

CHEMICAL MECHANICAL POLISHING COMPOSITION, CHEMICAL
MECHANICAL POLISHING SLURRY AND METHOD
FOR POLISHING SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from PCT International Patent Application No. PCT/KR2019/008849, filed on July 17, 2019, which claims priority from Korean Patent Application No.10-2018-0084631, filed on July 20, 2018, and Korean Patent Application No.10-2019-0085560, filed on July 16, 2019, the entire contents of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The invention relates to a chemical mechanical polishing composition, a chemical mechanical polishing slurry and a method for polishing a substrate, and specifically to a chemical mechanical polishing composition, a chemical mechanical polishing slurry and a method for polishing a substrate that are used to form a conductor consisting of tungsten when preparing semiconductor.

BACKGROUND OF THE INVENTION

[0003] In the manufacturing process of semiconductor, a polishing slurry for a conductor is applied in the process of removing a metal film, for example a tungsten film, formed on interlayer dielectric (ILD) while filling the inside of holes formed in the interlayer dielectric, to leave the tungsten film only in the holes.

[0004] Thus, most importantly, a polishing slurry for a conductor should not only minimize contamination by residual metal impurities using a small amount of catalyst metal, but also maximize a polishing rate of metal films, should have high selectivity for lower interlayer dielectric, and should not generate pattern defects such as dishing, and the like.

[0005] However, so far commercialized or developed slurries do not sufficiently meet all the requirements.

SUMMARY OF THE INVENTION

[0006] Technical Problem

[0007] It is an object of the invention to provide a chemical mechanical polishing composition, chemical mechanical polishing slurry and a method for polishing a substrate that can realize a polishing rate equivalent to or higher than the conventional polishing agent, while decreasing total metal content.

[0008] It is another object of the invention to provide a chemical mechanical polishing composition, chemical mechanical polishing slurry and a method for polishing a substrate that can realize remarkably higher polishing rate than the conventional polishing agent when using total metal content identical as before.

[0009] It is another object of the invention to provide a chemical mechanical polishing composition, chemical mechanical polishing slurry and a method for polishing a substrate having high polishing selectivity.

[0010] It is another object of the invention to provide a chemical mechanical polishing composition, chemical mechanical polishing slurry and a

method for polishing a substrate that do not generate pattern defects such as dishing.

[0011] Technical Solution

[0012] The chemical mechanical polishing composition according to the embodiments of the invention comprises an iron-based metal catalyst; and a magnesium-based metal catalyst, wherein in the total metal content of the metal catalyst mixture, the metal content of the iron-based metal catalyst may be equal to or greater than the metal content of the magnesium-based metal catalyst.

[0013] The chemical mechanical polishing slurry according to the embodiments of the invention comprises a first solution comprising multi-metallic catalysts comprising an iron-based metal catalyst and a magnesium-based metal catalyst, a polishing agent, and the remaining amount of water, and a second solution comprising an oxidant, wherein in the total metal content of the multi-metallic catalyst mixture, the metal content of the iron-based metal catalyst may be equal to or greater than the metal content of the magnesium-based metal catalyst.

[0014] The method for polishing a substrate according to the embodiments of the invention comprises the steps of: respectively providing the first solution and the second solution; mixing the first solution and the second solution before applying on a substrate; applying the chemical mechanical polishing slurry including the mixture of the first solution and the second solution on a substrate; and contacting a pad with the substrate, and moving the pad

against the substrate, thereby removing at least a part of tungsten layers formed on the substrate.

[0015] Advantageous Effects

[0016] The chemical mechanical polishing composition and chemical mechanical polishing slurry according to the embodiments of the invention can realize a polishing rate equivalent to or higher than the conventional polishing agent, even if total metal content is decreased.

[0017] The chemical mechanical polishing composition and chemical mechanical polishing slurry according to the embodiments of the invention can realize remarkably higher polishing rate than the conventional chemical mechanical polishing composition and chemical mechanical polishing slurry, when using total metal content identical as before.

[0018] The chemical mechanical polishing composition and chemical mechanical polishing slurry according to the embodiments of the invention can improve polishing selectivity.

[0019] The chemical mechanical polishing composition and chemical mechanical polishing slurry according to the embodiments of the invention can conduct a semiconductor manufacturing process without generating pattern defects.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0020] Hereinafter, embodiments of the invention will be explained in detail so that a person having ordinary knowledge in the art can easily practice

them. However, the invention may be realized in different forms, and is not limited to the embodiments explained herein.

[0021] The “chemical mechanical polishing composition” and “chemical mechanical slurry” of the invention are useful for polishing, for example, multi-metal layers including integrated circuit thin films, and semiconductor thin films, and other films, surfaces and substrates for which CMP process is useful. Particularly, they are used to polish at least one metal layers related to substrates selected from the group consisting of integrated circuit, thin film, multilayered semiconductor and wafer-related silicon substrate, TFT-LCD glass substrate, GaAs substrate and other substrates, for example, a tungsten layer. Particularly, the chemical mechanical polishing composition of the invention may be used to polish one or more tungsten layers, titanium and titanium nitride layers filled in the holes of an insulation film and also formed on the insulation film, to form a conductor in the holes of the insulation film in one step.

[0022] Wherein, throughout the specification, the chemical mechanical polishing composition may mean a first solution included in the chemical mechanical polishing slurry used to polish a semiconductor substrate. And, the chemical mechanical polishing slurry may mean a composition consisting of the first solution, and a second solution comprising an oxidant. The first solution and the second solution will be described below.

[0023] Hereinafter, the invention will be explained in detail.

[0024] According to one embodiment of the invention, there is provided a chemical mechanical polishing composition comprising an iron-based metal

catalyst; and a magnesium-based metal catalyst, wherein in the metal content of the metal catalyst mixture, the metal content of the iron-based metal catalyst is equal to or greater than the metal content of the magnesium-based metal catalyst.

[0025] The chemical mechanical polishing composition comprises multi-catalysts comprising an iron-based metal catalyst and a magnesium-based metal catalyst together, instead of a single catalyst component. As the result of creative efforts for finding out various catalysts capable of exhibiting synergistic effects among the existing numerous catalysts, the inventors confirmed that in case an iron-based metal catalyst and a magnesium-based metal catalyst are used together, polishing performance equivalent to or more excellent than before may be exhibited while decreasing the amount of catalysts used, and very remarkable polishing performance may be exhibited when using the same amount as before.

[0026] The iron-based metal catalyst may be selected from the group consisting of iron(II) nitrate, iron(III) nitrate, iron chloride, iron(II) sulfate, inorganic salts of iron including iron(III) sulfate, iron(II) halide, iron(III) halide (for example, fluoride, chloride, bromide and iodide), perchlorate, perbromate, and periodate, ferrosilicon, and organic iron(II) or organic iron(III) acetate, acetylacetonate, citrate, gluconate, malonate, oxalate, phthalate, succinate, or a mixture thereof. Wherein, the iron(II) nitrate and iron(III) nitrate may be in the form of hydrates as well known. For example, as the iron nitrate, iron(III) nitrate nonahydrate may be used.

[0027] According to one embodiment of the invention, the iron-based metal catalyst may be iron(II) nitrate, iron(III) nitrate, iron chloride, iron(II) sulfate, iron(III) sulfate or ferrosilicon.

[0028] The magnesium-based metal catalyst may be selected from the group consisting of magnesium nitrate, magnesium chloride, magnesium sulfate, magnesium citrate, magnesium diglutamate, magnesium formate, magnesium gluconate, magnesium glycinate, magnesium lactate, and magnesium oxalate. Wherein, the magnesium nitrate and magnesium sulfate may be in the form of hydrates as well known. For example, as the magnesium nitrate, magnesium nitrate hexahydrate may be used, and as the magnesium sulfate, magnesium sulfate hexahydrate may be used.

[0029] According to one embodiment of the invention, the magnesium-based metal catalyst may be magnesium nitrate, magnesium chloride or magnesium citrate.

[0030] Meanwhile, in the total metal content of the metal catalyst mixture, the metal content of the iron-based metal catalyst may be equal to or greater than the metal content of the magnesium-based metal catalyst.

[0031] According to one embodiment, based on the total metal content of the metal catalyst mixture, the metal content of the iron-based metal catalyst may be 1 to 20 times greater than the metal content of the magnesium-based metal catalyst.

[0032] And, in the metal catalyst mixture using the two metal catalyst in combination, on the basis of the total metal content, the minimum metal content

of the magnesium-based metal catalyst may be 0.0001wt% (1 ppm) based on the chemical mechanical polishing composition. And, on the basis of the total metal content of the metal catalyst mixture, the maximum metal content of the iron-based metal catalyst may be 0.0295wt% (295ppm). Wherein, in case the minimum metal content of the magnesium-based metal catalyst is less than 0.0001wt% based on the chemical mechanical polishing composition, a polishing rate may be remarkably low. And, in case the maximum metal content of the iron-based metal catalyst is greater than 0.0295wt%, increase in a polishing rate may slow down, and thus, it may not be economically efficient.

[0033] According to one embodiment of the invention, the total metal content of the iron-based metal catalyst and magnesium-based metal catalyst may be 0.002wt% to 0.03wt%, based on the chemical mechanical polishing composition. For example, the total metal content of the iron-based metal catalyst and magnesium-based metal catalyst may be 0.003wt% to 0.03wt%, based on the chemical mechanical polishing composition.

[0034] According to one embodiment of the invention, the maximum metal content of the iron-based metal catalyst may be 0.0295wt% based on the chemical mechanical polishing composition, the minimum metal content of the magnesium-based metal catalyst may be 0.0001wt% based on the chemical mechanical polishing composition, and the total metal content of the iron-based metal catalyst and magnesium-based metal catalyst may be 0.002wt% to 0.03wt% based on the chemical mechanical polishing composition.

[0035] Wherein, the chemical mechanical polishing composition may further comprise a dispersion stabilizer selected from tributylamine, methanesulfonic acid, or a mixture thereof.

[0036] The dispersion stabilizer may be included in the content of 0.0001 to 0.04wt%, or 0.003 to 0.01wt%, based on the chemical mechanical polishing composition.

[0037] In addition, the chemical mechanical polishing composition may further comprise a polishing agent. The content of the polishing agent is not specifically limited, but it may be included in the content of 0.01 to 8 wt%, based on the chemical mechanical polishing composition.

[0038] Further, the chemical mechanical polishing composition may further comprise the remaining amount of water.

[0039] The chemical mechanical polishing composition may further comprise well known additives, for example, a pH control agent, disinfectant, and the like.

[0040] The explanations about the metal catalyst are also applied to the multi-metallic catalyst included in the first solution of the following chemical mechanical polishing slurry.

[0041] Thus, according to another embodiment of the invention, there is provided a chemical mechanical polishing slurry comprising: a first solution, namely a chemical mechanical polishing composition, comprising multi-metallic catalysts comprising an iron-based metal catalyst and a magnesium-based metal catalyst; a polishing agent; and the remaining amount of water, and a second

solution comprising an oxidant, wherein in the total metal content of the multi-metallic catalyst mixture, the metal content of the iron-based metal catalyst is equal to or greater than the metal content of the magnesium-based metal catalyst.

[0042] And, according to yet another embodiment of the invention, there is provided a method for polishing a substrate comprising one or more tungsten layers, comprising the steps of: respectively providing the first solution and the second solution; mixing the first solution and the second solution before applying on a substrate; applying the chemical mechanical polishing slurry including the mixture of the first solution and the second solution on a substrate; and contacting a pad with the substrate, and moving the pad against the substrate, thereby removing at least a part of the tungsten layers formed on the substrate.

[0043] Namely, the chemical mechanical polishing composition may comprise a first solution comprising multi-metallic catalysts comprising an iron-based metal catalyst and a magnesium-based metal catalyst, a polishing agent and the remaining amount of water, wherein the metal content of the iron-based metal catalyst may be equal to or greater than the metal content of the magnesium-based metal catalyst. The first solution may be stored separately from a second solution comprising an oxidant, and they may be mixed before applying on a substrate, and then, applied on the substrate. And then, by contacting a polishing pad with the substrate, and moving the pad against the substrate, at least a part of the metal layers(for example, tungsten layers) on the

substrate may be removed. Meanwhile, the first solution may comprise a polishing agent. The polishing agent may be included in the content of 0.01 to 8 wt%, for example, 0.02 to 5wt%, specifically 0.1 to 3wt%, based on the first solution. The polishing agent is typically a metal oxide polishing agent. The metal oxide polishing agent may be selected from the group consisting of alumina, titania, zirconia, germania, silica, cerium oxide, and a mixture thereof. The polishing agent may have an average aggregate size of 10 to 150nm. The metal oxide polishing agent is mixed with the aqueous medium of the first solution as an aqueous dispersion of metal oxide.

[0044] The first solution may further comprise a pH control agent to maximize colloidal stability in the slurry. As the pH control agent, nitric acid, hydrochloric acid, phosphoric acid, acetic acid, malonic acid, quaternary ammonium compounds, potassium hydroxide, and the like may be used. The pH control agent may be added such that the pH of the first solution may become 1 to 6, for example, 2 to 4.

[0045] The first solution may further comprise a disinfectant. The disinfectant may inhibit the growth of microorganism or remove microorganism. As the disinfectant, CMIT (chloromethylisothiazolinone), BIT (benzisothiazolinone), and the like may be used. The disinfectant may be included in the content of 0.0001 to 0.1 wt%, for example, 0.001 to 0.08 wt%, specifically 0.01 to 0.05 wt%, based on the first solution.

[0046] The first solution may further comprise a dispersion stabilizer. As the dispersion stabilizer, tributylamine, methanesulfonic acid, or a mixture

thereof may be used. The dispersion stabilizer may be included in the content of 0.0001 to 0.04wt%, for example, 0.003 to 0.01wt%, based on the first solution.

[0047] The second solution may comprise an oxidant. As the oxidant, inorganic or organic per-compound may be used. The per-compound is a compound including one or more peroxy groups (-O-O-) or a compound including an element of the highest oxidation state. As the examples of the compound including one or more peroxy groups, although not limited hereto, hydrogen peroxide and adducts thereof, for example, urea hydrogen peroxide and percarbonate, organic peroxide, benzyl peroxide, peracetic acid, and di-t-butyl peroxide, monopersulfate(SO_5^{2-})-based compounds, disulfate($\text{S}_2\text{O}_8^{2-}$)-based compounds, and sodium peroxide may be mentioned. Specifically, the oxidant may be hydrogen peroxide. The second solution may be mixed with the first solution such that the content may become 0.1 to 5wt%, for example, 0.5 to 3.5 wt%, specifically 1 to 2.5 wt%, based on the total content of the slurry mixed.

[0048] Hereinafter, preferable embodiments of the invention will be explained in detail through examples. However, these examples are presented only for explanation, and the scope of the invention is not limited thereto.

[0049] Comparative Examples 1 to 13 and Examples 1 to 18

[0050] Preparation of polishing slurry and evaluation of polishing

[0051] For test, a 8 inch tungsten blanket wafer, a blanket wafer on which a 8 inch PE-TEOS insulation film is formed, and a 8 inch SKW5-3 Damascene pattern wafer were used (hereinafter, referred to as a semiconductor substrate).

[0052] As a polishing apparatus, Mirra 3400 (Applied Materials, Inc.) was used, and as a polishing pad, IC-1010(Rohm & Haas) was used, and polishing conditions were set as described in the following Table 1.

[0053] Table 1

platen	head	IC pressure	RR pressure	EC pressure	UC pressure	Slurry flow
Rpm	rpm	psi	psi	psi	psi	ml/min
84	78	3.6	10.4	5.2	5.2	200

[0054] After polishing, the thickness of the tungsten film was measured using CMT-2000(4 point probe, Changmin Tech Co., Ltd.), and the thickness of the insulation film was measured using Thermawave OP-2600 (KLA TENCOR), and then, a polishing rate was calculated by subtracting the thickness after CMP from the thickness before CMP. The results are shown in Tables 2 to 4.

[0055] For particle size analysis, ELS-Z(Otsuka Electronics) was used.

[0056] 1) Preparation of chemical mechanical polishing slurry
(Preparation of first solution and second solution)

[0057] Colloidal silica was used as a polishing agent, and stirred with the catalysts of the contents described in the following Tables 2 to 6 using a stirrer, and then, pH was adjusted to a target pH using a pH control agent, thus preparing a first solution. And, before polishing the semiconductor substrate, a separately prepared second solution comprising hydrogen peroxide was mixed with the first solution to prepare a chemical mechanical polishing slurry, and then, CMP(chemical mechanical polishing) evaluation was progressed.

[0058] Specifically, in the case of Comparative Examples 1 to 6, and 8, and Examples 1 to 9 in Table 2 and Table 5, 1.3wt% of colloidal silica having particle size of 90nm was used together with metal catalysts, and after adding 0.03wt% of CMIT, pH was adjusted to 3 using nitric acid and tetramethylammonium hydroxide. As the second solution, 31wt% hydrogen peroxide solution was used, and mixed with the first solution such that the final content became 1.5wt%. When preparing the first solution, water was used in the remaining amount. Wherein, in Comparative Example 7, a slurry comprising hydrogen peroxide only was prepared by the same method as described above, except that a metal catalyst was not used.

[0059] In the case of Comparative Examples 9 to 12 and Examples 10 to 12 in Table 3, 0.85wt% of colloidal silica having particle size of 90nm was used together with metal catalyst, and after adding 0.03wt% of BIT, pH was adjusted to 2.8 using nitric acid and tetramethylammonium hydroxide. As the second solution, 31wt% hydrogen peroxide solution was used, and mixed with the first solution such that the final content became 1.5wt%. When preparing the first solution, water was used in the remaining amount.

[0060] In the case of Comparative Example 13 and Examples 13 to 14 in Table 4, 2.0wt% of colloidal silica having particle size of 90nm was used together with metal catalyst, and after adding 0.03wt% of BIT, pH was adjusted to 2.5 using nitric acid and tetramethylammonium hydroxide. As the second solution, 31wt% hydrogen peroxide solution was used, and mixed with the first

solution such that the final content became 1.5wt%. When preparing the first solution, water was used in the remaining amount.

[0061] In the case of Examples 15 to 17 in Table 6, 1.3wt% of colloidal silica having particle size of 90nm was used together with metal catalyst, and after adding 0.03wt% of CMIT, and adding a dispersion stabilizer in the content described in Table 5, pH was adjusted to 3 using nitric acid and tetramethylammonium hydroxide. As the second solution, 31wt% hydrogen peroxide solution was used, and mixed with the first solution such that the final content became 1.5wt%. When preparing the first solution, water was used in the remaining amount.

[0062] 2) Measurement of polishing rate of tungsten blanket wafer

[0063] Table 2

No.	Kind and content of catalyst	Metal content	Total metal content	Tungsten polishing rate (Å/min)
Comparative Example 1	iron nitrate 0.0362 wt%	Fe 50 ppm	50 ppm	1,113
Comparative Example 2	iron nitrate 0.2170 wt%	Fe 300 ppm	300 ppm	2,202
Comparative Example 3	magnesium nitrate 0.00053 wt%	Mg 0.5 ppm	0.5 ppm	105
Comparative Example 4	magnesium nitrate 0.0011 wt%	Mg 1 ppm	1 ppm	315
Comparative Example 5	magnesium nitrate 0.0844 wt%	Mg 80 ppm	80 ppm	991
Comparative Example 6	ferrosilicon 0.0075 wt%	Fe 50 ppm	50 ppm	1,380
Comparative Example 7	-	-	0 ppm	98
Example 1	iron nitrate 0.0145 wt% magnesium nitrate 0.0211 wt%	Fe 20 ppm Mg 20 ppm	40 ppm	1,816
Example 2	ferrosilicon 0.0023 wt% magnesium nitrate 0.0158 wt%	Fe 15 ppm Mg 15 ppm	30 ppm	1,447
Example 3	iron nitrate 0.0072 wt% magnesium nitrate 0.0032 wt%	Fe 10 ppm Mg 3 ppm	13 ppm	1,098
Example 4	iron nitrate 0.0109 wt% magnesium nitrate 0.0053 wt%	Fe 15 ppm Mg 5 ppm	20 ppm	1,228
Example 5	iron nitrate 0.0289 wt%	Fe 40 ppm	45 ppm	2,007

	magnesium nitrate 0.0053 wt%	Mg 5 ppm		
Example 6	iron nitrate 0.0253 wt% magnesium nitrate 0.0011 wt%	Fe 35 ppm Mg 1 ppm	36 ppm	1,685
Example 7	iron nitrate 0.1772 wt% magnesium nitrate 0.0369 wt%	Fe 245 ppm Mg 35 ppm	280 ppm	3,119
Example 8	iron nitrate 0.1809 wt% magnesium nitrate 0.0527 wt%	Fe 250 ppm Mg 50 ppm	300 ppm	3,335
Example 9	iron nitrate 0.2134 wt% magnesium nitrate 0.0158 wt%	Fe 295 ppm Mg 15 ppm	310 ppm	3,218
Comparative Example 8	iron nitrate 0.2134 wt%	Fe 295 ppm	295 ppm	2,411

[0064] In the Table 2, iron nitrate was iron(III) nitrate nonahydrate, and magnesium nitrate was magnesium nitrate hexahydrate.

[0065] From the results of Table 2, it can be confirmed that compared to Comparative Examples 1, 5 and 6 using magnesium nitrate, iron nitrate, or ferrosilicon alone, when using an iron catalyst and a magnesium catalyst in combination as in Examples 1 to 6, higher tungsten polishing rates are exhibited despite smaller metal contents of the catalysts. Specifically, it can be seen that in the Examples wherein the metal contents of the catalysts are smaller, polishing rates are relatively higher than Comparative Examples. Thus, the Examples of the invention can realize a polishing rate equivalent to or higher than the conventional polishing agent, while decreasing total metal content.

[0066] Wherein, in case the total content of the iron catalyst and magnesium catalyst is 0.0132 wt% or less(the total content of iron metal and magnesium metal is 20ppm or less)(Example 3), catalyst content is too small, and thus, a polishing rate is not sufficient, and in case the total content of the iron catalyst and magnesium catalyst is 0.023 wt% or more(the total content of iron metal and magnesium metal is 300ppm or more)(Example 9), a polishing rate decreases to the contrary. And, in the case of Example 9, even if the content of

Fe metal catalyst is the maximum value of 295 ppm(0.0295wt%), the total content of Fe+Mg is 300ppm or more, and thus, a polishing rate does not increase any longer and rather decreases, but the polishing rate is excellent. However, in the case of Comparative Example 8 wherein only an iron-based metal catalyst is used, even if the Fe content becomes 295ppm(0.0295wt%) as in Example 9, a polishing rate is lower than Example 9. It can be seen from these results that it is preferable to use iron-based and magnesium-based metal catalysts in combination within the content range described herein.

[0067] Meanwhile, in the case of Examples 7 to 8 wherein total metal content is identical or similar as before, remarkably higher polishing rate than Comparative Example 2 can be realized. Namely, the Examples of the invention can realize remarkably higher polishing rate than before, when using the same total metal content as before.

[0068] In addition, in the case of Comparative Examples 3 and 4, the total metal catalyst content is smaller and only one kind of metal catalyst is used, and thus, a polishing rate is very inferior. Namely, in the case of Comparative Example 3, the content of the magnesium-based metal catalyst is too small (0.5 ppm, which is less than 1 ppm (0.0001 wt%)), and thus, a polishing rate is very low. In addition, the polishing rate is almost similar to the polishing rate of Comparative Example 7 wherein the slurry comprises only hydrogen peroxide without metal catalysts, and thus, improvement in the polishing rate cannot be anticipated. In the case of Comparative Example 4, the metal catalyst content is

1 ppm, and thus, a polishing rate is improved compared to Comparative Example 3, but the polishing rate is very inferior to the Examples of the invention.

[0069] Table 3

No.	Kind and content of catalyst	Content of metal	Total content of metal	Tungsten polishing rate (Å/min)
Comparative Example 9	iron chloride 0.0339 wt%	Fe 70 ppm	70 ppm	1,472
Comparative Example 10	iron chloride 0.0290 wt% nickel nitrate 0.0030 wt%	Fe 60 ppm Ni 6 ppm	66 ppm	1,308
Comparative Example 11	iron chloride 0.0290 wt% aluminum nitrate 0.0083 wt%	Fe 60 ppm Al 6 ppm	66 ppm	1,175
Comparative Example 12	iron chloride 0.0290 wt% calcium nitrate 0.0035 wt%	Fe 60 ppm Ca 6 ppm	66 ppm	998
Example 10	iron chloride 0.0290 wt% magnesium nitrate 0.0063 wt%	Fe 60 ppm Mg 6 ppm	66 ppm	2,388
Example 11	iron chloride 0.0290 wt% magnesium chloride 0.0024 wt%	Fe 60 ppm Mg 6 ppm	66 ppm	2,071
Example 12	iron chloride 0.0290 wt% magnesium citrate 0.0053 wt%	Fe 60 ppm Mg 6 ppm	66 ppm	2,150

[0070] The catalyst used in Comparative Examples 10 to 12 of Table 3 are nickel nitrate hexahydrate, aluminum nitrate nonahydrate, and potassium nitrate tetrahydrate.

[0071] As can be seen from the results of Table 3, even if multi-catalysts are used, in case multi-catalysts combining an iron-based catalyst and a nickel, aluminum, or calcium-based catalyst, different from the present disclosure, are used, tungsten polishing rate decreases to the contrary (Comparative Example 10 to 12). And, in the case of Comparative Example 9, only a single catalyst is used, and the polishing rate is higher than Comparative Example 10 to 12, but lower than Examples 10 to 12.

[0072] On the contrary, it can be confirmed that in case an iron-based catalyst and magnesium nitrate, magnesium chloride or magnesium citrate are combined, a tungsten polishing rate remarkably increases (Examples 10 to 12).

[0073] 3) Polishing rates of tungsten blanket wafer and insulation blanket wafer, and measurement of pattern wafer dishing

[0074] Table 4

No.	Kind and content of catalyst	Content of metal	Total content of metal	Blanket			Pattern Dishing(Å)	
				Polishing rate of tungsten (Å/min)	Polishing rate of insulation film (Å/min)	Selectivity (tungsten/insulation film)	10 μm (50% density)	1 μm (50% density)
Comparative Example 13	iron nitrate 0.0362 wt%	Fe 50 ppm	50 ppm	1,321	355	3.7	780	533
Example 13	ferrosilicon 0.0023 wt% magnesium nitrate 0.0158 wt%	Fe 15 ppm Mg 15 ppm	30 ppm	1,924	348	5.5	596	399
Example 14	iron nitrate 0.0289 wt% magnesium nitrate 0.0053 wt%	Fe 40 ppm Mg 5 ppm	45 ppm	2,359	370	6.4	492	358

[0075] In the Table 4, iron nitrate is iron(III) nitrate nonahydrate, and magnesium nitrate is magnesium nitrate hexahydrate.

[0076] From the results of Table 4, it can be confirmed that in case an iron-based catalyst and a magnesium-based catalyst are used in combination, despite smaller metal content of the catalysts, the polishing rate of tungsten increases, the polishing rate of an insulation film is maintained, and selectivity

increases. In addition, from the results of polishing pattern wafer, it can be seen that dishing decreases in 1 μm (50% density), 10 μm (50% density) patterns. Thus, it can be seen that in case the polishing slurries according to Examples of the invention are used, not only polishing rate can be improved, but also pattern dishing can be decreased, compared to Comparative Examples.

[0077] 4) Analysis of residual metal impurities

[0078] After polishing, the wafer was cleaned with DIW(deionized water) and an ammonia solution, and dried, and then, using TXRF 3750 equipment (Rigaku Corporation), the content of metal impurities on the wafer surface after polishing was analyzed for Comparative Example 2 and Example 5. The detection limit of the equipment used was 10^8 atoms/cm². The results were shown in Table 5.

[0079] Table 5

[0080] unit: $\times 10^{10}$ atoms/cm²

No.	Kind and content of catalyst	Content of metal	Total content of metal	Co	Cu	Zn	Na	Mg	Al	Cr	Mn	Fe	Ni	Mg
Blanket wafer				N.D	0.8	2.3	N.D	N.D	N.D	3.2	N.D	5.2	1.7	0.9
Comparative Example 2	iron nitrate 0.2170 wt%	Fe 300 ppm	300 ppm	N.D	1.7	2.1	1.5	0.3	0.1	3.4	0.8	196	2.2	1.3
Example 5	iron nitrate 0.0289 wt% magnesium nitrate 0.0053 wt%	Fe 40 ppm Mg 5 ppm	45 ppm	N.D	1.4	2.1	1.3	0.5	0.1	3.5	1.1	18	2	1.4

[0081] In the Table 5, iron nitrate is iron(III) nitrate nonahydrate, and magnesium nitrate is magnesium nitrate hexahydrate.

[0082] As shown in the results of Table 5, as the result of analyzing metal impurities on the wafer surface after polishing, compared to Comparative Example 2 comprising an iron-based catalyst only, in the case of Example 8 exhibiting similar tungsten polishing rate, the amount of metal impurities remaining on the wafer surface after polishing is remarkably smaller (91% decrease).

[0083] 5) Particle size stability test

[0084] Using ELS-Z(Otsuka Electronics), particle size stabilities immediately after preparation, after 60 days, and after 180 days were evaluated for the chemical mechanical polishing slurries of some Comparative Examples and Examples. The results are shown in Table 6.

[0085] Table 6

No.	Kind and content of catalyst	Content of metal	Total content of metal	Dispersion stabilizer	Immediately after preparation	After 60 days	After 180 days
Comparative Example 2	iron nitrate 0.2170 wt%	Fe 300 ppm	300 ppm	-	97nm	109nm	135nm
Example 5	iron nitrate 0.0289 wt% magnesium nitrate 0.0053 wt%	Fe 40 ppm Mg 5 ppm	45 ppm	-	98nm	99nm	109nm
Example 8	iron nitrate 0.1809 wt% magnesium nitrate 0.0527 wt%	Fe 250 ppm Mg 50 ppm	300 ppm	-	96nm	104nm	131nm

Example 15	iron nitrate 0.1809 wt% magnesium nitrate 0.0527 wt%	Fe 250 ppm Mg 50 ppm	300 ppm	tributylamine 0.01 wt%	98nm	97nm	100nm
Example 16	iron nitrate 0.1809 wt% magnesium nitrate 0.0527 wt%%	Fe 250 ppm Mg 50 ppm	300 ppm	Methanesulfonic acid 0.003 wt%	97nm	100nm	107nm
Example 17	iron nitrate 0.1809 wt% magnesium nitrate 0.0527 wt%	Fe 250 ppm Mg 50 ppm	300 ppm	tributylamine 0.005wt%+methane sulfonic acid 0.001wt%	97nm	97nm	98nm

[0086] In the Table 6, iron nitrate is iron(III) nitrate nonahydrate, and magnesium nitrate is magnesium nitrate hexahydrate.

[0087] As shown in Table 6, in the case of Comparative Example 2 comprising a large quantity of iron nitrate catalyst, as time elapses, dispersion stability of colloidal silica is lowered and particle size remarkably increases.

[0088] On the contrary, in the case of Examples 5 and 8, increase in particle size is small. And, in case tributylamine or methansulfonic acid is additionally used as a dispersion stabilizer, the effect of stabilizing particle size can be further enhanced (Examples 15 to 17).

[0089] Although preferable Examples of the invention have been explained in detail, the scope of the right of the invention is not limited thereby, and many modifications and improvements by a person having ordinary knowledge in the art using the basic concept of the invention as defined in the claims are also within the scope of the right of the invention.

What is claimed is:

1. A chemical mechanical polishing composition comprising
an iron-based metal catalyst; and
a magnesium-based metal catalyst,
wherein in the metal content of the metal catalyst mixture, the metal content of the iron-based metal catalyst is equal to or greater than the metal content of the magnesium-based metal catalyst.
2. The chemical mechanical polishing composition according to claim 1, wherein the magnesium-based metal catalyst is selected from the group consisting of magnesium nitrate, magnesium chloride, magnesium sulfate, magnesium citrate, magnesium diglutamate, magnesium formate, magnesium gluconate, magnesium glycinate, magnesium lactate, and magnesium oxalate.
3. The chemical mechanical polishing composition according to claim 1, wherein the iron-based metal catalyst is selected from the group consisting of iron(II) nitrate, iron(III) nitrate, iron chloride, iron(II) sulfate, iron(III) sulfate, iron(II) halide, iron(III) halide, inorganic iron salts including perchlorate, perbromate and periodate, ferrosilicon, and organic iron(II) or organic iron(III) acetate, acetylacetonate, citrate, gluconate, malonate, oxalate, phthalate, succinate or a mixture thereof.

4. The chemical mechanical polishing composition according to claim 2, wherein the magnesium-based metal catalyst is magnesium nitrate, magnesium chloride or magnesium citrate.

5. The chemical mechanical polishing composition according to claim 3, wherein the iron-based metal catalyst is iron(II) nitrate, iron(III) nitrate, iron chloride, iron(II) sulfate, iron(III) sulfate or ferrosilicon.

6. The chemical mechanical polishing composition according to claim 1, wherein the metal content of the iron-based metal catalyst is 1 to 20 times greater than the metal content of the magnesium-based metal catalyst.

7. The chemical mechanical polishing composition according to claim 1, wherein the metal content of the magnesium-based metal catalyst is minimum 0.0001wt%.

8. The chemical mechanical polishing composition according to claim 7, wherein the metal content of the iron-based metal catalyst is maximum 0.0295wt%.

9. The chemical mechanical polishing composition according to claim 1, wherein total metal content of the iron-based metal catalyst and magnesium-based metal catalyst is 0.002wt% to 0.03wt%.

10. The chemical mechanical polishing composition according to claim 1, further comprising a dispersion stabilizer selected from tributylamine, methanesulfonic acid, or a mixture thereof.

11. The chemical mechanical polishing composition according to claim 10, wherein the dispersion stabilizer is included in the content of 0.0001 to 0.04wt%, based on the chemical mechanical polishing composition.

12. The chemical mechanical polishing composition according to claim 11, wherein the dispersion stabilizer is included in the content of 0.003 to 0.01wt%, based on the chemical mechanical polishing composition.

13. A chemical mechanical polishing slurry comprising:
a first solution comprising
multi-metallic catalysts comprising an iron-based metal catalyst and a magnesium-based metal catalyst;
a polishing agent; and
the remaining amount of water, and
a second solution comprising an oxidant,
wherein in the total metal content of the multi-metallic catalyst mixture, the metal content of the iron-based metal catalyst is equal to or greater than the metal content of the magnesium-based metal catalyst.

14. The chemical mechanical polishing slurry according to 13, wherein the metal content of the iron-based metal catalyst is 1 to 20 times greater than the metal content of the magnesium-based metal catalyst.

15. The chemical mechanical polishing slurry according to 13, comprising the first solution in which the metal content of the magnesium-based metal catalyst is minimum 0.0001wt%.

16. The chemical mechanical polishing slurry according to 13, comprising the first solution in which the metal content of the iron-based metal catalyst is maximum 0.0295wt%.

17. The chemical mechanical polishing slurry according to 13, comprising the first solution in which the total metal content of the iron-based metal catalyst and magnesium-based metal catalyst is 0.002wt% to 0.03wt%.

18. The chemical mechanical polishing slurry according to 13, wherein the first solution further comprises a dispersion stabilizer selected from tributylamine, methansulfonic acid, or a mixture thereof.

19. The chemical mechanical polishing slurry according to 18, wherein the dispersion stabilizer is included in the content of 0.0001 to 0.04wt%, based on the first solution.

20. A method for polishing a substrate including one or more tungsten layers, comprising:

respectively providing the first solution and the second solution according to any one of claims 13 to 19;

mixing the first solution and the second solution before applying on a substrate;

applying the chemical mechanical polishing slurry including the mixture of the first solution and the second solution on a substrate; and

contacting a pad with the substrate, and moving the pad against the substrate, thereby removing at least a part of the tungsten layers formed on the substrate.