



(51) International Patent Classification:
H01L 21/306 (2006.01)

(21) International Application Number:
PCT/US2015/028593

(22) International Filing Date:
30 April 2015 (30.04.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/987,204 1 May 2014 (01.05.2014) US

(71) Applicant: **ADVANCED TECHNOLOGY MATERIALS, INC.** [US/US]; 7 Commerce Drive, Danbury, Connecticut 06810 (US).

(72) Inventors: **BARNES, Jeffrey A.**; 2 Tulip Tree Lane, Bethlehem, Connecticut 06751 (US). **COOPER, Emanuel I.**; 25 Atherstone Road, Scarsdale, New York 10583 (US).

(74) Agent: **FUIERER, Tristan**; Moore & Van Allen PLLC, P.O. Box 13706, Research Triangle Park, North Carolina 27709 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Published:

— with international search report (Art. 21(3))

(54) Title: Ni SELECTIVE ETCHING COMPOSITION THAT IS COMPATIBLE WITH NiGe AND Ge

(57) Abstract: Compositions and methods for selectively removing unreacted metal material (e.g., unreacted nickel) relative to metal germanide (e.g., NiGe) from microelectronic devices having same thereon. The compositions are substantially compatible with other materials present on the microelectronic device such as low-k dielectrics and silicon nitride.



WO 2015/168449 A1

Ni SELECTIVE ETCHING COMPOSITION THAT IS COMPATIBLE WITH NiGe AND Ge**FIELD**

[0001] The present invention generally relates to a composition and process for the selective removal of metal relative to metal germanide and germanium layers. More specifically, the present invention relates to a composition and process for the selective removal of nickel relative to nickel germanide and Ge. The compositions are formulated to be substantially compatible with other materials present on the microelectronic device (e.g., low-k dielectrics, silicon nitride, etc.) and result in less etching of the metal germanide layer.

DESCRIPTION OF THE RELATED ART

[0002] An approach for modifying the electronic properties of a semiconductor element (e.g., to reduce the resistivity of a semiconductor region in a substrate, so as to change the work-function of a semiconductor gate electrode formed upon this substrate) is to deposit a metal over at least the particular semiconductor element. The stack that includes the metal and the semiconductor material is then heated to produce a semiconductor-metal compound layer. This layer has a lower resistivity than the resistivity of the starting semiconductor material and, thus, has a different work-function. Unreacted metal is then removed from the substrate, such as selectively from the semiconductor-metal compound. Such a process leaves the semiconductor-metal compound layer intact and removes excess unreacted metal from the deposition and heating operations. The semiconductor layers formed by such processes may be referred to as semiconductor metalide layers.

[0003] A semiconductor metalide layer that is obtained by selectively removing unreacted metal without performing any subsequent masking step to pattern the metalide layer is typically referred to as a self-aligned structure. In certain embodiments, an additional heating step is performed to further reduce the resistivity of the semiconductor metalide layer, e.g., by changing the crystal phase of this layer.

[0004] Examples of such semiconductor-metal compounds are silicides. Metal silicide thin films are commonly used in microelectronic circuits in a variety of applications, such as interconnects, contacts and for the formation of transistor gates. For example, titanium disilicide (TiSi_2), cobalt disilicide (CoSi_2), and/or nickel silicide (NiSi) are used in Ultra Large Scale Integration Semiconductor devices having submicron feature sizes. As is known, silicide layers have a lower sheet resistance than the corresponding sheet resistance of the silicon from which they are formed.

[0005] Due to its electronic properties, germanium and SiGe are, for various MOS technologies, considered to be suitable replacements for silicon as the semiconductor material of choice to form substrates and/or gate electrodes. Germanides, e.g., compounds resulting from the reaction between

germanium and a metal, such as Ni, are used to reduce the resistivity of source and drain regions, or to reduce the resistivity of gate electrodes and, thus, modify the work-function of the gate electrodes.

[0006] In practice, a metal layer (e.g., a nickel layer) will react with germanium regions of a semiconductor structure to form a nickel germanide film, or layer. This nickel germanide layer, in turn, may be located between germanium substances of the structure and source and drain metal contacts for purposes of reducing contact resistances between the germanium substances and these contacts. After the metal layer to form the germanide layer is deposited, the resulting metal germanide and silicide regions are annealed. Subsequently the structure is selectively wet etched with an etching fluid to remove the excess or unreacted metal regions (unreacted or excess nickel regions, for example) relative to the germanide layer and the unreacted germanium.

[0007] Germanium-based substances, such as germanide films, germanium-doped regions and SiGe and elemental germanium substrates, may be highly susceptible to the etchant, or etching fluid, that is conventionally used to etch nickel. For example, a typical etching fluid for nickel contains an acid, such as sulfuric acid, and an oxidant, such as hydrogen peroxide or nitric acid, which are highly oxidizing in nature. Although these etching fluids may be used in a standard silicon-based process, these etching fluids undesirably pit the metal germanide films and cause galvanic corrosion of germanium (Ge) when Ge or SiGe is exposed and coupled with nickel germanide (NiGe) or NiPtGe.

[0008] Accordingly, it is an object of the present invention to provide a composition that selectively removes unreacted metal (e.g., Ni), while not substantially removing other layers (e.g., metal germanide such as NiGe, germanium and/or SiGe) that may be present on the surface of the microelectronic device.

SUMMARY

[0009] The present invention generally relates to a composition and process for the selective removal of metal relative to metal germanide, germanium, and/or SiGe layers. More specifically, the present invention relates to a composition and process for the selective removal of nickel relative to nickel germanide, Ge, and/or SiGe. The compositions are formulated to be substantially compatible with other materials present on the microelectronic device and result in less pitting of the metal germanide layer as well as less galvanic corrosion of the germanium.

[0010] In one aspect, a composition comprising at least two non-oxidizing acids and at least one solvent is described, wherein the at least two non-oxidizing acids are selected from the group consisting of sulfonic acid, methanesulfonic acid, p-toluenesulfonic acid, hypophosphorous acid, sulfuric acid, phosphoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, and combinations thereof.

[0011] In another aspect, a method of selectively removing unreacted metal material relative to metal germanide from a microelectronic device having same thereon is described, said method comprising

contacting the microelectronic device with a composition useful for the selective removal of unreacted metal material relative to metal germanide, said composition comprising at least two non-oxidizing acids and at least one solvent.

[0012] Other aspects, features and advantages will be more fully apparent from the ensuing disclosure and appended claims.

DETAILED DESCRIPTION, AND PREFERRED EMBODIMENTS THEREOF

[0013] The present invention generally relates to a composition and process for the selective removal of metal relative to metal germanide, germanium, and/or SiGe layers. More specifically, the present invention relates to a composition and process for the selective removal of nickel relative to nickel germanide, Ge, and/or SiGe. The compositions are formulated to be substantially compatible with other materials present on the microelectronic device (e.g., low-k dielectrics, silicon nitride, etc.) and result in less pitting of the metal germanide layer as well as less galvanic corrosion of germanium.

[0014] Compositions that substantially and selectively remove unreacted metal or metals from germanium layers, germanide and SiGe layers and/or dielectric layers without substantially adversely affecting those layers are disclosed. The term “selective removal of unreacted metal” or “selective etching of unreacted metal,” and the like, refer to the substantial removal of such unreacted metal from a germanide layer without substantially affecting (etching) the germanide layer, the germanium layer, and/or the SiGe layer. The term “substantial” or “substantially,” in reference to the removal (etching) of unreacted metal(s), means that more than 95% of the unreacted metal layer is removed, more than 98% of the unreacted metal layer is removed, or 99% or more of the unreacted metal is removed. In one embodiment, the metal is nickel and the germanide is a nickel germanide.

[0015] For ease of reference, “microelectronic device” corresponds to semiconductor substrates, flat panel displays, phase change memory devices, solar panels and other products including solar cell devices, photovoltaics, and microelectromechanical systems (MEMS), manufactured for use in microelectronic, integrated circuit, energy collection, or computer chip applications. It is to be understood that the terms “microelectronic device,” “microelectronic substrate” and “microelectronic device material” are not meant to be limiting in any way and include any substrate or structure that will eventually become a microelectronic device or microelectronic assembly.

[0016] As defined herein, the “germanium” or “germanium regions” may be a bulk germanium wafer, a germanium-on-insulator (GOI) wafer in which case the layer is a germanium layer formed on a dielectric layer on top of the substrate, or may also be formed by selectively depositing germanium on a substrate. The germanium can be a continuous layer that at least partially extends over the substrate or can be divided into separate regions. These regions can be insulated from other regions by field regions, wherein

the field regions can be formed by etching grooves into the substrate and filling the grooves with a dielectric material, such as an oxide. This insulation method is also known as shallow-trench-insulation (STI).

[0017] As defined herein, the “SiGe” corresponds to a silicon germanium alloy comprising about 30 wt % to about 80 wt% Ge. The SiGe can be a continuous layer that at least partially extends over the substrate or can be divided into separate regions. These regions can be insulated from other regions by field regions, wherein the field regions can be formed by etching grooves into the substrate and filling the grooves with a dielectric material, such as an oxide.

[0018] As defined herein, a “non-oxidizing acid” corresponds to an acid that has a standard oxidation/reduction potential of less than about +0.25 V versus the standard hydrogen electrode. Examples of non-oxidizing acids include sulfuric acid, hydrochloric acid, phosphoric and phosphonic acids, and most organic (e.g., carboxylic) acids, but not nitric or any “halate” acids (i.e., halogen + oxygen such as iodate, perchlorate, hypochlorite etc.).

[0019] As defined herein, “low-k dielectric material” corresponds to any material used as a dielectric material in a layered microelectronic device, wherein the material has a dielectric constant less than about 3.5. Preferably, the low-k dielectric materials include low-polarity materials such as silicon-containing organic polymers, silicon-containing hybrid organic/inorganic materials, organosilicate glass (OSG), TEOS, fluorinated silicate glass (FSG), silicon dioxide, and carbon-doped oxide (CDO) glass. It is to be appreciated that the low-k dielectric materials may have varying densities and varying porosities.

[0020] As defined herein, “phosphoric acid” is understood to have the formula H_3PO_4 and is also known as orthophosphoric acid.

[0021] It is understood that some chemical components naturally include negligible amounts of water when in their lowest energy, i.e., stable, state. Naturally present water is not considered “added water.”

[0022] “Substantially devoid” is defined herein as less than 2 wt. %, preferably less than 1 wt. %, more preferably less than 0.5 wt. %, even more preferably less than 0.1 wt. %, and most preferably 0 wt%.

[0023] As used herein, “about” is intended to correspond to $\pm 5\%$ of the stated value.

[0024] Compositions described herein may be embodied in a wide variety of specific formulations, as hereinafter more fully described.

[0025] In all such compositions, wherein specific components of the composition are discussed in reference to weight percentage ranges including a zero lower limit, it will be understood that such components may be present or absent in various specific embodiments of the composition, and that in instances where such components are present, they may be present at concentrations as low as 0.001 weight percent, based on the total weight of the composition in which such components are employed.

[0026] In a first aspect, a composition for selectively etching unreacted metal relative to metal germanide is described, wherein the composition does not substantially etch the metal germanide layer, low-k dielectric layer, silicon nitride layer, and/or STI material. More specifically, the composition selectively etches unreacted nickel relative to nickel germanide, wherein the composition does not substantially etch the nickel germanide layer, germanium, SiGe, low-k dielectric layers, and/or silicon nitride layers. In one embodiment, said composition comprises, consists of, or consists essentially of at least two non-oxidizing acids and at least one solvent. In another embodiment, said composition comprises, consists of, or consists essentially of at least three non-oxidizing acids and at least one solvent. In yet another embodiment, said composition comprises, consists of, or consists essentially of phosphoric acid, one of sulfuric acid or hydrochloric acid, and at least one solvent. In another embodiment, said composition comprises, consists of, or consists essentially of phosphoric acid, one of sulfuric acid or hydrochloric acid, and water. In still another embodiment, said composition comprises, consists of, or consists essentially of sulfuric acid, hydrochloric acid, phosphoric acid, and at least one solvent. In yet another embodiment, said composition comprises, consists of, or consists essentially of sulfuric acid, hydrochloric acid, phosphoric acid, and water. In another embodiment, said composition comprises, consists of, or consists essentially of sulfuric acid, hydrochloric acid, and phosphoric acid, wherein the composition is substantially devoid of added water.

[0027] The non-oxidizing acids are present to principally dissolve the unreacted metal, i.e., nickel. Non-oxidizing acids contemplated herein include, but are not limited to, sulfonic acid, methanesulfonic acid, p-toluenesulfonic acid, hypophosphorous acid, sulfuric acid, phosphoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, and combinations thereof. Preferably, the non-oxidizing acids comprise two or more of sulfuric acid, phosphoric acid, and hydrochloric acid. Although not wishing to be bound by theory, the use of HBr and/or HI is preferred when the removal selectivity of metal (i.e., Ni) relative to metal germanide (i.e., NiGe) is less important (e.g., when it is desired to remove the metal and metal germanide at substantially the same rate or to remove the metal germanide at a rate higher than the rate of removal of the metal).

[0028] Solvents contemplated include, but are not limited to, water, alcohols, glycols, glycol ethers, carbonates, and combinations thereof, such as straight-chained or branched alcohols (e.g., methanol, ethanol, isopropanol, butanol, pentanol, hexanol, 2-ethyl-1-hexanol, heptanol, octanol, and higher alcohols (including diols, triols, etc.), 4-methyl-2-pentanol), ethylene glycol, propylene glycol, butylene glycol, butylene carbonate, ethylene carbonate, propylene carbonate, dipropylene glycol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether (i.e., butyl carbitol), triethylene glycol monobutyl ether, ethylene

glycol monohexyl ether, diethylene glycol monohexyl ether, ethylene glycol phenyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether (DPGME), tripropylene glycol methyl ether (TPGME), dipropylene glycol dimethyl ether, dipropylene glycol ethyl ether, propylene glycol n-propyl ether, dipropylene glycol n-propyl ether (DPGPE), tripropylene glycol n-propyl ether, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, and combinations thereof. Preferably, the at least one solvent comprises water. The amount of solvent in the composition is preferably in a range from about 10 wt% to about 99.9 wt%, more preferably in a range from about 50 wt% to about 99.9 wt%, and most preferably in a range from about 90 wt% to about 99.9 wt%.

[0029] An optional component of the compositions described herein is at least one passivation agent for the germanium and metal germanide, i.e., nickel germanide, species. Passivation agents can include, but are not limited to, ascorbic acid, L(+)-ascorbic acid, isoascorbic acid, ascorbic acid derivatives, boric acid, ammonium baborate, borate salts (e.g., ammonium pentaborate, sodium tetraborate, and ammonium baborate), sodium bromide, potassium bromide, rubidium bromide, magnesium bromide, calcium bromide, ammonium bromides having the formula $\text{NR}^1\text{R}^2\text{R}^3\text{R}^4\text{Br}$, wherein R^1 , R^2 , R^3 and R^4 can be the same as or different from one another and are selected from the group consisting of hydrogen and branched or straight-chained C_1 - C_6 alkyls (e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl).

[0030] The compositions of the first aspect have pH in a range from less than 0 to about 3, preferably less than 0 to about 2. Further, the compositions of the first aspect are preferably substantially devoid of chemical mechanical polishing abrasive; oxidizing agents including, but not limited to, hydrogen peroxide, other peroxides, nitric acid and salts thereof, salts of copper, salts of iron, bromates, and metal oxides; halate acids (i.e., halogen + oxygen such as iodate, perchlorate, hypochlorite etc.); carboxylic acid or carboxylate complexing agents; sulfur compounds with an oxidation state between -2 and +5 (e.g., thiosulfate, sulfide, sulfite, bisulfite, metabisulfite, phosphorus pentasulfide); fluoride-containing sources; and combinations thereof. The selectivity of removal of unreacted metal (e.g., nickel):metal germanide (e.g., NiGe) is preferably greater than 1:1, more preferably greater than 5:1, even more preferably greater than 10:1, and most preferably greater than 50:1.

[0031] In an embodiment of the composition of the first aspect, the composition comprises, consists of, or consists essentially of phosphoric acid, one of sulfuric acid or hydrochloric acid, and at least one solvent, present in the following ranges, based on the total weight of the composition:

Component	% by weight	more preferred % by weight	most preferred % by weight
phosphoric acid (86%)	about 1 wt% to about 20 wt%	about 2 wt% to about 15 wt%	about 4 wt% to about 12 wt%

sulfuric acid (conc) or hydrochloric acid (37%)	about 0.1 wt% to about 15 wt%	about 0.5 wt% to about 12 wt%	about 1 wt% to about 10 wt%
solvent(s)	about 65 to about 98.9 wt %	about 73 to about 97.5 wt %	about 78 to about 95 wt %

[0032] In another embodiment of the composition of the first aspect, the composition comprises, consists of, or consists essentially of phosphoric acid, sulfuric acid, hydrochloric acid, and at least one solvent, present in the following ranges, based on the total weight of the composition:

Component	% by weight	more preferred % by weight	most preferred % by weight
phosphoric acid (86%)	about 1 wt% to about 20 wt%	about 2 wt% to about 15 wt%	about 4 wt% to about 12 wt%
sulfuric acid (conc)	about 0.1 wt% to about 10 wt%	about 0.5 wt% to about 8 wt%	about 1 wt% to about 5 wt%
hydrochloric acid (37%)	about 0.1 wt% to about 10 wt%	about 0.5 wt% to about 8 wt%	about 1 wt% to about 6 wt%
solvent(s)	about 60 to about 98.8 wt %	about 69 to about 97 wt %	about 77 to about 94 wt %

[0033] In yet another embodiment of the composition of the first aspect, the composition comprises, consists of, or consists essentially of phosphoric acid, sulfuric acid, and hydrochloric acid, wherein the composition is substantially devoid of added water, present in the following ranges, based on the total weight of the composition:

Component	% by weight	more preferred % by weight
phosphoric acid (86%)	about 40 wt% to about 80 wt%	about 50 wt% to about 70 wt%
sulfuric acid (conc)	about 2 wt% to about 20 wt%	about 5 wt% to about 15 wt%
hydrochloric acid (37%)	about 10 wt% to about 50 wt%	about 15 wt% to about 45 wt%

[0034] In another embodiment, the compositions of the first aspect further include dissolved nickel ions, wherein the unreacted nickel is solubilized by the composition to yield said nickel ions. For example, the composition of the first aspect may include at least two non-oxidizing acids, at least one solvent, and nickel ions. In another embodiment, the composition of the first aspect may include phosphoric acid, at least one of hydrochloric acid and sulfuric acid, at least one solvent, and nickel ions.

[0035] Advantageously, the composition described herein is low cost, easily diluted, readily available in electronic grade, and selectively removes nickel relative to nickel germanide at low temperatures (e.g., 20-25°C) and hence can be reused without changing out the chemistry each time.

[0036] The compositions of the first aspect described herein is easily formulated by simple addition of the respective ingredients and mixing to homogeneous condition. Furthermore, the compositions may be readily formulated as single-package formulations or multi-part formulations that are mixed at or before the point of use, e.g., the individual parts of the multi-part formulation may be mixed at the tool or in a storage tank upstream of the tool. The concentrations of the respective ingredients may be widely varied in specific multiples of the composition, i.e., more dilute or more concentrated, and it will be appreciated that the compositions described herein can variously and alternatively comprise, consist or consist essentially of any combination of ingredients consistent with the disclosure herein. Dilution ratios may be in a range from about 0.1 part diluent:1 part composition concentrate to about 100 parts diluent:1 part composition concentrate.

[0037] In use of the compositions for selectively removing unreacted metal material (e.g., unreacted nickel) relative to metal germanide (e.g., NiGe), germanium, and/or SiGe from microelectronic devices having same thereon, the compositions typically are contacted with the device for a time of from about 10 sec to about 180 minutes, preferably about 1 minute to about 5 minutes, at temperature in a range of from about 15°C to about 100°C, preferably about 20°C to about 70°C. Such contacting times and temperatures are illustrative, and any other suitable time and temperature conditions may be employed that are efficacious to at least partially remove the unreacted metal (e.g., unreacted nickel) from the device. Such contacting times and temperatures are illustrative, and any other suitable time and temperature conditions may be employed that are efficacious to at least partially remove unreacted metal (e.g., unreacted nickel) from the device, within the broad practice of the method. "At least partially remove" corresponds to the removal of at least 85 % of the unreacted metal (e.g., unreacted nickel), more preferably at least 90 %, even more preferably at least 95 %, and most preferred at least 99 %. Advantageously, the compositions of the first aspect selectively remove unreacted metal (e.g., unreacted nickel) relative to metal germanide (e.g., NiGe), germanium, and/or SiGe without substantially removing other materials present on the microelectronic device such as low-k dielectric materials, shallow trench isolation materials, and silicon nitride.

[0038] Following the achievement of the desired removal action, the composition may be readily removed from the device to which it has previously been applied, as may be desired and efficacious in a given end use application of the compositions described herein. Preferably, the rinse solution for the composition includes deionized water. Thereafter, the device may be dried using nitrogen or a spin-dry cycle.

[0039] Yet another aspect relates to the improved microelectronic devices made according to the methods described herein and to products containing such microelectronic devices. Preferably, the microelectronic device comprises the germanide NiGe.

[0040] A still further aspect relates to methods of manufacturing an article comprising a microelectronic device, said method comprising contacting the microelectronic device with a composition for sufficient time to selectively remove unreacted metal material (e.g., unreacted nickel) relative to metal germanide (e.g., NiGe), germanium, and SiGe from the microelectronic device, and incorporating said microelectronic device into said article, using a composition described herein. Preferably, the microelectronic device comprises the germanide NiGe.

[0041] Another aspect relates to an article of manufacture comprising a composition, a microelectronic device wafer, and material selected from the group consisting of NiGe, Ni, Ge, SiGe, and combinations thereof, wherein the composition comprises at least two or three non-oxidizing acids and at least one solvent. Preferably, the composition comprises sulfuric acid, phosphoric acid, hydrochloric acid, and water.

[0042] Yet another aspect relates to the removal of resist and resist residue removal (e.g., post-etch residue and/or post-ash residue) using the compositions described herein. It was surprisingly discovered by the inventor that the low pH compositions described herein are effective at removing polymeric layers such as resist and polymeric-containing material such as resist residue. Accordingly, a method of removing polymeric material is described herein, said method comprising contacting a microelectronic device having the polymeric material thereon with a composition described herein at conditions useful to remove the polymer material from the surface of the microelectronic device.

[0043] The features and advantages are more fully shown by the illustrative examples discussed below.

Example 1

[0044] Formulations A-L were prepared and were tested using electrochemical methods to determine Ni corrosion in Å/min using Tafel potentiodynamic plots, Ni:Ge corrosion in Å/min using Tafel potentiodynamic plots, and Ni:NiGe selectivity at ambient temperature. The formulations and results are reported in Table 1.

[0045] It can be seen that the selectivity of Ni:NiGe is much improved using formulations comprising HCl over HBr or HI.

Example 2

[0046] Formulations M-T were prepared and were tested using electrochemical methods to determine Ni corrosion in Å/min, Ni:Ge corrosion in Å/min, and Ni:NiGe selectivity at ambient temperature. The formulations and resulted are reported in Table 2.

[0047] Interesting, with Formulation S, if it is aged for 7 days at 55°C, the NiGe corrosion rate is 0.669 Å/min, the Ni corrosion rate is 8.8036 Å/min, and the Ni:NiGe selectivity is 13.2. Similarly, with Formulation T, if it is aged for 7 days at 55°C, the NiGe corrosion rate is 1.418 Å/min, the Ni corrosion rate is 213.2 Å/min, and the Ni:NiGe selectivity is 150.4.

Example 3

[0048] Formulations U-V were prepared and were tested using electrochemical methods to determine Ni corrosion in Å/min, Ni:Ge corrosion in Å/min, and Ni:NiGe selectivity at ambient temperature. The formulations and resulted are reported in Table 3.

[0049] Although not wishing to be bound by theory, under some conditions, having the third non-oxidizing acid (e.g., sulfuric acid) resulted in a slight lowering of the NiGe corrosion rates.

Example 4

[0050] Formulations AA-OO were prepared and were tested using electrochemical methods to determine Ni corrosion in Å/min at 20°C, Ni:Ge corrosion in Å/min at 20°C, Ge corrosion in Å/min at 25°C, and Ni:NiGe selectivity. The formulations and resulted are reported in Table 4.

[0051] Interestingly, as the amount of phosphoric acid in the composition dropped from 100wt% to a range from 50 wt% to 70 wt%, the nickel corrosion rate increases.

[0052] In Table 5, the nickel etch rate at 25°C in Å/min is also reported.

[0053] The results show that formulations without added water have a higher Ni etch rate and a better Ni:NiGe selectivity. That said, formulations with added water typically have a lower NiGe etch rate and thus the user can design the formulation to obtain the preferred results.

Table 1: Electrochemical experiments for Formulations A-L

Formulation	H ₃ PO ₄ (86%)/wt%	HCl (37%)/wt%	HBr (47%)/wt%	HI (55%)/wt%	DI water/wt%	NiGe corrosion rate/ Å/min	Ni corrosion rate/ Å/min	Ni:NiGe selectivity
A	8	1			91	0.310	4.12	13.29
B	12	1			87	0.322	5.46	16.95
C	8	2			90	0.355	5.96	16.77
D	12	2			86	0.233	5.33	22.85
E	8		1.7		903.	0.353	1.00	2.83
F	12		1.7		86.3	0.415	1.45	3.51
G	8		3.4		88.6	0.403	1.23	3.06
H	12		3.4		84.6	0.322	1.26	3.90
I	8			2.3	89.7	6.205	0.87	0.14
J	12			2.31	85.69	8.522	3.82	0.45
K	8			4.62	87.38	27.474	2.32	0.08
L	12			4.62	83.38	23.360	1.43	0.06

Table 2: Electrochemical experiments for Formulations M-T

Formulation	H ₃ PO ₄ (86%)/wt%	HCl (37%)/wt%	methanesulfonic acid/wt%	H ₂ SO ₄ (conc)/wt%	DI water/wt%	NiGe corrosion rate/ Å/min	Ni corrosion rate/ Å/min	Ni:NiGe selectivity
M	6	3			91	0.3462	5.022	14.51
N	6	3	3		88	0.3721	7.191	19.33
O	6			2	92	0.2918	3.713	12.72
P	6	3		2	89	0.5064	8.197	16.19
Q	6		3		91	0.2544	2.986	11.74
R	6		3	2	89	0.3438	2.545	7.40
S	12	6		2	80	0.405	4.4234	10.9
T	60	30		10		1.588	121.5	76.5

Table 3: Electrochemical experiments for Formulations U-V

Formulation	H ₃ PO ₄ (86%)/wt%	HCl (37%)/wt%	DI water/wt%	NiGe corrosion rate/ Å/min	Ni corrosion rate/ Å/min	Ni:NiGe selectivity
U	4	12	84	0.40154	2.2503	5.6042
V	6	12	82	0.35558	18.591	52.284

Table 4: Electrochemical experiments for Formulations AA-OO

Formulation	H ₃ PO ₄ (86%)/wt%	HCl (37%)/wt%	H ₂ SO ₄ (conc)/wt%	NiGe corrosion rate/ Å/min	Ni corrosion rate/ Å/min	Ge corrosion rate/ Å/min	Ni:NiGe selectivity
AA	70.00	25.00	5.00	1.23	187.32	0.031	152.8
BB	66.92	25.00	8.08	2.32	172.18	0.138	74.2
CC	59.49	29.63	10.88	1.40	458.85	0.162	327.5
DD	55.98	35.00	9.02	1.53	176.9	0.103	115.5
EE	63.6	27.9	8.5	1.29	87.64	0.075	68.1
FF	54.66	30.34	15.00	1.30	201.83	0.096	155.0
GG	50.00	35.00	15.00	1.63	217.91	0.172	134.0
HH	63.02	25.00	11.98	1.70	93.765	0.109	55.3
II	62.00	33.00	5.00	1.69	171.65	0.091	101.5
JJ	60.00	25.00	15.00	1.49	163.92	0.307	109.7
KK	65.78	29.22	5.00	6.66	588.05	0.191	88.2
LL	59.5	29.6	10.9	1.45	191.43	0.080	132.1
MM	100.00	0.00	0.00	203.74	6.615	0.030	<0.1
NN	70.00	30.00	0.00	1.23	121.57	0.339	99.1
OO	90.00	0.00	10.00	0.11	6.837	0.046	65.1

Table 5: Nickel etch rates for Formulations AA-OO

Formulation	Ni ER/ $\text{\AA min}^{-1}$
AA	86.95
BB	153.85
CC	171.43
DD	193.55
EE	166.67
FF	300
GG	230.77
HH	133.33
II	285.71
JJ	200
KK	200
LL	222.22
MM	
NN	166.67
OO	

* * *

[0054] Although the invention has been variously disclosed herein with reference to illustrative embodiments and features, it will be appreciated that the embodiments and features described hereinabove are not intended to limit the invention, and that other variations, modifications and other embodiments will suggest themselves to those of ordinary skill in the art, based on the disclosure herein. The invention therefore is to be broadly construed, as encompassing all such variations, modifications and alternative embodiments within the spirit and scope of the claims hereafter set forth.

What is claimed is:

1. A method of selectively removing unreacted metal material relative to metal germanide from a microelectronic device having same thereon, said method comprising contacting the microelectronic device with a composition useful for the selective removal of unreacted metal material relative to metal germanide, said composition comprising at least two non-oxidizing acids and at least one solvent.
2. The method of claim 1, wherein the at least two non-oxidizing acids are selected from the group consisting of sulfonic acid, methanesulfonic acid, p-toluenesulfonic acid, hypophosphorous acid, sulfuric acid, phosphoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, and combinations thereof.
3. The method of claim 1, wherein the at least two non-oxidizing acids comprise phosphoric acid and at least one of sulfuric acid and hydrochloric acid.
4. The method of any of the preceding claims, wherein the solvent comprises a species selected from the group consisting of water, methanol, ethanol, isopropanol, butanol, pentanol, hexanol, 2-ethyl-1-hexanol, heptanol, octanol, and higher alcohols, 4-methyl-2-pentanol, ethylene glycol, propylene glycol, butylene glycol, butylene carbonate, ethylene carbonate, propylene carbonate, dipropylene glycol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, ethylene glycol phenyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether (DPGME), tripropylene glycol methyl ether (TPGME), dipropylene glycol dimethyl ether, dipropylene glycol ethyl ether, propylene glycol n-propyl ether, dipropylene glycol n-propyl ether (DPGPE), tripropylene glycol n-propyl ether, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, and combinations thereof, preferably water.
5. The method of any of the preceding claims, wherein the pH of the composition is in a range from less than 0 to about 3.
6. The method of any of the preceding claims, wherein the composition is substantially devoid of chemical mechanical polishing abrasive; oxidizing agents including, but not limited to, hydrogen peroxide, other peroxides, nitric acid and salts thereof, halate acids, salts of copper, salts of iron,

bromates, and metal oxides; carboxylic acid or carboxylate complexing agents; sulfur compounds with an oxidation state between -2 and +5; fluoride-containing sources; and combinations thereof. .

7. The method of any of the preceding claims, wherein the unreacted metal is nickel.

8. The method of any of the preceding claims, wherein the metal germanide is nickel germanide.

9. The method of any of the preceding claims, wherein the selectively of removal of unreacted metal:metal germanide is preferably greater than 1:1, more preferably greater than 5:1, even more preferably greater than 10:1, and most preferably greater than 50:1.

10. The method of any of the preceding claims, wherein the conditions comprise temperature in a range from about 15°C to about 100°C and time in a range from about 10 sec to about 180 min.

11. A composition comprising at least two non-oxidizing acids and at least one solvent, wherein the at least two non-oxidizing acids are selected from the group consisting of sulfonic acid, methanesulfonic acid, p-toluenesulfonic acid, hypophosphorous acid, sulfuric acid, phosphoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, and combinations thereof.

12. The composition of claim 11, wherein the at least two non-oxidizing acids comprise phosphoric acid and at least one of sulfuric acid and hydrochloric acid.

13 The composition of claims 11 or 12, wherein the at least one solvent comprises a species selected from the group consisting of water, methanol, ethanol, isopropanol, butanol, pentanol, hexanol, 2-ethyl-1-hexanol, heptanol, octanol, and higher alcohols, 4-methyl-2-pentanol, ethylene glycol, propylene glycol, butylene glycol, butylene carbonate, ethylene carbonate, propylene carbonate, dipropylene glycol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, ethylene glycol phenyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether (DPGME), tripropylene glycol methyl ether (TPGME), dipropylene glycol dimethyl ether, dipropylene glycol ethyl ether, propylene glycol n-propyl ether, dipropylene glycol n-propyl ether (DPGPE), tripropylene glycol n-propyl ether, propylene glycol n-butyl ether, dipropylene

glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, and combinations thereof, preferably water.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/028593**A. CLASSIFICATION OF SUBJECT MATTER****H01L 21/306(2006.01)i**

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)

H01L 21/306; H01L 21/302; C09K 13/06; H01L 21/336; H01L 31/0224

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: non-oxidizing acid, sulfuric acid, hydrochloric acid, phosphoric acid, germanide, composition, etching

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005-0196962 A1 (CAROLINE DEMEURISSE et al.) 08 September 2005 See abstract, paragraphs [0025]-[0034] and claims 1, 11.	1-4, 11-13
A	US 2001-0004553 A1 (GARRY A. MERCALDI et al.) 21 June 2001 See abstract, paragraphs [0019]-[0022] and claims 1-9.	1-4, 11-13
A	US 2013-0137210 A1 (LAP-TAK ANDREW CHENG) 30 May 2013 See abstract, paragraphs [0039]-[0040] and claims 1-2.	1-4, 11-13
A	US 2013-0130500 A1 (FUYUKI SATO et al.) 23 May 2013 See abstract, paragraphs [0029]-[0030] and claim 1.	1-4, 11-13
A	US 2012-0231632 A1 (TOMONORI TAKAHASHI et al.) 13 September 2012 See abstract, paragraphs [0015]-[0016] and claim 1.	1-4, 11-13



Further documents are listed in the continuation of Box C.



See patent family 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 application or patent 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

29 July 2015 (29.07.2015)

Date of mailing of the international search report

29 July 2015 (29.07.2015)

Name and mailing address of the ISA/KR

International Application Division
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

CHOI, Sang Won

Telephone No. +82-42-481-8291



INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2015/028593**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/028593

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005-0196962 A1	08/09/2005	EP 1575082 A2 EP 1575082 A3 EP 1898452 A1 JP 2005-256173 A US 2007-0032025 A1 US 7517765 B2	14/09/2005 31/05/2006 12/03/2008 22/09/2005 08/02/2007 14/04/2009
US 2001-0004553 A1	21/06/2001	AU 2000-41958 A1 EP 1177575 A1 JP 2002-541662 A KR 10-0535603 B1 US 6316370 B1 US 6833084 B2 WO 00-60651 A1	23/10/2000 06/02/2002 03/12/2002 08/12/2005 13/11/2001 21/12/2004 12/10/2000
US 2013-0137210 A1	30/05/2013	CN 102792465 A TW 201133916 A US 8647910 B2 WO 2011-097430 A2 WO 2011-097430 A3	21/11/2012 01/10/2011 11/02/2014 11/08/2011 02/08/2012
US 2013-0130500 A1	23/05/2013	CN 103069548 A EP 2602815 A1 KR 10-1388937 B1 KR 10-2013-0060255 A SG 187737 A1 TW 201224212 A WO 2012-017819 A1	24/04/2013 12/06/2013 24/04/2014 07/06/2013 28/03/2013 16/06/2012 09/02/2012
US 2012-0231632 A1	13/09/2012	EP 2683792 A1 EP 2683792 A4 JP 2014-507815 A KR 10-2014-0022006 A SG 192574 A1 TW 201241158 A US 2014-0120734 A1 US 8647523 B2 US 8889025 B2 WO 2012-125401 A1	15/01/2014 03/12/2014 27/03/2014 21/02/2014 30/09/2013 16/10/2012 01/05/2014 11/02/2014 18/11/2014 20/09/2012