



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B44C 1/22, C03C 15/00, C09K 13/00, 13/02		A1	(11) International Publication Number: WO 98/13218 (43) International Publication Date: 2 April 1998 (02.04.98)
(21) International Application Number: PCT/US97/17503 (22) International Filing Date: 26 September 1997 (26.09.97)		(81) Designated States: CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(30) Priority Data: 60/027,277 27 September 1996 (27.09.96) US 08/802,829 19 February 1997 (19.02.97) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(71) Applicant: RODEL, INC. [US/US]; 451 Bellevue Road, Newark, DE 19713 (US).			
(72) Inventors: HOSALI, Sharath, D.; 108 E. Green Valley Circle, Newark, DE 19711 (US). SETHURAMAN, Anantha, R.; 34152 Finnigan Terrace, Fremont, CA 94555 (US). WANG, Jun-Fang; 5 White Briar Circle, Hockessin, DE 19707 (US). COOK, Lee, Melboure; 190 Bryson Road, Steelville, PA 19310 (US).			
(74) Agent: BENSON, Kenneth, A.; Rodel, Inc., 451 Bellevue Road, Newark, DE 19713 (US).			

(54) Title: COMPOSITION AND METHOD FOR POLISHING A COMPOSITE

(57) Abstract

A composition is provided for polishing a composite comprised of silica and silicon nitride comprising: an aqueous medium, abrasive particles, a surfactant, and a compound which complexes with the silica and silicon nitride wherein the complexing agent has two or more functional groups each having a dissociable proton, the functional groups being the same or different.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

5

COMPOSITION AND METHOD FOR POLISHING A COMPOSITE

10

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to compositions which are useful as slurries for the chemical-mechanical polishing of substrates, especially substrates comprised of silica and silicon nitride. More specifically the slurries of the present invention include an aqueous medium, 15 abrasive particles, a surfactant, and a compound which complexes with silica and silicon nitride.

Description of Related Art

In integrated circuit technology, various active and passive elements generally must be isolated from one another within the integrated circuit structure. This has often been accomplished by deep or shallow trench isolation techniques. These techniques typically use 20 silicon dioxide (silica) as a dielectric material and silicon nitride as a stop layer, requiring chemical-mechanical polishing (planarization) of each circuit layer. To achieve efficient polishing and adequate planarization, a polishing slurry is generally useful and should provide a high selectivity involving the removal rate of silica relative to silicon nitride.

In Silvestri et al., U. S. Patent 4526631, a slurry of 6 weight percent colloidal silica adjusted to a pH of about 12 with KOH provides a polishing ratio of about 10 SiO_2 to 1 Si_3N_4 . Beyer et al., U.S. Patent 4671851, states that the polishing ratios between SiO_2 and Si_3N_4 preferably should be between a lower limit of 4 to 1 and a higher limit of 40 to 1. Beyer describes obtaining a ratio of 6.2 to 1 using a colloidal silica in water with small amounts of a sodium salt of dichloroisocyanuric acid and sodium carbonate.

30 Even more recent patents such as Murase, U.S. Patent 5502007, also describe obtaining selectivities of about 10 SiO_2 to 1 Si_3N_4 removal rates using a colloidal silica slurry as a polishing agent. Kodera et al., U. S. Patent 5445996, use ceria as well as silica for the abrasive particles in slurries, but they also report selectivities for SiO_2 to Si_3N_4 removal rates in the range of 2 to 3.

SUMMARY OF THE INVENTION

A composition is provided for polishing a composite comprised of silica and silicon nitride comprising: an aqueous medium, abrasive particles, a surfactant and a compound which complexes with the silica and silicon nitride wherein the complexing agent has two or more functional groups each having a dissociable proton, the functional groups being the same or different.

A further aspect of the invention is the method for polishing a composite comprised of silica and silicon nitride comprising: applying a slurry at a polishing interface between a polishing pad and the composite comprised of silica and silicon nitride, the slurry comprising: an aqueous medium, abrasive particles, a surfactant and a compound which complexes with the silica and silicon nitride wherein the complexing agent has two or more functional groups each having a dissociable proton, the functional groups being the same or different.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that the addition of a compound which complexes with silica and silicon nitride to polishing slurries used in the chemical-mechanical polishing of composites comprised of silica and silicon nitride can provide a very high selectivity of rate of removal of SiO_2 to the rate of removal of Si_3N_4 when a surfactant is used in conjunction with the complexing agent and when the concentration of the complexing agent in the slurry is sufficient to block the removal of Si_3N_4 while not greatly affecting the removal of SiO_2 at the pH of the polishing slurry.

Compounds which act as complexing agents or chelating agents for SiO_2 and Si_3N_4 are described in great detail in U. S. Patent 5391258 and U. S. Patent 5476606 which are made part of this specification by reference. These compounds must have at least two acid groups present in the structure which can affect complexation to the silica and silicon nitride surface. Acid species are defined as those functional groups having a dissociable proton. These include, but are not limited to, carboxylate, hydroxyl, sulfonic and phosphonic groups. Carboxylate and hydroxyl groups are preferred as these are present in the widest variety of effective species. Particularly effective are structures which possess two or more carboxylate groups with hydroxyl groups in an alpha position, such as straight chain mono- and di-carboxylic acids and salts including, for example, malic acid and malates, tartaric acid and tartarates and gluconic acid and gluconates. Also effective are tri- and polycarboxylic acids and salts with secondary or tertiary hydroxyl

groups in an alpha position relative to a carboxylic group such as citric acid and citrates. Also effective are compounds containing a benzene ring such as ortho di- and polyhydroxybenzoic acids and acid salts, phthalic acid and acid salts, pyrocatecol, pyrogallol, gallic acid and gallates and tannic acid and tannates. In the examples to follow, a salt of phthalic acid is used as the 5 complexing agent and, therefore, such salts are preferred complexing agents for this invention. Potassium hydrogen phthalate, "KHP", was the phthalate salt used in the experiments described below.

The surfactant used in conjunction with the complexing agent in this invention is not present to perform the usual function of surfactants in slurries of stabilizing the particulate 10 dispersion. As shown in the examples which follow, the surfactant in combination with the complexing agent affects the rate of removal of Si_3N_4 from the composite surface. It is believed that any surfactant, whether it be an anionic, cationic, non-ionic or zwitter-ionic surfactant, might be effective in the compositions of this invention. Particularly useful would be fluorocarbons or hydrocarbons with phosphate end groups. In the following examples several 15 different surfactants were shown to be effective. "ZFSP", ZONYLTM FSP Fluorosurfactant, manufactured by the DuPont Company, was shown to be a particularly effective surfactant additive to the slurries of this invention. It is a long straight chain hydrocarbon with phosphate groups at one end and a fluoride at the other end.

In these examples, ceria was used for the abrasive particles in the slurry because it is an 20 effective polishing abrasive for chemical-mechanical polishing at all pH conditions and is stable against gelation. Any other polishing abrasive, such as alumina, zirconia, silica, titania and barium carbonate could also be used.

To adjust the slurries of this invention to the pH range in which the highest selectivities of SiO_2 removal to Si_3N_4 removal are obtained any base or amine compound might be used. In 25 the examples to follow KOH is used to adjust the pH of the slurry compositions. Potassium hydroxide, ammonium hydroxide, and all types of soluble amine compounds may be used to adjust the pH of chemical-mechanical polishing slurries.

EXAMPLE 1

30 Table 1 shows the results of polishing silicon dioxide and silicon nitride wafers with slurries containing various amounts of complexing agent at selected pH levels. These experiments were carried out on a Strasbaugh 6DS SP Planarizer using an IC1000/SubaIV

polishing pad stack under the conditions of 7 psi down pressure, 1.5 psi back pressure, 30 rpm carrier speed and 32 rpm table speed with a slurry flow rate of 125 ml/min. 6 inch wafers were used and the pad was conditioned after each wafer was polished. All slurries in this series of experiments contained 0.45% colloidal ceria and 0.2% ZFSP surfactant and the pH of the slurry 5 was adjusted using potassium hydroxide.

Table 1

<u>Sample</u>	<u>%KHP*</u>	<u>pH</u>	<u>RR SiO₂</u>	<u>RR Si₃N₄</u>	<u>Selectivity</u>
1	0	4	1419	256	5.5
2	3.1	4	6	3	2
10	3	0.5	3019	189	16
	4	1	3000	15	200
	5	3.1	1185	4	296
	6	1	3397	994	3.5
	7	2	3246	920	3.5

15 *Potassium hydrogen phthalate

These results clearly show that selectivities of silicon dioxide to silicon nitride removal rates much higher than reported heretofore can be obtained by using slurries comprising a complexing agent and a surfactant at a pH level where these additives effectively shut down the 20 removal rate of silicon nitride while not greatly affecting the removal rate of silicon dioxide. As shown above, selectivities of 200 and greater can be obtained by this inventive method of polishing.

EXAMPLE 2

25 The following experiments show the necessity of using a surfactant in the slurries of this invention. They were carried out on a Strasbaugh 6DS SP Planarizer under the same conditions described in Example I. Slurries were similar to the one used for Sample 4 on Table I in that the slurries were comprised of 1%KHP, 0.45% colloidal ceria and the pH was adjusted to 7 using KOH. Percent surfactant, ZFSP, was either 0.2% as in Sample 4 or 0.0%. Removal rates for 30 Si₃N₄ in Angstroms per minute are shown in Table 2 below:

Table 2

	<u>%ZFSP</u>	<u>RR Si₃N₄</u>
	0	793
	0	768
5	0	736
	0.2	10
	0.2	8

It is obvious from these data that the surfactant is critical to the shutting down of the Si₃N₄ removal rate so that such extraordinary selectivities can be obtained.

10

EXAMPLE 3

In the following experiments the abrasive in the slurries was commercial opaline ceria which was milled before use. Polishing of wafers was accomplished under the same conditions as in Example 1. Results are given in Table 3 below:

15

Table 3

<u>Sample</u>	<u>%Abrasive</u>	<u>%KHP</u>	<u>%ZFSP</u>	<u>pH</u>	<u>RR SiO₂</u>	<u>RR Si₃N₄</u>	<u>Selectivity</u>
8	2	0	0	7	5804	3504	2
9	2	1	0.2	7	2642	22	120
20	10	3.5	1	0.2	6.5	3195	13
	11	5	1	0.2	6.5	3705	33
	12	3.5	2	0.4	7	2123	10
	13	5	2	0.4	7.5	3609	1105

25

These results show that a complexing agent and a surfactant effectively shut down the removal rate of Si₃N₄ when used in a slurry adjusted to a desired pH range. At a pH of 6.5 and 7 the removal rate of Si₃N₄ is greatly shut down giving selectivities for the removal of silica over that of silicon nitride of over 100 (samples 9 - 12). However, at a pH of 7.5 (sample 13), the removal rate of silicon nitride is no longer depressed and selectivities are very poor.

30

EXAMPLE 4

In these experiments several surfactants were found to be effective in reducing the removal rate of silicon nitride at a pH of 6.5. The surfactants used were FC-93, FluoradTM FC-93, an anionic fluorochemical surfactant available from the 3M Company; "PVS", the sodium salt of polyvinyl sulphonate available commercially; and "ZFSN", ZONYLTM FSN, a non-ionic surfactant available from the DuPont Company. The slurries in this Example all contained 1.5% KHP (potassium hydrogen phthalate) and 0.45% commercial opalene ceria as the abrasive.

Polishing of wafers was accomplished under the same conditions as in Example 1. Results are given in Table 4 below:

10

Table 4

<u>Sample</u>	<u>Surfactant</u>	<u>%Surfactant</u>	<u>RR SiO₂</u>	<u>RR Si₃N₄</u>	<u>Selectivity</u>
14	FC-93	0.2	2975	464	6
15	PVS	0.3	3406	35	98
15 16	ZFSN	0.3	2678	39	68

These results show that several surfactants are effective in slurries made to reduce the removal rate of silicon nitride. A given surfactant might be even more effective should pH and slurry compositions be optimized.

20

EXAMPLE 5

In this Example the abrasive used was WS2000 available from Rodel, Inc. WS2000 is an abrasive which contains both ceria and silica. The slurry used for this experiment contained 3.5% abrasive, 1.5% KHP (potassium hydrogen phthalate), and 0.2% ZFSP (ZONYLTM FSP). The pH was about 6.5. Results from the polishing of wafers under the same conditions as in Example 1 are shown on Table 5 below:

Table 5

<u>Sample</u>	<u>RR SiO₂</u>	<u>RR Si₃N₄</u>	<u>Selectivity</u>
17	2209	9	244

30 The above Examples show many embodiments of this invention and are not meant to restrict the invention in any way. The scope of the invention is defined only by the claims which follow:

CLAIMS

1. A method of polishing a composite comprised of silica and silicon nitride comprising: applying a slurry at a polishing interface between a polishing pad and said composite comprised of silica and silicon nitride, said slurry comprising: an aqueous medium, abrasive particles, a surfactant, and a compound which complexes with said silica and silicon nitride, wherein said compound has two or more functional groups each having a dissociable proton, the functional groups being the same or different.

10 2. A method according to claim 1 wherein said compound which complexes with silica and silicon nitride contains a benzene ring.

15 3. A method according to claim 1 wherein said compound which complexes with silica and silicon nitride is a straight chain mono- or di-carboxylic acid or salt which has a secondary hydroxyl group in an alpha position relative to a carboxylate group.

4. A method according to claim 1 wherein said compound which complexes with silica and silicon nitride is a tri- or poly-carboxylic acid or salt which has a secondary or tertiary hydroxyl group in an alpha position relative to a carboxylate group.

20 5. A method according to claim 1 wherein said abrasive particles comprise ceria.

6. A method according to claim 1 wherein said surfactant comprises a fluorosurfactant.

25 7. A method according to claim 2 wherein said compound which complexes with silica and silicon nitride is potassium hydrogen phthalate.

30 8. A method according to claim 2 wherein said polishing composition comprises: water, about 0.2% to about 5% ceria, about 0.5% to about 3.5% potassium hydrogen phthalate, about 0.1% to about 0.5% fluorosurfactant, all percentages by weight, and wherein the pH of said polishing composition is adjusted from about 6 to about 7 by the addition of a base or an amine compound to said polishing composition.

35 9. A composition for polishing a composite comprised of silica and silicon nitride comprising: an aqueous medium, abrasive particles, a surfactant, and a compound which complexes with said

silica and silicon nitride, said compound having two or more functional groups each having a dissociable proton, said functional groups being the same or different.

10. A composition according to claim 9 wherein said compound which complexes with silica

5 and silicon nitride contains a benzene ring.

11. A composition according to claim 9 wherein said compound which complexes with silica and silicon nitride is a straight chain mono- or di-carboxylic acid or salt which has a secondary hydroxyl group in an alpha position relative to a carboxylate group.

10

12. A composition according to claim 9 wherein said compound which complexes with silica and silicon nitride is a tri- or poly-carboxylic acid or salt which has a secondary or tertiary hydroxyl group in an alpha position relative to a carboxylate group.

15

13. A composition according to claim 9 wherein said abrasive particles comprise ceria.

14. A composition according to claim 9 wherein said surfactant comprises a fluorosurfactant.

20

15. A composition according to claim 10 wherein said compound which complexes with silica and silicon nitride is potassium hydrogen phthalate.

25

16. A composition according to claim 9 comprising: water, about 0.2% to about 5% ceria, about 0.5% to about 3.5% potassium hydrogen phthalate, about 0.1% to about 0.5% fluorosurfactant, all percentages by weight, and wherein the pH of said composition is adjusted from about 6 to about 7 by the addition of a base or an amine compound to said composition.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/17503

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B44C 1/22; C03C 15/00; C09K 13/00, 13/02

US CL :252/79.1, 79.5; 438/693, 756, 757; 216/89, 99

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)

U.S. : 252/79.1, 79.5; 438/692, 693, 756, 757; 216/89, 99

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

NONE

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

APS/USPAT; STN/CAS; ORBIT/WPAT, JAPIO, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,448,634 A (LAMPERT) 15 MAY 1984 (15-05-84), COLUMNS 1-4.	1-16
A	US 5,502,007 A (MURASE) 26 MARCH 1996 (26-03-96), COLUMNS 4-7.	1-16
Y	US 5,476,606 A (BRANCALEONI ET AL) 19 DECEMBER 1995 (19-12-95), COLUMNS 3-8.	9-16
A	US 5,445,996 A (KODERA ET AL) 29 AUGUST 1995 (29-08-95), COLUMN 23.	1-16
Y	US 5,391,258 A (BRANCALEONI ET AL) 21 FEBRUARY 1995 (21-02-95), COLUMNS 4-8.	9-16
A	US 4,671,851 A (BEYER ET AL) 09 JUNE 1987 (09-06-87), COLUMNS 6-8.	1-16

 Further documents are listed in the continuation of Box C.

See patent family annex.

•	Special categories of cited documents:	*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
A	document defining the general state of the art which is not considered to be of particular relevance	*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
E	earlier document published on or after the international filing date	*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
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)	*A*	document member of the same patent family
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		

Date of the actual completion of the international search

28 JANUARY 1998

Date of mailing of the international search report

23 FEB 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

GEORGE GOUDREAU

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/17503

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 4,526,631 A (SILVESTRI ET AL) 02 July 1985 (02-07-85), columns 6-7.	1-16