111 wetting and dispersing additive (available from BYK-Chemie USA, Inc. of Wallingford, CT). To this mixture was added 125.4 grams of 2-hydroxyethyl methacrylate (available from Rohm and Haas Co. of Philadelphia, PA), 317.5 grams of 2-phenoxyethyl acrylate (available as SR 339, from Sartomer Co. or Exton, PA)), 2.435 kg of trimethylolpropane triacrylate (available as SR 351 from Sartomer Co.), 136.6 grams of β-carboxyethyl acrylate (available from Bimax Inc. of Cockeysville, MD), 502.5 grams TERGITOL 15-7-S (available from Sigma Aldrich Inc.,) and 15.07 grams of phenothiazine dissolved in 464.3 grams of 1-methoxy-2-propanol. The mixture was mixed using a polytetrafluoroethylene-coated blade for 30 minutes, and then transferred to a rotary evaporator to remove the 1-methoxy-2-propanol. The slurry was cooled to room temperature, and then 27.0 grams of free-radical photoinitiator (phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide, available as Ciba IRGACURE 819 from Ciba Specialty Chemicals of Tarrytown, NY), 27.0 grams of thermal free-radical initiator (2,2'-azobis(2,4-dimethylvaleronitrile, available as VAZO 52 from E. I. du Pont de Nemours and Co. of Wilmington, DE) and 6.75 grams of hydroquinone monomethyl ether were added, followed by mixing for two hours.

Example 2

A roll of polypropylene production tool, 30 inches (76 cm) in width, was provided. The polypropylene production tool was polypropylene film that had a hexagonal array (350 μm on center) of hexagonal columnar cavities (125 μm wide and 30 micrometers deep), corresponding to a 10 percent cavitation area. The production tool was essentially the inverse of the desired shape, dimensions, and arrangement for the abrasive composites in the ultimate structured abrasive article. SLURRY 2 was coated between the cavities of production tool and roll of translucent polycarbonate/PBT based film backing material (7 mils (0.18 mm) thickness available a BAYFOL CR6-2 from Bayer Corp., Pittsburgh, PA) using a casting roll and a nip roll (nip force of 1300 pounds (5.78 kN)) and then passed through UV light source (V Bulb, Model EPIQ available from Fusion Systems), at a line speed of 10 feet/min (3.0 m/min) and a total exposure of 6000 watts/inch (2.36 kJ/hr-cm). The resultant structured abrasive article (SA2) was removed from the production tool after being UV cured.

SA2 was used to polish thermal oxide blanket wafers (200 mm in diameter with a micrometer film thickness of silicon oxide on its surface) using CMP polisher available under the trade designation REFLEXION polisher from Applied Materials, Inc. of Santa Clara, CA using a wafer pressure of 3.0 lb/in^2 (20.7 kPa), a platen speed of 30 revolutions per minute, and a web index speed of 8 millimeters for 1 minute. The measured removal rate averaged 2011 Å/min for thermal oxide wafers, with an unexpected center fast wafer profile, as shown in the graph above, which provides an option to fine tone the wafer profile to its optimal uniformity by adjusting pressures applying to the wafers.

Comparative Example 1 – Fixed Abrasive Web Without Surfactant

Preparation of Slurry 3

Into a mixing vessel were mixed 45.000 kg Ceria Dispersion 2, 663.3 grams of DISPERBYK-111 wetting and dispersing additive (available from BYK-Chemie USA, Inc. of Wallingford, CT). To this mixture was added 125.4 grams of 2-hydroxyethyl methacrylate (available from Rohm and Haas Co. of Philadelphia, PA), 317.5 grams of 2-phenoxyethyl acrylate (available as SR 339, from Sartomer Co. or Exton, PA)), 2.4354 kg of trimethylolpropane triacrylate (available as SR 351 from Sartomer Co.), 136.6 grams of β-carboxyethyl acrylate (available from Bimax Inc. of Cockeysville, MD), and 15.07 grams of phenothiazine dissolved in 464.3 grams of 1-methoxy-2-propanol. The mixture was mixed using a polytetrafluoroethylene-coated blade for 30 minutes, then transferred to a rotary evaporator to remove the 1-methoxy-2-propanol. The slurry was cooled to room temperature, and then 20.04 grams of free-radical photoinitiator (phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide, available as Ciba IRGACURE 819 from Ciba Specialty Chemicals of Tarrytown, NY), 20.04 grams of thermal free-radical initiator (2,2'-azobis(2,4-dimethylvaleronitrile, available as VAZO 52 from E. I. du Pont de Nemours and Co. of Wilmington, DE) and 5.01 grams of hydroquinone monomethyl ether were added, followed by mixing for two hours.

Comparative Example 1

A roll of polypropylene production tool, 30 inches (76 cm) in width, was provided. The polypropylene production tool was polypropylene film that had a hexagonal array (350 μm on center) of hexagonal columnar cavities (125 μm wide and 30 μm deep), corresponding to a 10 percent cavitation area. The production tool was essentially the inverse of the desired shape, dimensions, and arrangement for the abrasive composites in the ultimate structured abrasive article. Slurry 3 was coated between the cavities of production tool and roll of translucent polycarbonate/PBT based film backing material (7 mils (0.18 mm) thickness available as BAYFOL CR6-2 from Bayer Corp., Pittsburgh, PA) using a casting roll and a nip roll (nip force of 1300 pounds (5.78 kN)) and then passed through UV light source (V Bulb, Model EPIQ available from Fusion Systems), at a line speed of 10 feet/min (3.0 m/min) and a total exposure of 6000 watts/inch (2.36 kJ/hr-cm). The resultant structured abrasive article (SA3) was removed from the production tool after being UV cured.

SA3 was used to polish thermal oxide blanket wafers (200 mm in diameter with a micrometer film thickness of silicon oxide on its surface) using CMP polisher available under the trade designation REFLEXION polisher from Applied Materials, Inc. of Santa

Clara, CA using a wafer pressure of 3.0 lb/in^2 (20.7 kPa), a platen speed of 30 revolutions per minute, and a web index speed of 5 millimeters for 1 minute. The measured removal rate averaged 742 Å/min for thermal oxide wafers, with a typical center slow and edge fast cross wafer profile, which is hard to overcome, as shown in the graph above.

Comparative Example 2 – Fixed Abrasive Web with 3% Surfactant

Preparation of Slurry 4

Into a mixing vessel were mixed 1.0747 kg Ceria Dispersion 2, 15.8 grams of DISPERBYK-111 wetting and dispersing additive (available from BYK-Chemie USA, Inc. of Wallingford, CT). To this mixture was added 3.00 grams of 2-hydroxyethyl methacrylate (available from Rohm and Haas Co. of Philadelphia, PA), 7.58 grams of 2-phenoxyethyl acrylate (available as SR 339, from Sartomer Co. or Exton, PA)), 58.16 grams of trimethylolpropane triacrylate (available as SR 351 from Sartomer Co.), 3.26 grams of β-carboxyethyl acrylate (available from Bimax Inc. of Cockeysville, MD), 18.0 grams TERGITAL 15-7-S (available from Sigma Aldrich Inc.,) and 0.36 grams of phenothiazine dissolved in 20 grams of 1-methoxy-2-propanol. The mixture was mixed using a polytetrafluoroethylene-coated blade for 30 minutes, and then transferred to a rotary evaporator to remove the 1-methoxy-2-propanol. The slurry was cooled to room temperature, and then 0.65 grams of free-radical photoinitiator (phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide, available as IRGACURE 819 from Ciba Specialty Chemicals of Tarrytown, NY), 0.65 grams of thermal free-radical initiator (2,2’-azobis(2,4-dimethylvaleronitrile, available as VAZO 52 from E. I. du Pont de Nemours and Co. of Wilmington, DE) and 0.16 grams of hydroquinone monomethyl ether were added, followed by mixing for two hours.

A roll of polypropylene production tool, 30 inches (76 cm) in width, was provided. The polypropylene production tool was polypropylene film that had a hexagonal array (350 micrometers on center) of hexagonal columnar cavities (125 micrometers wide and 30 micrometers deep), corresponding to a 10 percent cavitation area. The production tool was essentially the inverse of the desired shape, dimensions, and arrangement for the abrasive composites in the ultimate structured abrasive article. Slurry 4 was coated between the cavities of production tool and roll of translucent polycarbonate/PBT based film backing material (7 mils (0.18 mm) thickness available a BAYFOL CR6-2 from Bayer Corp., Pittsburgh, PA) using a casting roll and a nip roll (nip force of 1300 pounds (5.78 kN)) and then passed through UV light source (V Bulb, Model EPIQ available from Fusion Systems), at a line speed of 10 feet/min (3.0 m/min) and a total exposure of 6000 watts/inch (2.36 kJ/hr-cm). The resultant structured abrasive article (SA4) was removed from the production tool after being UV cured.

SA4 was used to polish thermal oxide blanket wafers (200 mm in diameter with a micrometer film thickness of silicon oxide on its surface) using CMP polisher available under the trade designation REFLEXION polisher from Applied Materials, Inc. of Santa Clara, CA using a wafer pressure of 3.0 lb/in^2 (20.7 kPa), a platen speed of 30 revolutions per minute, and a web index speed of 8 millimeters for 1 minute. The film was found to fall apart during the polish, and was unable to polish the wafers.

Comparative Example 3 – Surfactant Added to Polish Fluid

SA3 was used to polish thermal oxide blanket wafers (200 mm in diameter with a micrometer film thickness of silicon oxide on its surface) using CMP polisher available under the trade designation REFLEXION polisher from Applied Materials, Inc. of Santa Clara, CA using a wafer pressure of 3.0 lb/in^2 (20.7 kPa), a platen speed of 30 revolutions per minute, and a web index speed of 5 millimeters for 1 minute. An amount of TERGITOL was added the polish fluid equivalent to that in the FA web in Example 2, based on the calculations. The measured removal rate averaged 793 Å/min for thermal oxide wafers, with a typical center slow and edge fast cross wafer profile as shown in Fig. 3.

The removal rates of the Examples and Comparative Examples are displayed in Table 1.

Table 1

Removal Rate on Thermal Oxide Wafers

Examples	**Surfactant**	**Removal Rate (A/min)**
Example 1	Tergitol at 1 % based on total (Resin + Abrasive)	1625
Example 2	Tergitol at 2 % based on total (Resin + Abrasive)	2011
Comparative 1	None	742
Comparative 2	Tergitol at 3 % based on total (Resin + Abrasive)	Fixed abrasive film fall apart during polishing
Comparative 3	Tergitol added into polish fluid	793

Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows. All references cited in this disclosure are herein incorporated by reference in their entirety.

What is claimed is:

1. A structured abrasive article comprising:

a backing having first and second opposed major surfaces;

a structured abrasive layer disposed on and secured to the first major surface wherein the structured abrasive layer comprises:

a polymeric binder;

abrasive particles dispersed in the binder; and

a nonionic polyether surfactant dispersed in the binder,

wherein the abrasive particles have a mean particle size of less than about 200 nm, wherein the nonionic polyether surfactant is not covalently bound to the crosslinked polymeric binder, and

wherein the nonionic polyether surfactant is present in an amount of from 0.75 to 2.2 percent by weight based on a total weight of the structured adhesive layer.

2. A structured abrasive article according to claim 1, wherein the nonionic polyether surfactant is present in an amount of from 1.0 to 2.2 percent by weight based on a total weight of the structured adhesive layer.

3. A structured abrasive article according to claim 1, wherein the shaped abrasive composites are precisely-shaped.

4. A structured abrasive article according to claim 1, wherein the crosslinked polymeric binder comprises an acrylic polymer.

5. A structured abrasive article according to claim 1, wherein the surfactant comprises a polyethylene oxide segment.

6. A structured abrasive article according to claim 1, wherein the surfactant comprises a polypropylene oxide segment.

7. A structured abrasive article according to claim 1, wherein the shaped abrasive composites further comprise an anionic phosphate polyether ester, and
wherein the anionic phosphate polyether ester is present in an amount by weight that is less than that of the nonionic polyether surfactant.

8. A structured abrasive article according to claim 1, wherein the backing comprises a polymer film.

9. A structured abrasive article according to claim 8, wherein the polymer film comprises an elastomeric polyurethane.

10. A structured abrasive article according to claim 1, wherein the backing comprises a polymer foam.

11. A structured abrasive article according to claim 1, further comprising an attachment interface layer directly bonded to the second major surface.

12. A structured abrasive article according to claim 11, wherein the attachment interface layer comprises a pressure-sensitive adhesive disposed on the second major surface.

13. A structured abrasive article according to claim 11, wherein the attachment interface layer comprises a looped fabric.

14. A method of abrading a workpiece comprising:

frictionally contacting at least a portion of a structured abrasive article with a surface of a workpiece while in the presence of an aqueous fluid; and

moving at least one of the workpiece or the structured abrasive layer relative to the other to abrade at least a portion of the surface of the workpiece,

wherein the structured abrasive article comprises:

a backing having first and second opposed major surfaces; and a structured abrasive layer disposed on and secured to the first major surface wherein the structured abrasive layer comprises:

a polymeric binder;

abrasive particles dispersed in the binder; and

a nonionic polyether surfactant dispersed in the binder,

wherein the abrasive particles have a mean particle size of less than about 200 nm, wherein the nonionic polyether surfactant is not covalently bound to the crosslinked polymeric binder, and

wherein the nonionic polyether surfactant is present in an amount of from 0.75 to 2.2 percent by weight based on a total weight of the structured adhesive layer.

15. A method of abrading a workpiece according to claim 14, wherein the workpiece is an oxide wafer.

16. A method of abrading a workpiece according to claim 14, wherein the workpiece comprises silicon.

17. A method of abrading a workpiece according to claim 14, wherein the aqueous fluid comprises tap water.

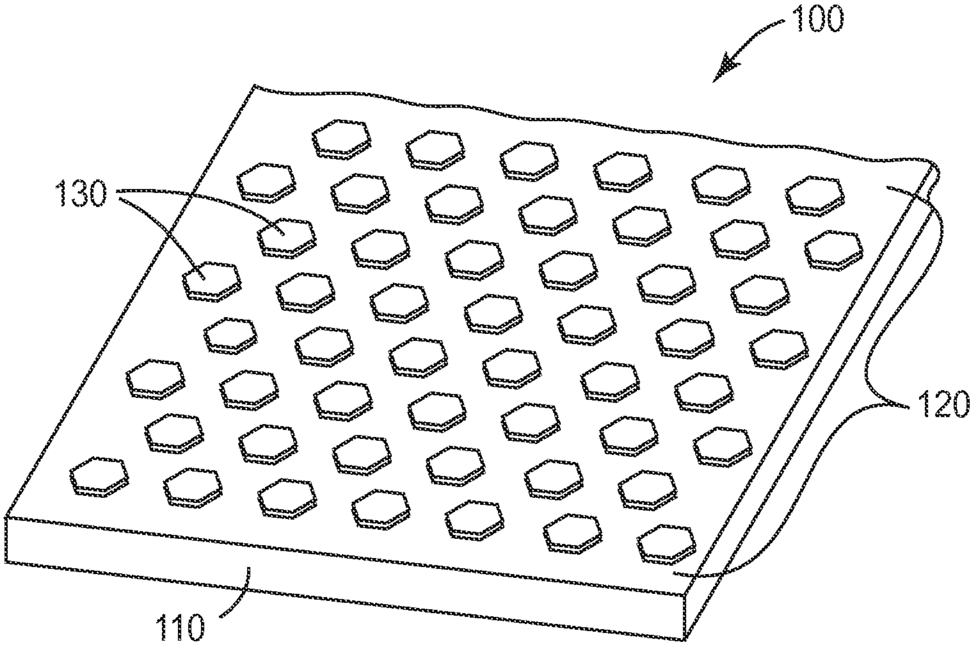
100
130
120
110

FIG. 1

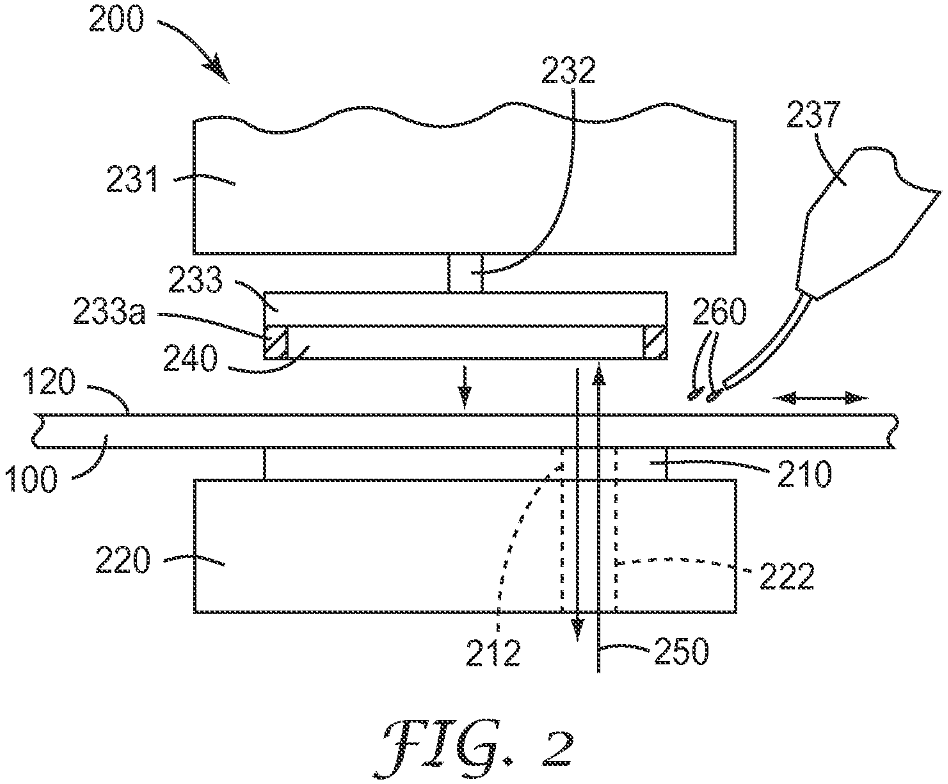
200
232
237
231
233
233a
260
240
120
100
210
220
222
212
250

FIG. 2

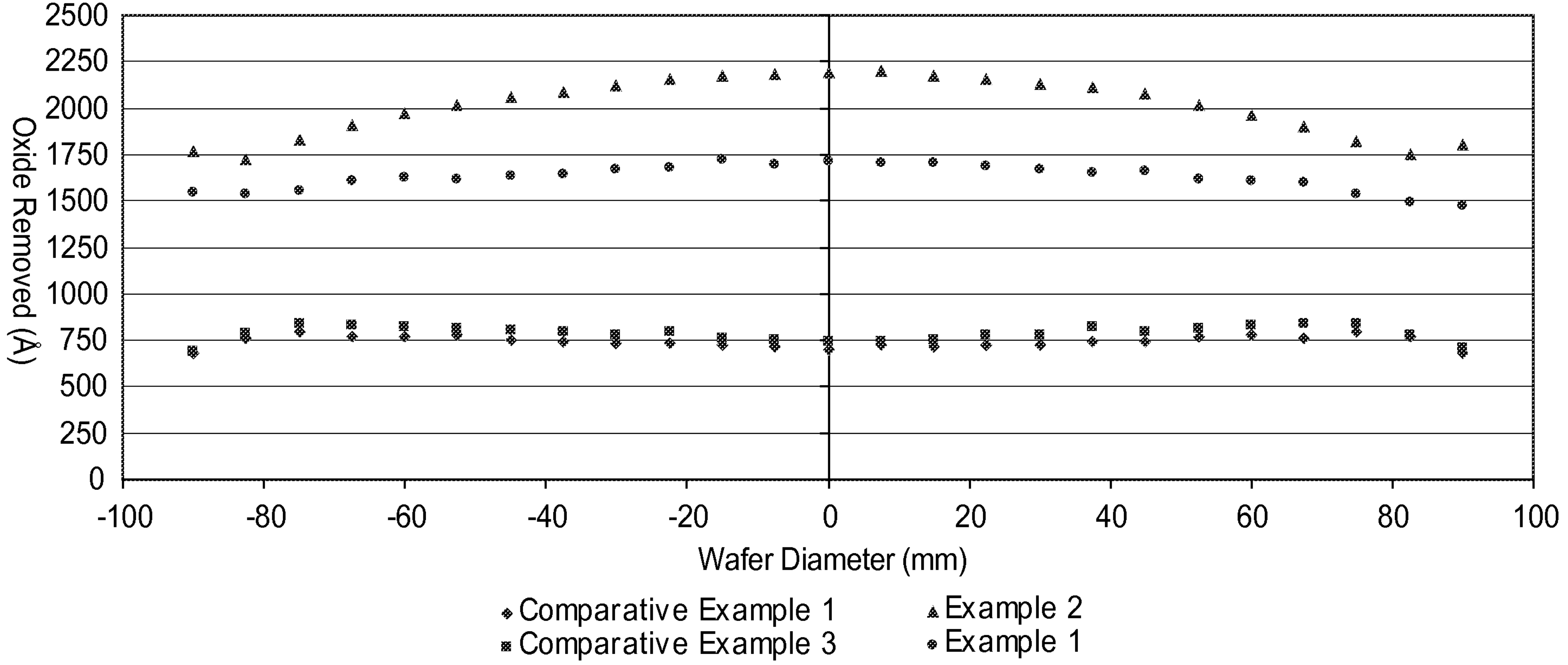
Oxide Removed (Å)
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
-100
-80
-60
-40
-20
0
20
40
60
80
100
Wafer Diameter (mm)
◆ Comparative Example 1
▨ Comparative Example 3
▲ Example 2
● Example 1

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/034439

A. CLASSIFICATION OF SUBJECT MATTER
INV. B24D3/34 B24B37/24 B24B37/26
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B24B B24D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/112909 A1 (SAINT GOBAIN ABRASIVES INC [US]; GAETA ANTHONY C [US]; YOU XIAORONG [U) 26 October 2006 (2006-10-26) figure 1 page 3, line 6 - page 6, line 23 page 16, line 7 - line 9 page 18, line 17 - line 18 page 19, line 25 - page 20, line 10 page 25, line 33 - page 26, line 4 -----	1-17
A	US 2002/026752 A1 (CULLER SCOTT R [US] ET AL) 7 March 2002 (2002-03-07) paragraphs [0002], [0094], [0106], [0118], [0135] ----- -/--	1,3-5, 8-13

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search 23 August 2011	Date of mailing of the international search report 30/08/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Endres, Mirja

1

International application No
PCT/US2011/034439

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/176443 A1 (KOLLODGE JEFFREY S [US] ET AL) 9 July 2009 (2009-07-09) figures 1,2 paragraphs [0002], [0005] - [0008], [0079], [0080] -----	1,3,4,8, 11,12, 14-17
X,P	WO 2011/034635 A1 (3M INNOVATIVE PROPERTIES CO [US]) 24 March 2011 (2011-03-24) the whole document -----	1-17

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/034439

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006112909 A1	26-10-2006	AR 052367 A1	14-03-2007
		AT 477084 T	15-08-2010
		AU 2006237653 A1	26-10-2006
		BR PI0608177 A2	17-11-2009
		CA 2603275 A1	26-10-2006
		CN 101175608 A	07-05-2008
		DK 1868770 T3	22-11-2010
		EP 1868770 A1	26-12-2007
		ES 2349429 T3	03-01-2011
		JP 2008537911 A	02-10-2008
		KR 20070121841 A	27-12-2007
		NZ 562513 A	29-10-2010
		RU 2374062 C2	27-11-2009
US 2002026752 A1	07-03-2002	NONE	
US 2009176443 A1	09-07-2009	WO 2010085587 A1	29-07-2010
WO 2011034635 A1	24-03-2011	US 2011065362 A1	17-03-2011