

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
16 July 2009 (16.07.2009)

PCT

(10) International Publication Number  
**WO 2009/088945 A1**

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

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(21) International Application Number:  
PCT/US2008/088669

(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, 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, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(22) International Filing Date:  
31 December 2008 (31.12.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
61/017,872 31 December 2007 (31.12.2007) US

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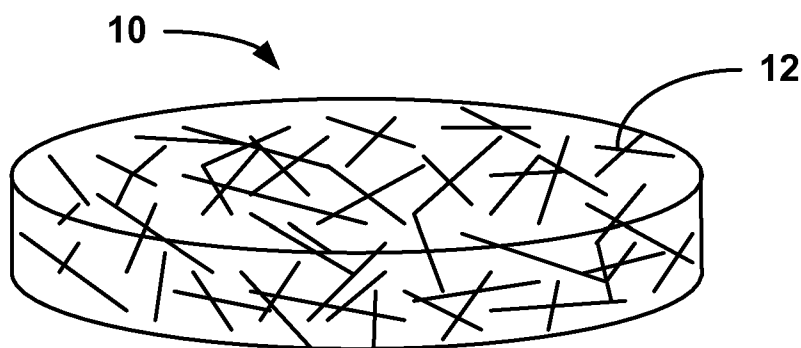
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT,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

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Published:  
— with international search report

(54) Title: CHEMICAL-MECHANICAL PLANARIZATION PAD



**FIG. 1**

(57) Abstract: The present disclosure relates to a polishing pad including a chemical agent present in an amount sufficient to be released and dissolving into an aqueous abrasive particle polishing medium during chemical mechanical planarization and reducing abrasive particle agglomeration and a binder. The pad includes a surface such that as the pad is abraded the surface is renewed exposing at least a portion of the chemical agent.

## CHEMICAL-MECHANICAL PLANARIZATION PAD

### Cross-Reference to Related Applications

This application claims the benefit of U.S. Provisional Patent Application Serial No.  
5 61/017,872, filed on December 31, 2007, which is fully incorporated herein by reference.

### Field of Invention

The present invention relates to a chemical-mechanical planarization pad and, in particular, a chemical-mechanical planarization pad incorporating chemical agents.

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### Background

Various chemicals are used in chemical-mechanical planarization (CMP) to enhance, stabilize and control the process of planarizing semiconductor substrates. Oxidizing agents such as hydrogen peroxide and monopersulfates may be used with ferric nitrate in the  
15 presence of an abrasive for CMP applications on metal polish. Alkaline solutions such as potassium hydroxide and ammonium hydroxide may be used to hydrolyze the silicon dioxide layer in a semiconductor wafer to facilitate mechanical abrasion and removal. In addition, carboxylic acid, nitrate salt and soluble cerium may be used to affect high removal rate of a silicon dioxide film and slow removal rate of the underlying silicon nitride film thus  
20 preventing erosion of the silicon nitride film.

Other classes of chemicals used in CMP may include surfactants and corrosion inhibitors. Polyvinyl alcohol (PVOH), for example, may be added for stabilizing abrasive particles thus preventing their agglomeration. Polyethylene glycol and sodium dodecylbenzenesulfone may likewise be utilized as a dispersant. Furthermore, triazole  
25 compounds, may be used as corrosion inhibitors in copper polish.

### Summary

An aspect of the present disclosure relates to a polishing pad. The polishing pad may include a binder and a chemical agent, which chemical agent is present in an amount sufficient to be released and dissolving into an aqueous abrasive particle polishing medium during chemical mechanical planarization and reducing abrasive particle agglomeration. The pad may also include a surface and as the pad is abraded, the surface may be renewed exposing at least a portion of the chemical agent.

A further aspect of the present disclosure relates to a method of forming a polishing pad. The method may include combining a chemical agent into a binder wherein the chemical agent is present in an amount sufficient to be released and dissolve into an aqueous abrasive particle polishing medium during chemical mechanical planarization and reducing abrasive particle agglomeration. In addition, the method may include forming the binder and chemical agent into a chemical mechanical planarization polishing pad.

Yet a further aspect of the present disclosure relates to a method of polishing with a polishing pad. The method may include contacting a polishing pad having a surface with a substrate. The pad may include a chemical agent combined into a binder wherein the chemical agent may be present in an amount sufficient to be released and dissolve into an aqueous abrasive particle polishing medium during chemical mechanical planarization and reducing abrasive particle agglomeration. The method may also include abrading the pad and exposing at least a portion of the chemical agent.

### Brief Description of Drawings

The above-mentioned and other features of this disclosure, and the manner of attaining them, will become more apparent and better understood by reference to the following description of embodiments described herein taken in conjunction with the accompanying drawings, wherein:

**FIG. 1** illustrates an example of a CMP pad contemplated herein.

**FIG. 2** illustrates another example of a CMP pad contemplated herein.

**FIG. 3** illustrates a further example of a CMP pad contemplated herein.

### Detailed Description

The present invention relates to a CMP pad and its method of use via the aspect of incorporating one or more organic chemicals and/or polymers into the CMP pad for releasing into the polishing medium during chemical mechanical polishing. Such release may then enhance, stabilize and/or control the process of planarization of semiconductor substrates.

Various chemical agents, including but not limited to those mentioned herein, may be incorporated into a CMP pad. The incorporation of the chemical agents in the CMP pad may be achieved through dispersion of the agent in liquid or solid particle form in the pad material during manufacture. In addition, the agent may be applied to one or more of the individual components of the pad prior to pad manufacture.

One example of a CMP pad, illustrated in **FIG. 1**, may include coating a chemical agent known as polyvinyl alcohol (PVOH) onto the surface of a three-dimensional network of polymeric fibers **12** (component 1), before mixing component 1 with a binder resin such as polyurethane pre-polymer (component 2) to form a CMP pad **10**. It may be appreciated herein that the poly(vinyl alcohol) may be selected with varying levels of alcohol (-OH) functionality, i.e., percentage of hydrolysis, and/or varying molecular weights (number average), thereby presenting varying levels of solubility in, e.g., aqueous based polishing media. In some examples, the poly(vinyl alcohol) may exhibit greater than 50 % hydrolysis of the poly(vinyl acetate) precursor, including all values and increments in the range of 50 to 99.9 % hydrolysis, such as 75% to 99.9% hydrolysis, etc. In addition, the molecular weight may vary in the range of 10,000 to 500,000, including all values and increments therein, such as 100,000 to 300,000, etc. The coated polymeric fibers may then be mixed in the polyurethane pre-polymer during the manufacturing process. The polymeric fibers **12** may include soluble or insoluble fibers, which may be coated with polyvinyl alcohol during the fiber forming process or after the fiber forming process. Solubility may be understood as the ability of the fibers to at least partially or completely dissolve in an aqueous solution.

As alluded to above, during processing, the polyvinyl alcohol coating on the fibers may then be dissolved and dispersed in a given aqueous abrasive medium during CMP to prevent and/or reduce the agglomeration of the abrasive particles, which may reduce scratching defects on the semiconductor wafer. In addition, it may be appreciated that where the fibers themselves are soluble or made selectively soluble in a given slurry environment,

the fibers may also dissolve upon exposure to the aqueous abrasive medium. The rate of release of the polyvinyl alcohol into the aqueous abrasive medium may be controlled, if desired, by the amount of coating, thickness of the coating and/or coating weight and/or the number of fibers exposed on the pad surface during CMP. This may be the case as the  
5 polyvinyl alcohol may only dissolve into the aqueous abrasive medium upon exposure to such medium.

Another example of a CMP pad, illustrated in **FIG. 2**, may include mixing polyvinyl alcohol in liquid or particle form into component 2, the polyurethane pre-polymer. As illustrated, the polyvinyl alcohol may form discrete domains **24** within the CMP pad **20**.  
10 During processing of the pad, the exposed polyvinyl alcohol on the pad surface may be dissolved, while the remaining unexposed polyvinyl alcohol may be kept within the bulk of the pad. As the pad is abraded during the CMP process, fresh surfaces may be exposed. Thus new or previously un-exposed polyvinyl alcohol may be dissolved and released into the aqueous abrasive medium. As in the above embodiment, the release of the polyvinyl alcohol  
15 may be controlled by the amount of the polyvinyl alcohol mixed into component 2 and the wear or abrasion rate of the pad.

A third example, illustrated in **FIG. 3**, may include using polyvinyl alcohol as the only ingredient to provide component 1. A three-dimensional network of polyvinyl alcohol fibers and/or particles **34** of polyvinyl alcohol may then be mixed with component 2  
20 (described above) in the CMP pad **30** during the manufacturing process. Again, the rates of dissolution and release of polyvinyl alcohol may be controlled by the size of the three-dimensional network or weight of the polyvinyl alcohol particles in the pad.

It may be appreciated that in additional embodiments the chemical agents incorporated into a CMP pad may not have to dissolve and release into the aqueous abrasive  
25 medium. One or more chemical agents may therefore be maintained as relatively captive or stationary on the pad surface during CMP procedures. Such agents may also play a beneficial role to CMP performance. For example, a captive or stationary chemical agent on a pad surface may be utilized to impart a desired level of hydrophilicity or hydrophobicity to the pad surface. Hydrophilicity or hydrophobicity may be understood as the affinity of a  
30 substance to water, which may be indicated by, for example, the contact angle of water on a surface. In some examples, a contact angle of greater than 90 ° may indicate a relatively

hydrophobic material and contact angles of 90 ° or less may indicate a relatively hydrophilic material.

An example of imparting hydrophilicity or hydrophobicity to the pad surface may include incorporating a surface wetting agent such as an organic ester of a carboxylic acid, such as an organic ester of stearic acid, which may provide hydrophilicity to the pad and facilitate contact between the aqueous abrasive medium, the pad and the semiconductor. Various methods may be used to incorporate such a hydrophilic or hydrophobic chemical agent into a CMP pad, including, but not limited to, chemical and/or irradiation grafting, and/or mixing a hydrophilic or hydrophobic chemical agent into one or more components of the pad.

In addition, as noted above oxidizing agents such as hydrogen peroxide and monopersulfates may be used with ferric nitrate in the presence of an abrasive for CMP applications on metal polish. Alkaline solutions such as potassium hydroxide and ammonium hydroxide may be used to hydrolyze the silicon dioxide layer in a semiconductor wafer to facilitate mechanical abrasion and removal. In addition, carboxylic acid, nitrate salt and soluble cerium may be used to affect high removal rate of a silicon dioxide film and slow removal rate of the underlying silicon nitride film thus preventing erosion of the silicon nitride film.

Other classes of chemicals used in CMP may include surfactants and corrosion inhibitors. Polyvinyl alcohol (PVOH), for example, may be added for stabilizing abrasive particles thus preventing their agglomeration. Polyethylene glycol and sodium dodecylbenzenesulfone may likewise be utilized as a dispersant. Furthermore, triazole compounds, may be used as corrosion inhibitors in copper polish.

The chemical agents herein may be present in a range of about 0.1 to 50.0 % by volume of the CMP pad, including all values and increments therein in 1.0% increments. In addition, the chemical agents may be localized to certain regions of the pad to provide a localized relative concentration. For example, the chemical agent may be provided to a core portion of the pad and/or to outer regions of the pad. Furthermore, the chemical agents may be dispersed relatively uniformly throughout the pad, wherein a given and relatively constant volume fraction of the chemical agent may be present throughout.

The method of use of the CMP pad in polishing a semiconductor substrate in the presence of an abrasive-containing or abrasive-free liquid medium may include placing the semiconductor substrate, pad and liquid medium in CMP polishing equipment. The polishing equipment may control one or more process parameters such as polishing time, pressure, temperature, relative speed of the pad on the substrate and flow rate of the liquid medium, etc. The results of CMP processes may be expressed in terms of polish or removal rate, uniformity of removal throughout the substrate surface (Within-Wafer-Non-Uniformity, WIWNU), planarity (Planarization Efficiency), Defectivity on the substrate surface, and useful life of the CMP pad.

The foregoing description of several methods and embodiments has been presented for purposes of illustration. It is not intended to be exhaustive or to limit the claims to the precise steps and/or forms disclosed, and obviously many modifications and variations are possible in light of the above teaching. It is intended that the scope of the invention be defined by the claims appended hereto.

## CLAIMS

1. A polishing pad, comprising:  
  
a chemical agent present in an amount sufficient to be released and dissolving into an aqueous abrasive particle polishing medium during chemical mechanical planarization  
5 and reducing abrasive particle agglomeration; and  
  
a binder, formed into the pad, wherein said pad includes a surface and wherein as said pad is abraded, the surface is renewed exposing at least a portion of said chemical agent.
2. The polishing pad of claim 1 wherein said chemical agent comprises poly(vinyl  
10 alcohol) sourced from poly(vinyl acetate) and exhibits greater than 50% hydrolysis of said poly(vinyl acetate) precursor wherein said poly(vinyl alcohol) is present in a range of 0.1 to 50.0 % by volume of said pad.
3. The polishing pad of claim 1 wherein the chemical agent forms a three-dimensional network within the pad.
- 15 4. The polishing pad of claim 1, wherein said chemical agent is coated on fibers.
5. The polishing pad of claim 3, wherein said fibers are soluble.
6. The polishing pad of claim 3, wherein said fibers are insoluble.
7. The polishing pad of claim 1, wherein said chemical agent comprises particles dispersed within said pad.
- 20 8. The polishing pad of claim 2, wherein said polyvinyl alcohol comprise fibers.
9. The polishing pad of claim 1, including a second chemical agent that does not dissolve in said aqueous abrasive particle polishing medium and wherein said second chemical agent imparts a desired level of hydrophobicity or hydrophilicity to said pad surface.
- 25 10. The polishing pad of claim 1, wherein said chemical agent is localized to a region of the pad providing a localized relative concentration.



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

combining a chemical agent into a binder wherein said chemical agent is present in an amount sufficient to be released and dissolve into an aqueous abrasive particle polishing medium during chemical mechanical planarization and reducing abrasive particle agglomeration; and

forming said binder and chemical agent into a chemical mechanical planarization polishing pad.

12. The method of claim 11 wherein said chemical agent comprises poly(vinyl alcohol) sourced from poly(vinyl acetate) and exhibits greater than 50% hydrolysis of said poly(vinyl acetate) precursor wherein said poly(vinyl alcohol) is present in a range of 0.1 to 50.0 % by volume of said pad.

13. The method of claim 11 wherein the chemical agent forms a three-dimensional network within the pad.

14. The method of claim 11, wherein said chemical agent is coated on fibers.

15. The method of claim 14, wherein said fibers are soluble.

16. The method of claim 14, wherein said fibers are insoluble.

17. The method of claim 11, wherein said chemical agent comprises particles dispersed within said pad.

18. The method of claim 12, wherein said polyvinyl alcohol comprise fibers.

19. The method of claim 11, including a second chemical agent that does not dissolve in said aqueous abrasive particle polishing medium and wherein said second chemical agent imparts a desired level of hydrophobicity or hydrophilicity to said pad surface.

20. The method of claim 11, wherein said chemical agent is localized to a region of the pad providing a localized relative concentration.

21. A method of polishing with a polishing pad, comprising:

contacting a polishing pad having a surface with a substrate,;

said pad comprising a chemical agent combined into a binder wherein said chemical agent is present in an amount sufficient to be released and dissolve into an aqueous

5 abrasive particle polishing medium during chemical mechanical planarization and reducing abrasive particle agglomeration; and

abrading said pad and exposing at least a portion of said chemical agent.

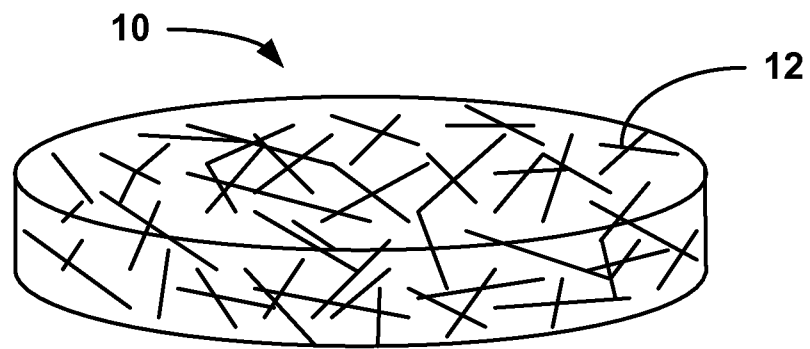


FIG. 1

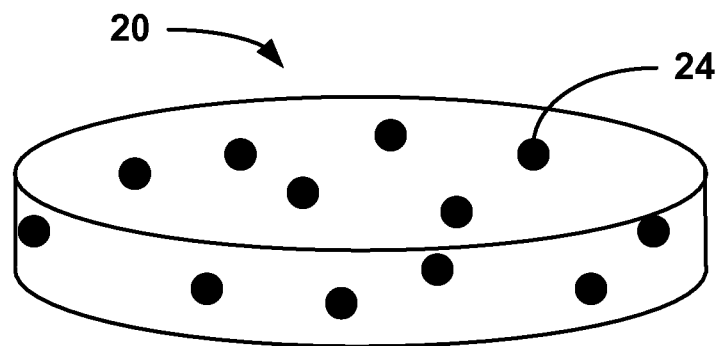
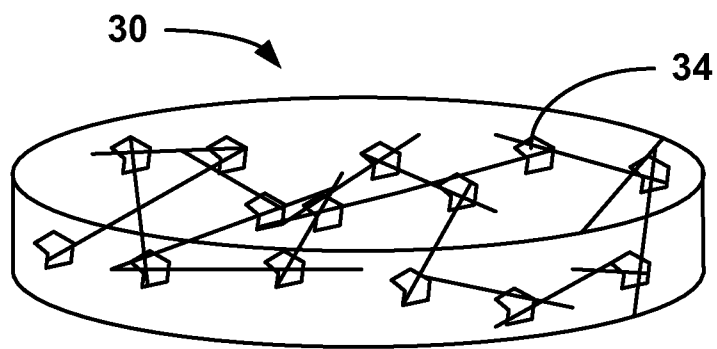


FIG. 2

**FIG. 3**

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 08/88669

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B24B 37/04 (2009.01)

USPC - 257/E21.304; 438/692, 693

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)

257/E21.304; 438/692, 693

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

257/E21.304; 438/692, 693 - text limited

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

PubWest (DB=PGPB,USPT,USOC,EPAB,JPAB), Google Scholar

Search terms: polishing pad, substrate, chemical agent, polyvinyl alcohol, fiber

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/0153643 A1 (Simpson et al.) 14 July 2005 (14.07.2005) see entire doc, esp Abstract	1, 3, 7, 10, 11, 13, 17, 20, 21
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Y		2, 4-6, 8, 9, 12, 14-16, 18, 19
Y	US 2007/0224806 A1 (Yamashita) 27 September 2007 (27.09.2007) para [0040]	2, 8, 12, 18
Y	US 2005/0133363 A1 (Hu et al.) 23 June 2005 (23.06.2005) para [0018]	4-6, 8, 14-16, 18
Y	US 2007/0202702 A1 (Fu Chen et al.) 30 August 2007 (30.08.2007) para [0030]	9, 19

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

\* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

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"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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

08 February 2009 (08.02.2009)

Date of mailing of the international search report

23 FEB 2009

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