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

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
5 April 2001 (05.04.2001)

PCT

(10) **International Publication Number**
WO 01/23486 A1

(51) **International Patent Classification**⁷: C09G 1/02, H01L 21/3105

(21) **International Application Number:** PCT/US00/24342

(22) **International Filing Date:** 5 September 2000 (05.09.2000)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
09/409,464 30 September 1999 (30.09.1999) US

(71) **Applicants: INFINEON TECHNOLOGIES NORTH AMERICA CORP.** [US/US]; 1730 North First Street, San Jose, CA 95112-4508 (US). **INTERNATIONAL BUSINESS MACHINES CORPORATION** [US/US]; New Orchard Road, Armonk, NY 10504 (US).

(72) **Inventors: NOJO, Haruki**; 236 Townview Drive, Wappingers Falls, NY 12590 (US). **SCHUTZ, Ronald, J.**; Box 1312 Reservoir Drive, Millbrook, NY 12545 (US). **RAMACHANDRAN, Ravikumar**; First floor, 12 1/2 Eldrige Avenue, Ossining, NY 10562 (US).

(74) **Agents: BRADEN, Stanton, C.** et al.; Siemens Corporation, Intellectual Property Dept., 186 Wood Ave. South, Iselin, NJ 08830 (US).

(81) **Designated States** *(national)*: CN, JP, KR.

(84) **Designated States** *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/23486 A1

(54) **Title:** COMPOSITIONS FOR AND METHODS OF REDUCING/ELIMINATING SCRATCHES AND DEFECTS IN SILICON DIOXIDE CMP PROCESS

(57) **Abstract:** An aqueous slurry-less composition for chemical-mechanical-polishing of a silicon dioxide workpiece comprising: a cationic surfactant that is soluble and ionized at neutral to alkaline pH conditions, in which the cationic surfactant is present in an aqueous slurry-less composition in an amount less than its critical micelle concentration.

COMPOSITIONS FOR AND METHODS OF REDUCING/ELIMINATING SCRATCHES AND DEFECTS IN SILICON DIOXIDE CMP PROCESS

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The invention relates to the use of cationic surfactants in slurry-less environments during chemical mechanical polishing (CMP) of silicon dioxide wafer surfaces to substantially eliminate or reduce scratches and defects produced during the CMP process.

Certain categories of cationic surfactants chemisorb onto the silicon dioxide portion of the wafer during VLSI processing under all pH conditions, namely, acidic, neutral and basic pHs.

2. DESCRIPTION OF THE PRIOR ART

In recent years new chemical mechanical polishing (CMP) techniques have come into use that use a slurry-less polishing scheme for silicon wafer surfaces where the polishing pad has abrasive particles embedded therein. In particular, the polishing pad contains CeO_2 as the abrasive material for silicon dioxide CMP applications.

During the CMP process, the wafer to be polished is abraded against the pad surface in an aqueous environment. However, during the CMP process at neutral or alkaline conditions these polishing pads produce defects and scratches, thereby causing yield losses.

Accordingly, it is desirable to devise compositions for and methods of, protecting the surface of silicon dioxide wafers from scratches and defects occasioned by abrasion during the slurry-less CMP process.

Somasundaran et al. "Surfactant adsorption at the solid-liquid interface Dependence of mechanism of chain length", J. Phys. Chem., Vol.68, pp.3562-3566 (1964), disclose that:

a) the concentration of surfactant required to neutralize the surface charge on silica decreases with increasing chain length; and

b) from the critical concentration to neutralize the surface charge (as observed indirectly from a zero zeta-potential measurement for silica particles in an aqueous solution), the van der Waals energy scales is 0.97 kT per CH_2 group or 580 cal/mole.

On the basis of the Somasundaran et al., reference it would appear that there is a lateral hydrophobic bonding between the alkyl chains that are adsorbed on the silica surface.

US Patent 5,769,689 discloses compositions for a method of polishing a workpiece comprised of silicon dioxide wherein the surface of the workpiece is exposed to a polishing composition comprising water, submicron SiO_2 particles, a soluble inorganic salt at a concentration below the critical coagulation concentration for the composition, and wherein the pH of the composition is adjusted to within a range of about 9-10 by the addition of a soluble amine.

Kumar et al., "CHEMICAL-MECHANICAL POLISHING OF COPPER IN GLYCEROL BASED SLURRIES", Mat. Res. Soc. Symp. Proc. Vol. 427, pps. 237-242 (1996), discloses the use of a slurry containing glycerol and Al_2O_3 abrasive for CMP processing of a copper metal surface to render the copper suitable as an interconnect fabrication. The process is an alternative to reactive ion etching of copper.

A chemical-mechanical polishing technique for LSI's to address the problem of dishing is disclosed in U.S. Patent 5,607,718, in which a number of compounds are added to decrease the solution velocity and suppress dishing. These compounds include a number of thickeners such as silicates, glucose, tragacanth gum and agar.

Nojo et al., "SLURRY ENGINEERING FOR SELF-STOPPING, DISHING FREE SiO_2 - CMP", IEDM, pages 349-352, © 1996 IEEE, disclose a slurry in which a surfactant was added to a conventional CeO_2 slurry for SiO_2 in chemical mechanical polishing (CMP) to obtain global planarization within a chip without any stopping layer or design limitations.

U.S. Patent 4,588,474 discloses a cleaning treatment on a metal surface wherein glycerin is added to the solution along with other additives to obtain a smoother and more uniform surface. These solutions contain a caustic, a nitrate or nitrite, and optionally, a diol or polyol such as ethylene glycol or glycerin, and the workpiece is an aluminum alloy.

An electrochemical polishing technique for metal removal and planarization of various components in various stages of microelectronic fabrication is disclosed in U.S. Patent 5,567,300. This patent is directed to feature removal, and uses a non-viscous polyol to enhance removal. Glycerin, which has a viscosity at room temperature of 1500 times that of water, is used in electroetching to increase the electrolyte viscosity and promote polishing.

A significant disadvantage of the processes in the foregoing patent and literature references is that, there is no acknowledgment of the need to improve defect control of silicon dioxide chemical mechanical polishing (CMP) in a slurry-less system through chemistry modifications to the aqueous medium.

SUMMARY OF THE INVENTION

One object of the present invention is to provide improved defect control of silicon dioxide during chemical mechanical polishing in a slurry-less system to reduce or eliminate polishing related scratches and defects.

Another object of the present invention is to provide improved defect control of silicon dioxide during chemical mechanical polishing in a slurry-less system by the addition of specific kinds of cationic surfactants that chemisorb onto silica surfaces under neutral and alkaline pH conditions.

A further object of the present invention is to provide improved defect control of silicon dioxide during chemical mechanical polishing in a slurry-less system by addition to the slurry-less system of cationic surfactants selected from the group that would produce the cationic ion from the group consisting of:

Alkyl-trimethyl-ammonium halides; alkyl-benzyl-dimethyl-ammonium halides; pyridinium-alkyl halides; alkyl-ammonium esters; and mixtures thereof. The aniomic group could be varied to obtain the respective cationic surfactant ion.

In general, the invention is accomplished by the addition of cationic surfactants selected from the group of: alkyl-trimethyl ammonium halides; akyl-benzyl-dimethyl-ammonium halides; pyridinium-alkyl halides; alkyl-ammonium esters, and mixtures thereof, in a slurry-less system, prior to chemical mechanical polishing of silicon dioxide wafers at neutral or alkaline pH conditions, in amounts below the critical micelle concentration (the concentration beyond which surfactants tend to self-aggregate) or less than 0.1 mole/L.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the effect of hydrocarbon chain length on the zero-potential of quartz in solutions of alkylammonium acetates and in solutions of ammonium acetate.

DETAILED DESCRIPTION OF THE INVENTION

The foregoing and other objects and advantages of the invention will be better understood by resort to the following detailed description of the preferred embodiments of the invention.

To protect or provide improved defect control of silicon dioxide wafers during chemical mechanical polishing (CMP) in a slurry-less system, the addition of certain kinds of cationic surfactants were added to reduce polishing scratches and defects. These cationic surfactants chemisorb onto the silica surfaces at neutral and alkaline pH conditions, thereby protecting the wafer surface from polish scratches and defects. The wafer to be polished is abraded against the pad surface and typically, the pads contain CeO_2 as the abrasive material, which is embedded therein.

In the tooling system employed for chemical mechanical polishing, an aqueous solution that is either neutral or alkaline is used for polishing, and while not wishing to be bound by any theory of how the invention works, it is believed that the addition of cationic surfactants chemisorbs onto the silica surface to affect interaction coupling between the silica surface and the positively charged head group.

The four classes of cationic surfactants useful in the context of the invention are selected from the group consisting of: 1) alkyl-trimethyl-ammonium halides, having an alkyl length of C_6-C_{18}, amongst which, hexadecyl-trimethyl-ammonium bromide is preferred; 2) alkyl-benzyl-dimethyl-ammonium halides, having an alkyl length of C_6-C_{18}, of which hexadecyl-benzyl-dimethyl-ammonium bromide and dodecyl-benzyl-dimethyl-ammonium bromide are preferred; 3) pyridinium-alkyl halides, having an alkyl group of C_6-C_{18}, of which cetyl-pyridinium-chloride is preferred; and 4) alkyl-ammonium esters, having an alkyl group from C_6-C_{18}, of which dodecylammonium acetate is preferred; and mixtures thereof.

In the context of the invention, mixtures of the cationic surfactants may be utilized to form a composite solution. Alternatively, mixtures of surfactants, of which one or more of the four classes of cationic surfactants are present in predominate amount may be mixed with small amounts of anionic and/or nonionic surfactants as well.

The phenomenon of cationic surfactants chemisorbing strongly to silica surfaces is established in the literature, and an example of cationic surfactant adsorption is explained with alkyl-amines interaction with SiO_2. The adsorption free energy has two main terms: the electrical interaction term, which contains the interaction coupling between the silicon surface and the positively charged head group; and the van der Waals terms, which contains the energy required to remove the hydrophobic groups from the aqueous solution noted in the Somasundaran et al. reference previously referred to. In the Somasundaran et al. reference, the following was found:

A) That the concentration of surfactant required to neutralize the surface charge (as is depicted in the graph of FIG. 1, which shows the effect of hydrocarbon chain length on the zeta-potential of quartz in solutions of alkylammonium acetates and ammonium acetate); and

B) That the critical concentration to neutralize the surface charge (as may be observed indirectly from a zero zeta-potential measurement for silica particles in an aqueous solution), estimated by the van der Waals energy scales is 0.97kT per CH_2 group or 580 cal/mole.

This would suggest that there is a lateral hydrophobic bonding between the alkyl chains that are adsorbed on the silica surface. Also, the critical concentration required for zeta-potential reversal decreases with increasing chain length.

In the case of the four above mentioned class of surfactants, the CMC or critical micelle concentrations (the concentration beyond which surfactants tend to self-aggregate) in the concentration range is less than 0.1 moles/liter.

Table I is the critical micelle concentrations for some of the alkyl-trimethyl ammonium halides and alkyl-pyridinium halides.

Table I

Surfactant	Solvent	CMC(moles/liter)
Dodecyl-trimethyl ammonium bromide	Water at 25°C	1.6E-2
Dodecyl-pyridinium chloride	Water at 25°C	1.5E-2
Tetradecyl-trimethyl ammonium chloride	Water at 30°C	3.5E-3
Tetradecyl-pyridinium bromide	Water at 30°C	2.6E-3
Hexadecyl-trimethyl ammonium chloride	Water at 30°C	1.3E-3
Cetyl-pyridinium chloride	Water at 25°C	9.0E-4

It can be seen from Table I that the critical micelle concentration (CMC) shifts to lower concentrations with increasing chain length.

Accordingly, in the context of the invention, use of the four classes of cationic compounds in chemical mechanical polishing tools in a slurry-less polishing scheme requires effective concentrations that is less than 0.1 moles/L.

In particular, the effective concentrations would be different for the varying chain lengths, and therefore, concentrations close to the concentration required to obtain zero zeta-potential values or higher are the most effective, and these are typically between 0.01 to 1 millimoles/liter. Preferably, the concentration of the cationic surfactant is lower than the critical micelle concentration (CMC) for the particular surfactant of choice.

In an alternative embodiment of the invention, small concentrations of common anionic polymer may be used in conjunction with a predominant amount of cationic surfactants in the slurry-less system. Use of the anionic polymers are useful because, the polishing pads in the chemical mechanical polishing tool may have CeO_2 particles embedded therein, and it may be necessary to coat these particles as they are stripped off from the pad during the CMP operation. For these situations, a small concentration, less than 2 weight percent, and more preferably from about 0.01 to about 1 wt% of a common anionic polymer like polyacrylic acid or ammonium acrylate may be used in conjunction with the cationic surfactant in the aqueous system.

To further reduce defects/scratches in the SiO_2 wafer during CMP in a slurry-less system, a non-ionic polymer such as polyacrylamide or polyvinyl alcohol of molecular weight<10,000 may be added to a composite solution mixture of surfactants at a concentration level lower than 1 weight percent, more preferably in the amount of about 0.01 wt%.

The toxicity data and the LD-50 values for some of the four classes of cationic surfactants as measured on rats are shown in Table II.

Table II

Surfactants	Average LD-50 values (mg/Kg)
Dodecyl-trimethyl-ammonium chloride	250-300
Hexadecyl-trimethyl-ammonium chloride	250-300
Hexadecyl-trimethyl-ammonium bromide	1000
Decyl-dimethyl-benzyl ammonium chloride	740
Dodecyl-dimethyl-benzyl ammonium chloride	910
Hexadecyl-dimethyl-benzyl ammonium chloride	1000
Octadecyl-dimethyl-benzyl ammonium chloride	3500
Cetyl-Pyridinium chloride	200

It should be noted that, at concentrations less than 1% there are no health-related issues in connection with human use.

From the foregoing, it is clear that amine based cationic surfactants chemisorb onto silica surfaces close to 1kT contribution to the adsorption free energy and the change in the zeta-potential to positive values with increasing additions of surfactant.

Accordingly, aqueous solutions containing a mixture of surfactants, primarily cationic, and to a smaller extent anionic and/or non-ionic surfactants, adsorb onto the silica part of the wafer surface, at neutral or alkaline conditions, to form a surfactant-coated protective layer, thereby reducing scratches or polishing defects during a slurry-less CMP operation.

While the mentioned examples focus on silicon dioxide wafers, it should be understood that the invention compositions may be utilized on other doped silicon dioxides, such as borophosphatesilicate glasses as well.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

WHAT IS CLAIMED IS:

1. An aqueous slurry-less composition for chemical-mechanical-polishing of a silicon dioxide workpiece comprising: a cationic surfactant that is soluble and ionized at neutral to alkaline pH conditions, said cationic surfactant being present in an aqueous slurry-less composition in an amount less than its critical micelle concentration.

2. The composition of claim 1 wherein said amount less than said critical micelle concentration is less than 0.1 moles/liter.

3. The composition of claim 2 wherein said cationic surfactant is an

alkyl-benzyl-dimethyl-ammoniun compound.

4. The composition of claim 3 wherein said alkyl-trimethyl-ammonium halide is hexadecyl-trimethyl-ammonium bromide.

5. The composition of claim 2 wherein said cationic surfactant is an alkyl-benzyl-dimethyl-ammonium halide.

6. The composition of claim 5 wherein said alkyl-benzyl-dimethyl-ammonium halide is selected from the group consisting of hexadecyl-benzyl-dimethyl ammonium bromide and dodecyl-benzyl-dimethyl-ammonium bromide.

7. The composition of claim 2 wherein said cationic surfactant is pyridinium alkyl halide.

8. The composition of claim 7 wherein said pyridinium alkyl halide is cetyl-pyridinium-chloride.

9. The composition of claim 2 wherein said cationic surfactant is an alkyl-ammonium ester.

10. The composition of claim 9 wherein said alkyl-ammonium ester is dodecylammonium acetate.

11. The composition of claim 2 wherein an anionic polymer is additionally present in an amount of about less than 2 weight percent based upon the weight of said cationic surfactant.

12. The composition of claim 11 wherein said anionic polymer is selected from the group consisting of polyacrylic acid and ammonium acrylate.

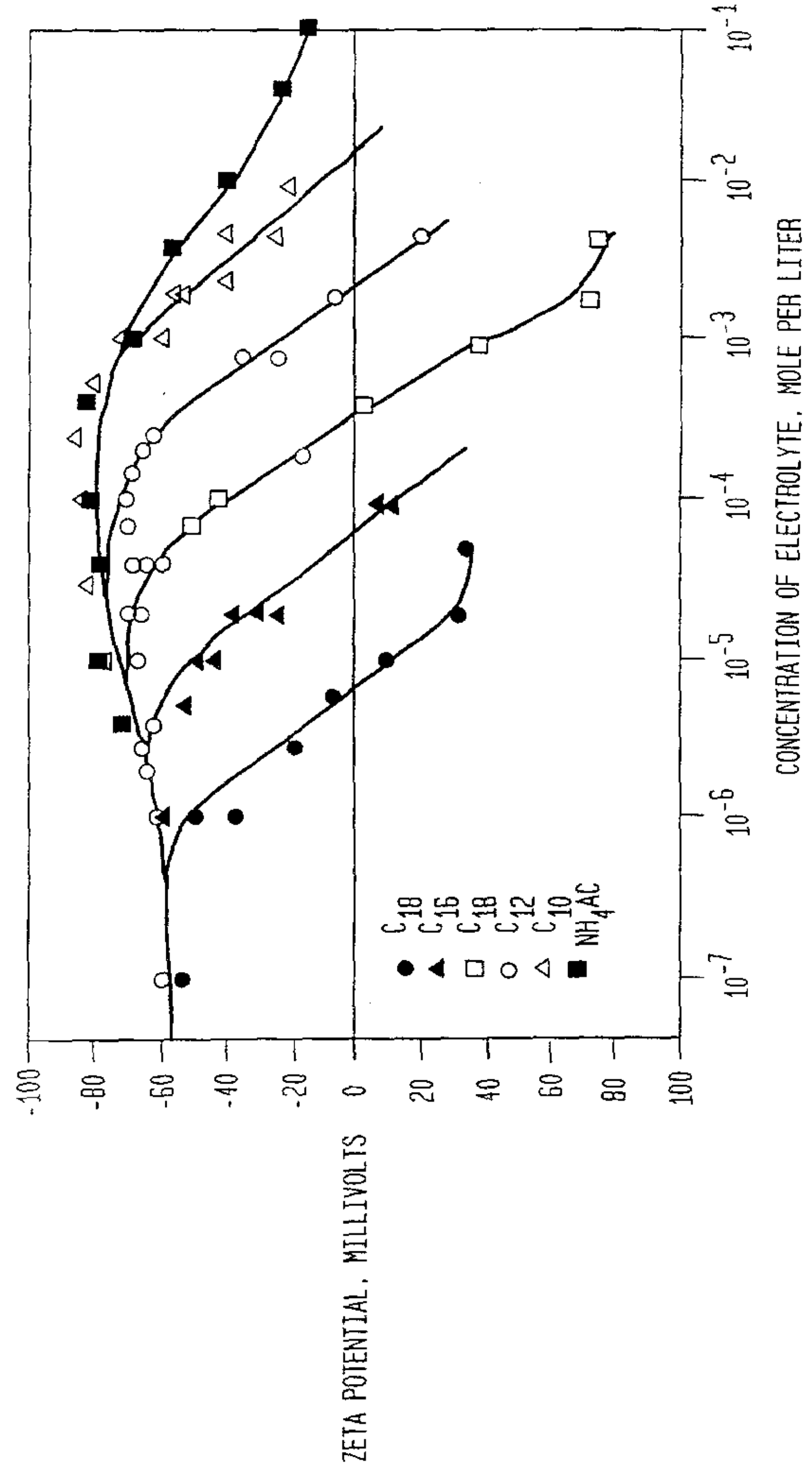
13. The composition of claim 2 wherein a non-ionic polymer is additionally present in an amount about less than 1 weight percent based upon the weight of said cationic surfactant.

14. The composition of claim 13 wherein said non-ionic polymer is selected from the group consisting of polyacrylamide and polyvinyl alcohol.

15. A method for reducing scratches and defects during chemical mechanical polishing of a silicon dioxide workpiece, comprising: exposing the surface of said workpiece to a slurry-less polishing composition comprising a cationic surfactant that is soluble and ionized at neutral to alkaline pH conditions, said cationic surfactant being present in an aqueous slurry-less composition in an amount less than its critical micelle concentration. The composition of claim 2 wherein said cationic surfactant is selected from the group consisting of an alkyl-trimethyl-ammonium halide, an alkyl-benzyl-dimethyl-ammonium halide, a pyridinium-alkyl halide, an alkyl ammonium ester, and mixtures thereof, in which the alkyl is from C_6 to C_{18}.

16. The composition of claim 2 wherein said cationic surfactant comprises bromide.

FIG. 1


ZETA POTENTIAL, MILLIVOLTS
-100
-80
-60
-40
-20
0
20
40
60
80
100
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
CONCENTRATION OF ELECTROLYTE, MOLE PER LITER
● C_{18}
▲ C_{16}
□ C_{18}
○ C_{12}
△ C_{10}
■ NH_4AC

INTERNATIONAL SEARCH REPORT

Inte. nal Application No
PCT/US 00/24342

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09G1/02 H01L21/3105

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)
IPC 7 C09G H01L

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.
A	DATABASE WPI Section Ch, Week 199826 Derwent Publications Ltd., London, GB; Class A60, AN 1998-292391 XP002155072 & JP 10 102040 A (HITACHI CHEM CO LTD), 21 April 1998 (1998-04-21) abstract ---	1,15
A	EP 0 913 442 A (HITACHI LTD.) 6 May 1999 (1999-05-06) column 11, line 11-15; claims 1,7,11 -----	1

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

☒ Patent family members are listed in 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 11 December 2000	Date of mailing of the international search report 27/12/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Girard, Y

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter .ial Application No
PCT/US 00/24342

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10102040 A	21-04-1998	NONE	
EP 913442 A	06-05-1999	JP 11135466 A	21-05-1999
		CN 1216727 A	19-05-1999
		US 6117775 A	12-09-2000

[19]中华人民共和国国家知识产权局

[51]Int. Cl⁷
C09G 1/02
H01L 21/3105

[12]发明专利申请公开说明书

[21]申请号 00808137.9

[43]公开日 2002年6月5日

[11]公开号 CN 1352673A

[22]申请日 2000.9.5 [21]申请号 00808137.9
[30]优先权
[32]1999.9.30 [33]US [31]09/409464
[86]国际申请 PCT/US00/24342 2000.9.5
[87]国际公布 WO01/23486 英 2001.4.5
[85]进入国家阶段日期 2001.11.27
[71]申请人 因芬尼昂技术北美公司
地址 美国加利福尼亚州
共同申请人 国际商业机器公司
[72]发明人 H·诺约 R·J·舒尔茨
R·拉马钱德兰

[74]专利代理机构 中国专利代理(香港)有限公司
代理人 卢新华 杨丽琴

权利要求书2页 说明书6页 附图页数1页

[54]发明名称 在二氧化硅化学机械抛光过程中减少/消除划痕和缺陷的组合物和方法

[57]摘要

一种用于化学机械抛光二氧化硅工件的水性无浆组合物，其包括：能在中性至碱性pH条件下溶解和离解的阳离子表面活性剂，其中阳离子表面活性剂在水性无浆组合物中的存在量低于其临界胶束浓度。

ISSN1008-4274

知识产权出版社出版

权利要求书

1. 一种用于二氧化硅工件的化学机械抛光的水性无浆组合物，其包括：能在中性至碱性的 pH 条件下溶解和离解的阳离子表面活性剂，所述的阳离子表面活性剂以水性无浆组合物的形式存在，其含量低于其临界胶束浓度.

2. 权利要求 1 的组合物，其中所述的低于所述临界胶束浓度的含量为低于 0.1 mol/l。

3. 权利要求 2 的组合物，其中所述的阳离子表面活性剂是烷基-苄基-二甲基-铵化合物

4. 权利要求 3 的组合物，其中所述的烷基-三甲基-卤化铵是十六烷基-三甲基-溴化铵.

5. 权利要求 2 的组合物，其中所述的阳离子表面活性剂是烷基-苄基-二甲基-卤化铵.

6. 权利要求 5 的组合物，其中所述的烷基-苄基-二甲基-卤化铵选自十六烷基-苄基-二甲基溴化铵和十二烷基-苄基-二甲基-溴化铵.

7. 权利要求 2 的组合物，其中所述的阳离子表面活性剂是吡啶鎓烷基卤.

8. 权利要求 7 的组合物，其中所述的吡啶鎓烷基卤是十六烷氯化吡啶鎓.

9. 权利要求 2 的组合物，其中所述的阳离子表面活性剂是烷基-铵酯。

10. 权利要求 9 的组合物，其中所述的烷基-铵酯是十二烷基铵乙酸酯.

11. 权利要求 2 的组合物，按照所述的阳离子表面活性剂重量计算，其中外加的阴离子聚合物的存在量约小于 2 重量%.

12. 权利要求 11 的组合物，其中所述的阴离子聚合物选自聚丙烯酸和丙烯酸铵.

13. 权利要求 2 的组合物，按照所述的阳离子表面活性剂重量计算，其中外加的非离子聚合物的存在量为约 1 重量%.

14. 权利要求 13 的组合物，其中所述的非离子聚合物选自聚丙烯酰胺和聚乙烯醇.

15. 一种减少二氧化硅工件在化学机械抛光过程中的划痕和缺陷的方法，其包括：将所述工件的表面暴露在包含阳离子表面活性剂的无浆抛光组合物中，该阳离子表面活性剂，能在中性至碱性的 pH 条件下溶解和离解，所述的阳离子表面活性剂在水性无浆组合物中的存在量低于其临界胶束浓度，权利要求 2 的组合物，其中所述的阳离子表面活性剂选自烷基-三甲基-卤化铵、烷基-苄基-二甲基-卤化铵、吡啶鎓-烷基卤、烷基铵乙酸酯、和它们的混合物，其中烷基为 C_6-C_{18}。

16. 权利要求 2 的组合物，其中所述的阳离子表面活性剂包括溴化物。

说　明　书

在二氧化硅化学机械抛光过程中减少/消除划痕和缺陷的组合物和方法

发明背景

1. 发明领域

本发明涉及在二氧化硅薄片表面化学机械抛光过程（CMP）中，阳离子表面活性剂在无浆环境中的应用，以基本上消除或减少在 CMP 过程中产生的划痕和缺陷.

在 VLSI（超大规模集成）加工过程中，在所有的 pH 条件下，即在酸性、中性和碱性 pH 条件下，某些类型的阳离子表面活性剂能化学吸附在薄片的二氧化硅部分上.

2. 对现有技术的说明

近年来，已经开始使用新的化学机械抛光（CMP）技术对硅晶片表面实施无浆抛光方案，其中抛光板具有嵌入其中的研磨剂颗粒. 特别是，对于二氧化硅 CMP 的应用，抛光板包含用作磨料的 CeO_2.

在 CMP 过程中，待抛光的晶片，在有水的环境下对着抛光板面进行研磨. 然而，在 CMP 过程中，在中性或碱性条件下，这些抛光盘能产生缺陷和划痕，因而造成产率下降.

因此，需要设计保护二氧化硅晶片表面以防止在无浆 CMP 过程中因研磨而产生划痕和缺陷的组合物和方法.

Somasundaran 等人在“表面活性剂在固-液界面上的吸附和对链长机制的关系”，物理化学杂志（J. Phys. Chem.），68 卷，3562-3566 页（1964）中公开:

a) 中和二氧化硅上的表面电荷所需的表面活性剂浓度，随链长的增加而下降; 和

b) 根据中和该表面电荷的临界浓度（是根据在水溶液中对二氧化硅颗粒 0 Zeta 电位的测量间接观测的），每个 CH_2 基团的范德华能量标度为 0.97 kT 或 580 cal/mol.

根据 Somasundaran 等人的观点，似乎与吸附在二氧化硅表面上的烷基链之间具有侧向疏水键有关.

美国专利 5,769,689 公开了在用于抛光由二氧化硅组成的加工件

的方法中使用的组合物，其中加工件的表面暴露在包含水、亚微细SiO_2颗粒、和可溶性无机盐的抛光组合物中，浓度低于组合物的临界凝聚浓度，其中通过加入可溶性胺，将组合物的pH调节到约9-10.

Kumar等人在“铜在甘油基浆体中的化学-机械抛光”，Mat. Res. Symp. Proc.（材料研究专题讨论会文集），427卷，237-242页（1996）中公开了对金属铜表面的CMP加工，应用包含甘油和Al_2O_3研磨剂的浆体，使铜适合用作连接件制造.用这种方法代替铜的反应性离子蚀刻方法.

在美国专利5,607,718中公开，对SLI（大规模集成）的化学-机械抛光技术，提出了表面凹陷的问题，其中加入许多化合物以降低溶液的速度和抑制表面凹陷.这些化合物包括若干种增稠剂，例如硅酸盐、葡萄糖、黄蓍胶和琼脂.

Nojo等人在“自停止，无凹陷的SiO_2-CMP浆体技术”，IEDM，349-352页，©1996 IEEE中公开一种浆体，其中将有表面活性剂的浆体加入到用于SiO_2化学机械抛光（CMP）的常规CeO_2浆体中，在没有任何终止层或设计限制的情况下，在一个芯片内获得完全的平面化。

美国专利4,588,474公开一种对金属表面清洁处理的方法，其中将甘油与其它添加剂一道加入溶液中，获得更光滑更均匀的表面.这些溶液包含苛性碱、硝酸盐或亚硝酸盐，以及还可有二元醇或多元醇如乙二醇或甘油，加工件是铝合金.

在美国专利5,567,300中公开了在微电子制造的各个阶段中，各种部件的金属去除和平面化的电化学抛光技术.该专利是针对特征清除，并采用非粘性的多元醇来增强清除.在电蚀刻中，采用在室温下粘度是水1500倍的甘油，以提高电解质的粘度和促进抛光.

在前述专利和参考文献中的这些方法中，一个明显的缺点是没有报导需通过对含水介质的化学改进来改善二氧化硅在无浆系统中化学机械抛光（CMP）中的缺陷控制.

发明概述

本发明的一个目的是在采用无浆系统进行化学机械抛光过程中，提供对二氧化硅改善缺陷的控制，以减少或消除与抛光有关的划痕和缺陷.

本发明的另一个目的是在采用无浆系统进行化学机械抛光过程中，通过加入在中性和碱性 pH 条件下能化学吸附在二氧化硅表面上的特种阳离子表面活性剂提供对二氧化硅改善缺陷的控制.

本发明的另一个目的，是在采用无浆系统进行化学机械抛光过程中，通过在无浆系统中加入阳离子表面活性剂，提供对二氧化硅改善缺陷的控制，这些阳离子表面活性剂，选自下列能产生阳离子的阳离子表面活性剂:

烷基-三甲基-卤化铵; 烷基-苄基-二甲基-卤化铵; 吡啶鎓-烷基卤; 烷基-铵酯; 和它们的混合物. 可以改变阴离子基团，以获得相应阳离子表面活性剂的离子.

本发明一般是在二氧化硅晶片在中性或碱性条件下化学机械抛光之前，在无浆系统中加入阳离子表面活性剂实现的，这些表面活性剂选自: 烷基-三甲基-卤化铵; 烷基-苄基-二甲基-卤化铵; 吡啶鎓-烷基卤; 烷基-铵酯，和它们的混合物，其用量低于临界胶束浓度（超过该浓度，表面活性剂往往倾向于自身聚集）或低于 0.1 mol/l.

附图简述

图 1 是表示烃链长度，对石英在烷基乙酸铵溶液和在乙酸铵溶液中 Zeta-电位的影响曲线.

发明详述

通过下面对本发明优选实施方案的详细说明，能更好地理解本发明前述的和其它的目的和优点.

为了在采用无浆系统进行的化学机械抛光过程（CMP）中，保护二氧化硅晶片或提供改善的缺陷控制，加入某些种类的阳离子表面活性剂，以减少抛光划痕和缺陷. 这些阳离子表面活性剂在中性和碱性 pH 条件下化学吸附在二氧化硅的表面上，从而保护晶片表面，以防止产生抛光划痕和缺陷. 待抛光的晶片对着抛光板的表面研磨，抛光板一般包含嵌入其中的 CeO_2 作为研磨材料.

在化学机械抛光采用的加工系统中，抛光采用的水溶液既可以是中性的，也可以是碱性的，虽然不希望本发明工作受任何理论上的约束，但确信，加入的阳离子表面活性剂，化学吸附在二氧化硅的表面上，能影响二氧化硅表面和带正电荷的端基之间的相互结合.

在本发明情况下有效的四类阳离子表面活性剂，选自：1）烷基-

三甲基-卤化铵，其烷基长度为 C_6-C_{18}，其中优选十六烷基-三甲基-溴化铵；2）烷基-苄基-二甲基-卤化铵，其烷基长度为 C_6-C_{18}，其中优选十六烷基-苄基-二甲基-溴化铵和十二烷基-苄基-二甲基-溴化铵；3）吡啶鎓-烷基卤，其烷基为 C_6-C_{18}，其中优选十六烷基氯化吡啶鎓；和 4）烷基-铵酯，其烷基为 C_6-C_{18}，其中优选十二烷基乙酸铵；和它们的混合物．

在本发明的情况下，可以利用阳离子表面活性剂的混合物，以制成复合溶液．采用另一种方案，也可使这四类阳离子表面活性剂中的一种或多种以占优势量存在的表面活性剂混合物与少量的阴离子和/或非离子表面活性剂混合．

在文献中已经确认，阳离子表面活性剂能强烈化学吸附在二氧化硅表面上的现象，并用烷基胺与 SiO_2 的相互作用解释阳离子表面活性剂吸附的实例．吸附自由能具有二个主要项：电相互作用项，该项包括硅表面和带正电荷的端基之间的相互结合；和范德华项，该项包括在前面提到的 Somasundaran 等人的文献中所指出的，从水溶液中除去疏水基团所需的能量．在 Somasundaran 等人的文献中，得到以下几点：

A) 中和表面电荷所需的表面活性剂浓度（如图 1 中的曲线所示，该曲线示出，烃链长度对石英在烷基乙酸铵溶液和乙酸铵溶液中 Zeta-电位的影响）；和

B) 中和表面电荷的临界浓度（是根据对二氧化硅颗粒在水溶液中 0 Zeta-电位的测量间接确定的），根据范德华能量标度估计，每个 CH_2 基团为 0.57 kT 或 580 cal/mol.

这表明，吸附在二氧化硅表面上的烷基链之间有一个侧向疏水键．Zeta-电位反向所需的临界浓度也随链长的增加而降低．

在上述四类表面活性剂的情况下，CMC 或临界胶束浓度（超过该浓度，表面活性剂倾向于自身聚集）低于 0.1 mol/l.

表 I 是一些烷基-三甲基卤化铵和烷基-卤化吡啶鎓的临界胶束浓度．

表 I

表面活性剂	溶剂	CMC（mol/l）
十二烷基-三甲基溴化铵	25℃的水	1.6E-2
十二烷基-氯化吡啶鎓	25℃的水	1.5E-2
十四烷基-三甲基氯化铵	30℃的水	3.5E-3
十四烷基-溴化吡啶鎓	30℃的水	2.6E-3
十六烷基-三甲基氯化铵	30℃的水	1.3E-3
十六烷基-氯化吡啶鎓	25℃的水	9.0E-4

从表 1 可以看出，临界胶束浓度（CMC）随链长的增加而降低.

因此，在本发明的情况下，在采用无浆抛光流程的化学机械抛光装置中，应用这四类阳离子化合物，需要的有效浓度低于 0.1 mol/l.

尤其是，对不同的链长度，有效浓度是不同的，因此，获得 0 Zeta-电位值和较高值所需的浓度是最有效的，这些浓度一般在 0.01-1 mmol/l 之间. 对于所选择的特定表面活性剂，阳离子表面活性剂的浓度优选低于临界胶束浓度（CMC）.

在本发明另一个实施方案中，可将低浓度的普通阴离子聚合物与在无浆系统中含量占优势的阳离子表面活性剂一起使用. 采用阴离子聚合物是有效的，因为化学机械抛光装置的抛光板可以有嵌入其中的 CeO_2 颗粒，当它们在 CMP 操作过程中从板上脱落时，必须包覆这些颗粒. 对于这些情况，可以与含水系统的阳离子表面活性剂一起使用的如聚丙烯酸或丙烯酸铵之类的普通阴离子聚合物的低浓度要低于 2 重量%，更优选约 0.01 至约 1 重量%.

为了进一步减少在采用无浆系统的 CMP 过程中二氧化硅晶片上的缺陷/划痕，可以将非离子聚合物如分子量<10,000 的聚丙烯酰胺或聚乙烯醇加入到表面活性剂混合物的复合溶液中，其浓度低于 1 重量%，更优选其含量为约 0.01 重量%.

在这四类阳离子表面活性剂中，一些表面活性剂的毒性数据和 LD-50 值，按照对小鼠的测定，示于表Ⅱ.

表 II

表面活性剂	平均 LD-50 值（mg/Kg）
十二烷基-三甲基氯化铵	250-300
十六烷基-三甲基氯化铵	250-300
十六烷基-三甲基溴化铵	1000
癸基-二甲基-苄基氯化铵	740
十二烷基-二甲基-苄基氯化铵	910
十六烷基-二甲基-苄基氯化铵	1000
十八烷基-二甲基-苄基氯化铵	3500
十六烷基-氯化吡啶鎓	200

应当指出，在浓度低于 1%时，人类使用，对健康没有任何问题．

从以上所述，可以清楚地看到，化学吸附在二氧化硅表面上的胺基阳离子表面活性剂，对吸附自由能的贡献约为 1kT，Zeta-电位随表面活性剂的增加向正值变化．

因此，包含表面活性剂，主要是阳离子表面活性剂，和较少的阴离子和/或非离子表面活性剂混合物的水溶液，在中性或碱性条件下在薄片表面的二氧化硅部分上吸附，以形成表面活性剂覆盖的保护层，从而在无浆 CMP 操作中减少了划痕或抛光缺陷．

虽然上述的实例都集中在二氧化硅晶片上，但应当理解，对其它掺杂的二氧化硅，例如磷硅酸硼玻璃，也可使用本发明的组合物．

本领域的技术人员会很容易发现本发明的另一些优点和改进．因此，在不偏离在所附权利要求和其等价物所规定的，本发明一般概念的内容或范围内，可以进行各种修改．

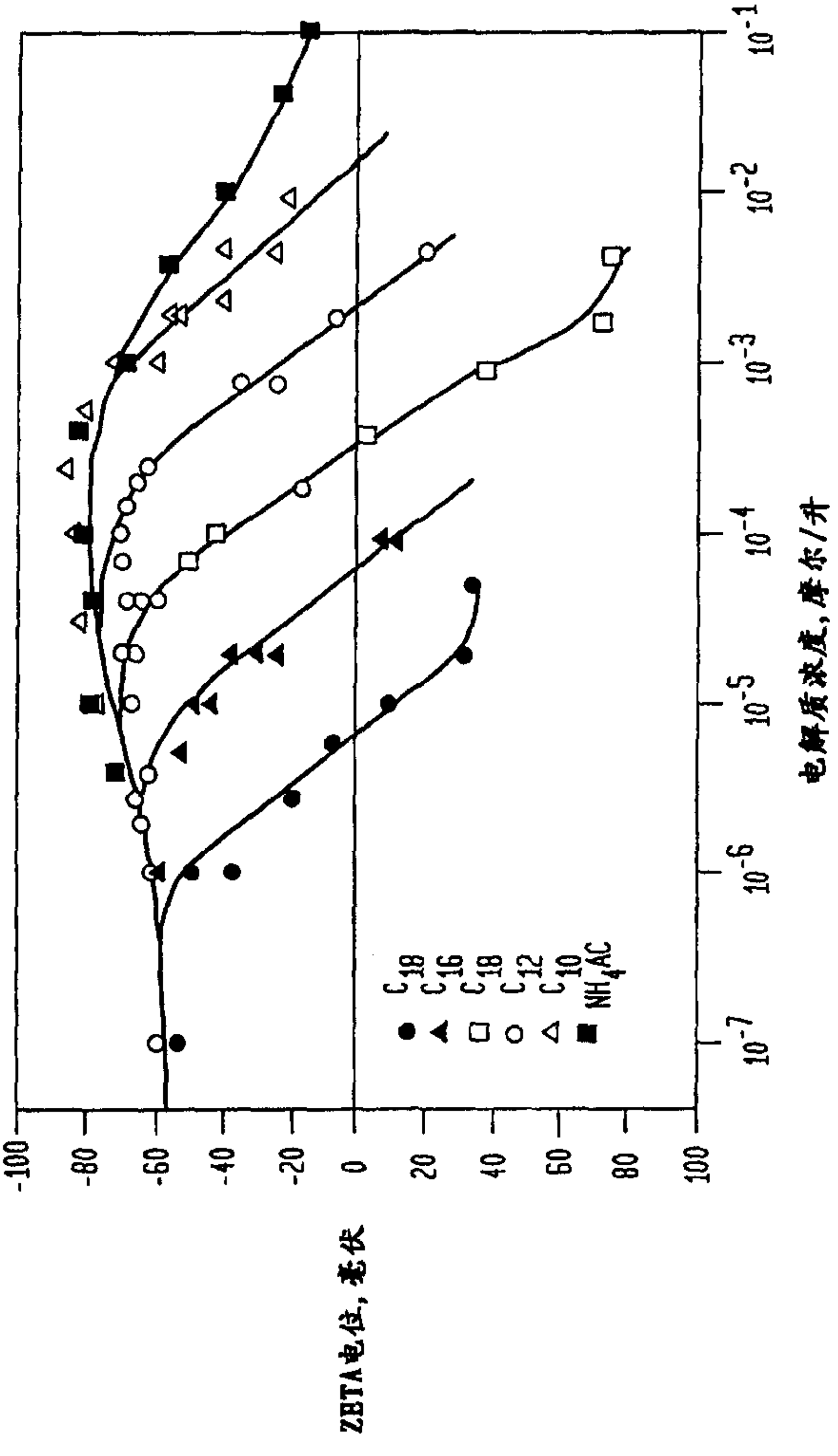

ZETA电位，毫伏
-100
-80
-60
-40
-20
0
20
40
60
80
100
电解质浓度，摩尔/升
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
● C_{18}
▲ C_{16}
□ C_{18}
○ C_{12}
△ C_{10}
■ NH_4AC

图 1