Description

CHEMICAL MECHANICAL POLISHING SLURRY COMPOSITION FOR POLISHING POLYCRYSTALLINE SILICON FILM AND METHOD FOR PREPARING THE SAME

Technical Field

[1] The present invention relates to a chemical mechanical polishing slurry for polishing a polycrystalline silicon (Poly-Si) film, and a method for producing the slurry. More particularly, the present invention relates to a method for fabricating a semiconductor device, which is useful in the formation of a self-alignment floating gate of a flash memory device, using a slurry capable of improving the within-wafer-non-uniformity (WIWNU) with a high polishing selectivity towards a poly-crystalline silicon film in preference to a device separation film, which functions as a polishing stop layer.

[2]

Background Art

[3] Integrated circuit technology enters the ultra large scale integration (ULSI) era, which is represented by 512M-bit and 1G-bit DRAMs, through high performance and high integration of semiconductor devices. As the minimum processing size required for the fabrication of devices becomes smaller, line widths of 60 nm and 70 nm are being currently applied to the fabrication of next-generation devices.

[4] Integration in integrated circuits (ICs) has resulted in a reduction in the size of devices and a need for multilevel interconnection. To meet this need, it is necessary to planarize the entire surface of materials being polished by through the use of effective lithography. Under such circumstances, chemical mechanical polishing is currently in the spotlight as a novel planarization technique. Highly integrated semiconductor devices are fabricated by repeatedly and alternately depositing conductive materials and insulating materials over one another to form patterns. When the surface of each material layer is not planarized upon pattern formation, it is very difficult to formnew pattern layers over the top. That is, in the case where new layers are continuously laminated on non-uniform surfaces between material layers, incident light is reflected at different angles from refracted films, resulting in inaccurate photo resist patterns upon development. Accordingly, the need for chemical mechanical polishing (hereinafter, referred to simply as "CMP") is widely recognized. CMP is of particular importance because polycrystalline silicon materials are widely used to form contacts and lines of devicesin semiconductor manufacturing processes.

[5] The principle of CMP techniques is that a slurry, which is an abrasive solution, is

supplied in a state where a wafer is placed in contact with the surface of a polishing pad so that the slurry chemically reacts with the surface of the wafer, and at the same time, the polishing pad is moved relative to the wafer to physically remove irregular portions present on the surface of the wafer.

[6] Slurries used in semiconductor CMP processes comprises deionized water, a metal oxide, a base or acid for pH adjustment, an additive for controlling the polishing rate and selectivity, and the like. The metal oxide mainly used is silica (SiO_2), alumina (Al_2O_3), ceria (CeO_2), zirconia (ZrO_2), titania (TiO_2), or the like, which are produced by a fuming or sol-gel process. As the additive, an amine type additive is mainly used to generate a number of hydroxyl ions in order to attain high polishing rates towards polycrystalline silicon films, and at the same time, to attain low polishing rates towards insulating layers.

[7] Various methods have been attempted to increase the polishing rate. For example, U.S. Patent No. 4,169,337 discloses the addition of an echant, such as aminoethylethanolamine. U.S. Patent Nos. 3,262,766 and 3,768,989 disclose the preparation of polishing compositions by co-precipitating small amounts of other particles, such as CeO_2 particles during production of SiO_2. Further, the addition of inorganic salts, such as $Ce(OH)_4$, NH_4SO_4 and $Fe(SO_4)$, to a slurry is disclosed in Mechanism of Glass Polishing Vol. 152, 1729, 1971. Many patent publications disclose slurries for increasing the polishing rate and selectivity. For example, U.S. Patent No. 4,169,337 describes a slurry composed of silica/amine/organic salt/ polyhydric alcohol, U.S. Patent No. 4,169,337 describes a slurry composed of silica/ amine, U.S. Patent No. 5,139,571 describes a slurry composed of silica/quaternary ammonium salt, U.S. Patent No. 5,759,917 describes a slurry composed ceria/ carboxylic acid/silica, U.S. Patent No. 5,938,505 describes a slurry composed of tetramethyl ammonium salt/hydrogen peroxide, and U.S. Patent No. 6,009,604 describes a slurry composed of electron-donor compound/TMAH/silica.

[8] Since slurries generally used for polishing polycrystalline silicon films have a high polishing selectivity for polycrystalline silicon films because insulating oxide films are used as stop layers. This high polishing selectivity results in dishing on the poly-crystalline silicon films due to the chemical mechanical action. The occurrence of dishing adversely affects the subsequent photo process, causing a height difference upon the formation of polycrystalline silicon lines. As a result, the electrical properties and contact characteristics inside cells are deteriorated.

[9] Thus, there is a need to develop a novel slurry capable of overcoming the problem of dishing and improving the within-wafer-non-uniformity.

[10]

Disclosure of Invention

Technical Problem

[11] Therefore, the present invention has been made in view of the above problems of the prior art, and it is an object of the present invention to provide a chemical mechanical polishing (CMP) slurry with a high selectivity that comprises a blend of metal oxide abrasive particles in ultrapure water and additives, including a non-ionic fluorine type surfactant and a quaternary ammonium base.

[12]

Technical Solution

[13] In accordance with one aspect of the present invention, there is provided a CMP slurry composition for polishing a polycrystalline silicon film, comprising:

[14] (a) a metal oxide;

[15] (b) a quaternary ammonium base and

[16] (c) a fluorine type surfactant of Formula 1 below:

[17] $CF_3(CF_2)_nSO_2X$ (1)

[18] wherein n is from 1 to 20, X is COOR, RO, $(OCH_2CH_2)_{n'}$ or $(OCH_2CH(OH)CH_2)_{n'}$, R is a $C_{1\sim20}$ alkyl group, and n' is from 1 to 100.

[19] The fluorine type surfactant of Formula 1 is preferably present in an amount of 0.001% to 1% by weight, based on the total weight of the slurry composition.

[20] The metal oxide is preferably at least one kind selected from SiO_2, Al_2O_3, CeO_2, ZrO_2 and TiO_2, and has preferably a primary particle size of 10 nm to 200 nm and a specific surface area of 10 to 300 m^2/g.

[21] The quaternary ammonium base is preferably at least one compound selected from tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, tetrapropyl ammonium hydroxide, and tetrabutyl ammonium hydroxide.

[22] A mixture of two or more kinds of the fluorine type surfactant represented by Formula 1 is simultaneously used in the present invention.

[23] In accordance with another aspect of the present invention, there is provided a method for preparing the CMP slurry composition by feeding 0.001 to 1% by weight of the fluorine type surfactant, 0.01 to 5% by weight of the quaternary ammonium base and 0.1 to 30% by weight of the metal oxide to ultrapure water, followed by mixing.

[24]

Best Mode for Carrying Out the Invention

[25] Hereinafter, the present invention will be described in more detail.

[26] The present invention provides a CMP slurry composition for polishing a poly-crystalline silicon film which comprises (a) a metal oxide, (b) a quaternary ammonium base, and (c) a fluorine type surfactant of Formula 1 below:

[27] $CF_3(CF_2)_nSO_2X$ (1)

[28] wherein n is from 1 to 20, X is COOR, RO, $(OCH_2CH_2)_{n'}$ or $(OCH_2CH(OH)CH_2)_{n'}$, R is a $C_{1\sim20}$ alkyl group, and n' is from 1 to 100.

[29] The metal oxide is not specifically restricted so long as it can be produced by a fuming or sol-gel process. Examples of suitable metal oxide include silica (SiO_2), alumina (Al_2O_3), ceria (CeO_2), zirconia (ZrO_2), and titania (TiO_2).

[30] These metal oxides preferably have a primary particle size of 10 nm to 200 nm, preferably 20 nm to 200 nm, as determined by transmission electron microscopy (TEM), and preferably have a specific surface area of 10 to 300 m^2/g. It is preferable to use silica particles as the metal oxide as this achieves better results. When the primary particle size is below 10 nm, the polishing rate (i.e. removal rate) is low and thus the throughput drops undesirably. On the other hand, when the primary particle size is above 200 nm, large particles are present in a large quantity, which unfavorably causes the formation of μ-scratches. The content of the metal oxide in the slurry is preferably from 0.1 to 30% by weight, and more preferably from 1 to 20% by weight, based on the total weight of the composition.

[31] The composition of the present invention is required to have a pH of 9 or greater in order to maintain the polishing rate of polycrystalline silicon layers at a suitable level. To this end, the composition of the present invention comprises a quaternary ammonium base as a pH-adjusting agent. Specific examples of the quaternary ammonium base include tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, tetrapropyl ammonium hydroxide, and tetrabutyl ammonium hydroxide. These quaternary ammonium bases may be used alone or in combination. It is preferable that the quaternary ammonium base be added in an amount ranging from 0.01 to 5% by weight, based on the total weight of the slurry. However, to improve the performance, it is more preferable that the quaternary ammonium base be added in an amount ranging from 0.01 to 1% by weight.

[32] The fluorine type surfactant is used to control the polishing rate and to improve the within-wafer-non-uniformity of a polycrystalline silicon film.

[33] The fluorine type surfactant used in the present invention is a non-ionic perfluoroalkane sulfonyl compound represented by Formula 1 below:

[34] $CF_3(CF_2)_nSO_2X$ (1)

[35] wherein n is from 1 to 20, X is COOR, RO, $(OCH_2CH_2)_{n'}$ or $(OCH_2CH(OH)CH_2)_{n'}$, R is a $C_{1\sim20}$ alkyl group, and n' is from 1 to 100.

[36] In Formula 1, the most preferred within-wafer-non-uniformity is achieved when n is between 1 and 8.

[37] Two or more kinds of the fluorine type surfactant represented by Formula 1 may be simultaneously used in the present invention. It is preferable that the fluorine type

surfactant be added in an amount ranging from 0.001 to 1% by weight, based on the total weight of the slurry. However, to improve the performance, it is more preferable that the fluorine type surfactant be added in an amount ranging from 0.001 to 0.5% by weight. When the fluorine type surfactant is used in an amount of less than 0.001% by weight, the polishing rate of a polycrystalline silicon film is too high, edge portions of a wafer are excessively polished, which tends to deteriorate the within-wafer-non-uniformity. Meanwhile, when the fluorine type surfactant is used in an amount exceeding 1% by weight, the polishing rate of a polycrystalline silicon film is too low, edge portions of a wafer are not adequately polished, unfavorably deteriora ting the within-wafer-non-uniformity. In addition, by appropriately controlling the amount of the fluorine type surfactant, the edge profile can be improved and occurrence of dishing can be diminished.

[38] Since the slurry composition comprising the fluorine type surfactant, the quaternary ammonium base and the metal oxide according to the present invention has an ap-propriate polishing rate, the selectivity towards a polycrystalline silicon film in preference to an insulating oxide film can reach the desired ratio 20:1 to 100:1, the most preferred within-wafer-non-uniformity can be attained, and the problem of dishing can be avoided.

[39] The present invention also provides a method for preparing the CMP slurry composition by feeding 0.001 to 1% by weight of the fluorine type surfactant, 0.01 to 5% by weight of the quaternary ammonium base and 0.1 to 30% by weight of the metal oxide to ultrapure water, followed by mixing.

[40]

Mode for the Invention

[41] The present invention will now be described in more detail with reference to the following examples. However, these examples are given for the purpose of illustration and are not to be construed as limiting the scope of the invention.

[42]

[43] Example 1

[44] First, 200g of 20 wt% TMAH was added to 12299.5g of ultrapure water. Ten minutes after the addition, 0.5g of polyoxyethylene perfluorobutyl sulfonyl ester was added thereto. To the mixture was added 2,500g of 20 wt% colloidal silica in a reactor. The resulting mixture was sufficiently stirred at 500 rpm and filtered through a 3 micron filter to obtain a slurry. A wafer was polished using the slurry for one minute under the following conditions. The thickness of the wafer before and after the polishing was measured, and the within-wafer-non-uniformity (WIWNU) was evaluated at portions other than 3 mm edges by 98-point analysis using an optiprobe.

The results are shown in Table 1 below.

[45] . Polishing Machine: UNIPLA 211 (Semicon Tech.)

[46] . Polishing Pad: IC1000/Suba IV K groove (Rodel)

[47] . Polishing substrate: F-Poly, PTEOS, 8" blanket wafer

[48] . Polishing conditions

[49] - Platen Speed: 70 rpm

[50] - Head Speed: 70 rpm

[51] - Pressure: 3.5 psi

[52] - Back Pressure: 0 psi

[53] - Temperature: 25℃

[54] - Slurry Flow: 200 ml/min.

[55]

[56] Example 2

[57] A slurry was obtained in the same manner as in Example 1, except that 1.0g of polyoxyethylene perfluorobutyl sulfonyl ester was added. The polishing performance of the slurry was evaluated in accordance with the procedure described in Example 1. The results are shown in Table 1 below.

[58]

[59] Example 3

[60] A slurry was obtained in the same manner as in Example 1, except that 1.5g of polyoxyethylene perfluorobutyl sulfonyl ester was added. The polishing performance of the slurry was evaluated in accordance with the procedure described in Example 1. The results are shown in Table 1 below.

[61] Table 1

	Colloidal silica (20%)	Amount		Polishing performance				
		Polyoxyethylene per-fluorobutyl sulfonyl ester	TMAH(20%)	Poly-Si		PTEOS		Selectivity
				Polishing rate (Å/min.)	WIWNU (%)	Polishing rate (Å/min.)	WIWNU (%)	
Example 1	2500g	0.5g	200g	2121	2.27	26	3.15	82
Example 2	2500g	1.0g	200g	1069	5.19	21	3.59	51
Example 3	2500g	1.5g	200g	708	7.66	29	3.36	24

[62] A slurry was obtained in the same manner as in Example 1, except that poly-oxyethylene perfluorobutyl sulfonyl ester was not added. The polishing performance of the slurry was evaluated in accordance with the procedure described in Example 1. The results are shown in Table 2 below.

[63]

[64] Comparative Example 2

[65] A slurry was obtained in the same manner as in Example 1, except that TMAH was not added. The polishing performance of the slurry was evaluated in accordance with the procedure described in Example 1. The results are shown in Table 2 below.

[66] Table 2

	Colloidal silica (20%)	Amount		Polishing performance				
		Polyoxyethylene per-fluorobutyl sulfonyl ester	TMAH(20%)	Poly-Si		PTEOS		Selectivity
				Polishing rate (Å/min.)	WIWNU (%)	Polishing rate (Å/min.)	WIWNU (%)	
Comp.Example 1	2500g	-	200g	3564	18.95	30	15.41	119
Comp. Example 2	2500g	0.5g	-	103	17.67	92	13	1

[67] As can be seen from the data shown in Tables 1 and 2, the simultaneous use of the fluorine type surfactant and the quaternary ammonium base enables a considerable reduction in the number of surface defects on the wafers and maintains a preferred selectivity, when compared to using the two components individually.

[68]

Industrial Applicability

[69] As apparent from the above description, the present invention provides a CMP slurry composition for polishing a polycrystalline silicon film that can solve the problem of dishing and has superior within-wafer-non-uniformity and optimal selectivity.

[70] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

Claims

[1] A chemical mechanical polishing (CMP) slurry composition for polishing a poly-crystalline silicon film, comprising:

(a) a metal oxide;

(b) a quaternary ammonium base; and

(c) a fluorine type surfactant of Formula 1 below:

$CF_3(CF_2)_nSO_2X$ (1)

wherein n is from 1 to 20, X is COOR, RO, $(OCH_2CH_2)_{n'}$ or $(OCH_2CH(OH)CH_2)_{n'}$, R is a $C_{1\sim20}$ alkyl group, and n' is from 1 to 100.

[2] The slurry composition according to claim 1, wherein the fluorine type surfactant is present in an amount of 0.001% to 1% by weight, based on the total weight of the slurry composition.

[3] The slurry composition according to claim 1, wherein the metal oxide is at least one kind selected from SiO_2, Al_2O_3, CeO_2, ZrO_2 and TiO_2 and has a primary particle size of 10 nm to 200 nm and a specific surface area of 10 to 300 m^2/g.

[4] The slurry composition according to claim 1, wherein the quaternary ammonium base is at least one compound selected from tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, tetrapropyl ammonium hydroxide, and tetrabutyl ammonium hydroxide.

[5] The slurry composition according to claim 1, wherein a mixture of two or more kinds of the fluorine type surfactant represented by Formula 1 is used.

[6] A method for preparing a CMP slurry composition by feeding 0.001 to 1% by weight of a fluorine type surfactant, 0.01 to 5% by weight of a quaternary ammonium base and 0.1 to 30% by weight of a metal oxide to ultrapure water, followed by mixing.