



(51) International Patent Classification:
H01L 21/3213 (2006.01) *C23F 1/30* (2006.01)
C23F 1/28 (2006.01)

(21) International Application Number:
PCT/EP2009/058240

(22) International Filing Date:
1 July 2009 (01.07.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/245,255 3 October 2008 (03.10.2008) US

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(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, 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, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (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, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: SELECTIVE CHEMICAL ETCH METHOD FOR MRAM FREELAYERS

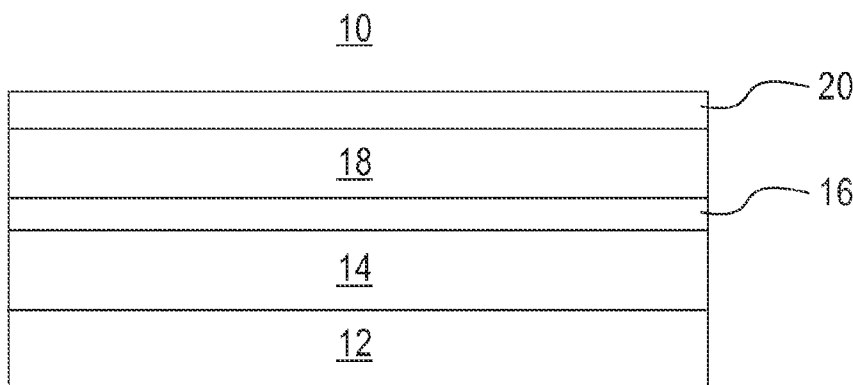


FIG. 1

(57) Abstract: An etching process is employed to selectively pattern an exposed magnetic layer of a magnetic thin film structure. The etching process includes exposing the magnetic layer to an etchant composition including at least one weakly absorbing acid, a surfactant inhibitor soluble in the at least one weakly absorbing acid, and at least one cation additive. The presence of the at least one cation additive increases dissolution inhibition of an underlying tunnel barrier layer (i.e., increases etch selectivity) and permits the use of more soluble surfactant inhibitors in the etchant composition.

SELECTIVE CHEMICAL ETCH METHOD FOR MRAM FREELAYERS

BACKGROUND

5 The present disclosure generally relates to semiconductor devices, and more particularly to the fabrication of magnetic memory devices.

10 A recent development in semiconductor memory devices involves spin electronics, which combines semiconductor technology and magnetics. The spin of electrons, rather than the charge, is used to indicate the presence of a "1" or "0." One such spin electronic device is a magnetic random access memory (MRAM) device which includes conductive lines (wordlines and bitlines) positioned in a different direction, e.g., perpendicular to one another in different metal layers, the conductive lines sandwiching a magnetic stack or magnetic tunnel junction (MTJ), which functions as a magnetic memory cell. A current flowing
15 through one of the conductive lines generates a magnetic field around the conductive line and orients the magnetic polarity into a certain direction along the wire or conductive line. A current flowing through the other conductive line induces the magnetic field and can partially turn the magnetic polarity, also. Digital information, represented as a "0" or "1," is storable in the alignment of magnetic moments. The resistance of the magnetic memory cell
20 depends on the moment's alignment. The stored state is read from the magnetic memory cell by detecting the component's resistive state.

25 An advantage of MRAM devices compared to traditional semiconductor memory devices such as dynamic random access memory (DRAM) devices is that MRAM devices are non-volatile. For example, a personal computer (PC) utilizing MRAM devices would not have a long "boot-up" time as with conventional PCs that utilize DRAM devices. Also, an MRAM device does not need to be powered up and has the capability of "remembering" the stored data. Therefore, it is expected that MRAM devices will replace flash memory, DRAM, and static random access memory devices (SRAM) devices in electronic applications where a
30 memory device is needed.

Because MRAM devices operate differently than traditional memory devices, they introduce

design and manufacturing challenges. The magnetic material layers used in MRAM devices require different etch chemistries and processes than traditional materials used in semiconductor processing, making them difficult to integrate into MRAM manufacturing processing schemes. For example, because of their small z-direction thickness, MTJ
5 freelayers are expected to require gentler etching solutions than typical microelectronic back end of line processes or utilize thicker films to minimize lateral etching and to maximize etching selectivity with respect to thin tunneling barrier, which are commonly fabricated from a metal oxide such as AlO_x , and the like.

10 The simplest case of tunnel barrier dissolution may be written as:

$$R_{\text{Tot}} = R_{\text{H}}^{+} + R_{\text{L}}$$

the linear combination of proton-promoted (R_{H}^{+}) and anion/ligand-promoted (R_{L}) dissolution reactions, assuming these reactions are independent and parallel. Typically R_{L} will depend not only on the surface concentration of ligand, but also on the type; for example, a 5- or 6-
15 membered ring forming chelate will promote higher rates of metal oxide dissolution than one which forms chelate rings of fewer or more than 5 or 6. The simplest way to reduce R_{L} to close to zero is to choose an acid with a non-surface interacting ligand, and to use pure solutions.

20 In the past, ultrapure perchloric acid HClO_4 has been the acid of choice where a non-adsorbing acid anion was used. However, due to safety considerations, HClO_4 has fallen out of favor; there is also the possibility of chloride contamination in HClO_4 solutions.

Accordingly, there is a need for improved etching processes for removing selected portions
25 of the magnetic layer disposed on the tunnel barrier.

BRIEF SUMMARY

Disclosed herein are processes for etching a magnetic film structure. In one embodiment,
30 the process for selectively patterning a magnetic film structure comprises providing a magnetic structure comprising at least one bottom magnetic layer, at least one top magnetic layer, wherein the at least one bottom magnetic layer is separated from the at least one top

magnetic layer by a tunnel barrier layer; and selectively etching the top magnetic layer with an etching solution comprising at least one weakly absorbing acid, a surfactant inhibitor soluble in the at least one weakly absorbing acid, and at least one cation additive.

5 In another embodiment, the process comprises providing a magnetic structure comprising at least one bottom magnetic layer, at least one top magnetic layer, wherein the at least one bottom magnetic layer is separated from the at least one top magnetic layer by a tunnel barrier layer; and selectively etching the top magnetic layer with an etching solution comprising at least one perfluoroalkane sulfonic acid, an alkylsulfonate salt soluble in the at
10 least one perfluoroalkane sulfonic acid, and at least one cation additive selected to replace bound protons on a surface of the tunnel barrier layer.

The disclosure may be understood more readily by reference to the following detailed description of the various features of the disclosure and the examples included therein.

15 BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

Referring now to the figures wherein the like elements are numbered alike:

Figure 1 illustrates a cross sectional view of an exemplary MRAM structure;

20 Figure 2 graphically illustrates log adsorption of surfactant as a function of log equilibrium bulk concentration of surfactant; and

Figure 3 graphically illustrates open circuit potential behavior as a function of time for a film stack including an aluminum oxide tunnel layer in various etchant solutions containing trifluoromethane sulfonic acid.

25 DETAILED DESCRIPTION

The present disclosure is generally directed to an etchant composition and process for selectively etching a magnetic layer disposed on a tunnel barrier layer. The etchant
30 composition increases the stability of the underlying tunnel barrier layer such that dissolution of the tunnel layer can be substantially prevented. The etchant composition generally includes at least one weakly adsorbing acid, a surfactant inhibitor soluble in the at

least one weakly absorbing acid, and at least one cation additive.

For illustrative purposes, an exemplary MRAM structure 10 is shown in FIG. 1. Specifically, the MRAM structure 10 generally includes a bottom magnetic layer 14, a tunnel barrier layer 16, a top magnetic layer 18, and a passivation layer 20, all of which are disposed on a substrate 12, typically silicon. The structure may further include additional layers such as adhesion layers, barrier layers, and the like. The top and bottom magnetic layers may be composed of the same or different magnetic layers in which each individual layer generally has a thickness of less than 150 Å. It should be noted that the top and/or bottom magnetic layers 14, 18 may comprise only one magnetic film or they may comprise a stack of magnetic films. In one embodiment, each individual magnetic film layer has a thickness of less than 100 Å.

Illustrative examples of magnetic materials that can be employed for the magnetic layers 14, 18 include, but are not intended to be limited to, Ni_xFe_y , $\text{Ni}_x\text{Co}_y\text{Fe}_z$, and other like magnetic materials. In the above formulas, x, y, and z are any integers whose sum adds up to 100.

In one embodiment, the top magnetic layer 14 is comprised of a Permalloy layer, i.e., a Ni_xFe_y type, or Co_xFe_y layer, while the bottom magnetic film layer 18 comprises a stack including Ni_xFe_y and Co_xFe_y .

The tunnel barrier layer 16 includes any conventional material such as Al_2O_3 , which is capable of sustaining a tunneling current and which does not chemically degrade the properties of the top and bottom magnetic layers (14 and 18, respectively). In some instances, the tunnel barrier layer 16 may also serve as a diffusion barrier. The tunnel barrier layer 16 is generally a thin layer, which has a thickness of less than about 15 Å.

The passivating layer 20 includes any metal layer such as, for example, Ti, TiN, Ta, or TaN which serves as a barrier layer preventing diffusion of moisture, air, and other contaminants from contacting the underlying magnetic layers 14, 18 and the tunnel barrier layer 16. The thickness of the passivation layer may vary, but typically has a thickness of from about 20 to about 1000 Å. The passivating layer 20 may contain a surface oxide, which is located on

the upper surface of the passivating layer 20 when the structure is exposed to air.

The processes for fabricating the MRAM structure include a number of conventional techniques. For example, the various magnetic and non-magnetic layers can be formed using chemical vapor deposition (CVD), plasma assisted CVD, plating, evaporation, sputtering, chemical solution deposition, or the like. The various magnetic and non-magnetic layers can be patterned using well known lithographic techniques. During the fabrication process, selected portions of the top magnetic layer are exposed such that a selective etching process is needed to remove the exposed portions of the magnetic layer so as to give the MRAM structure its desired structural characteristics. The exposed portions of the top magnetic layer are etched using an etchant solution having the etchant composition as generally described above.

The etchant composition generally includes at least one weakly absorbing acid, a surfactant inhibitor soluble in the at least one weakly absorbing acid, and at least one cation additive. In one embodiment, the at least one weakly absorbing acid is a perfluoroalkane sulfonic acid. By "a perfluoroalkane sulfonic acid" it is meant a sulfonic acid derivative that is substituted with a perfluoroalkyl group. By "a perfluoroalkyl" it is meant an alkyl in which all hydrogen atoms have been replaced by fluorine. Suitable perfluoroalkane sulfonic acids employed are $\text{CF}_3(\text{CF}_2)_n\text{SO}_3\text{H}$ or $(\text{CF}_2)_m(\text{SO}_3\text{H})_2$, wherein n can be zero or any integer from 1 to 6, m can be any integer from 1 to 6. Illustrative examples of perfluoroalkane sulfonic acids that can be used include, but are not limited to: $\text{CF}_3\text{SO}_3\text{H}$; $\text{CF}_3\text{CF}_2\text{SO}_3\text{H}$; $\text{CF}_2(\text{SO}_3\text{H})_2$; $(\text{CF}_2)_2(\text{SO}_3\text{H})_2$; and other analogous perfluoroalkane sulfonic acids with perfluoroalkyl chains having more than two carbon atoms. Other suitable perfluoroalkane sulfonic acids include analogs of the above illustrative examples wherein at least one of the F atom are substituted by $-\text{NH}_2$. In one embodiment, the perfluoroalkane sulfonic acid is trifluoromethane sulfonic acid (TFMSA). Due to the high electron-withdrawing tendency of the electronegative F atoms, TFMSA is one of the strongest acids ($\text{pK}_a = \text{ca. } -13$), and is essentially fully dissociated in aqueous solutions. Electrochemical and X-ray Absorption Near Edge Structure (XANES) studies have revealed a negligible tendency for TFMSA anion adsorption on noble metal surfaces. It is expected that TFMSA anion will similarly exhibit a negligible tendency for interacting with oxide surfaces, such as engaging in metal

ion complexation reactions, e.g., with Al^{+3} or related partially-hydrolyzed Al^{+3} species, i.e., R_L is essentially zero for this anion.

The surfactant inhibitor is selected to be soluble in the at least one weakly absorbing acid, e.g., soluble in the perfluoralkane sulfonic acid. The term "surfactant inhibitor" is used herein to denote a substance that, when present at a low concentration, adsorbs onto the surface of a solution or the interfaces of a multi-phase solution system, and substantially alters the free energy of the surface or the interfaces. The term "interface" is used herein to denote a surface forming a common boundary between any two immiscible phases. In one embodiment, the surfactant inhibitors are alkylsulfonic acid salts, also referred to herein as alkane sulfonates. By "alkylsulfonic acid salts or alkane sulfonates" it is meant to include any metal salt of a sulfonic acid derivative that is substituted with an alkyl group. By "alkyl" it is meant an acyclic alkyl that has more than 7 carbon atoms to less than 16 carbon atoms. Illustrative examples of surfactant inhibitors that can be employed in the present disclosure include, but are not limited to: $CH_3(CH_2)_hSO_3M$; and other analogous compounds; wherein M may be any metal cation, such as a sodium or potassium cation, and h can be any integer from 6 to 15. It is understood to one skilled in the art that the alkyl chain of the above illustrative examples can be straight or branched. Since the pH of zero charge (PZC) of bulk alumina is close to 9, the PCZ of the tunnel barrier 16 should be significantly greater than the pH of the etchant solutions. It is believed that the negatively charged SO_3^- group of the alkylsulfonic acid salts adsorbs on the positively charged sites on the tunnel barrier surface thereby protecting the tunnel barrier 16 from dissolution, or significantly slowing such dissolution. As a general rule, the longer the chain length of the surfactant inhibitor, the greater is the thermodynamic tendency for the surfactant inhibitor to come out of solution and adsorb on surfaces. That is, the AlO_x etch inhibitor ability of the alkane sulfonate surface active compounds is proportional to molecular weight: $CH_3(CH_2)_9SO_3^-Na^+ < CH_3(CH_2)_{11}SO_3^-Na^+ < CH_3(CH_2)_{13}SO_3^-Na^+ < CH_3(CH_2)_{15}SO_3^-Na^+$. Though an excellent AlO_x etch inhibitor in a trifluoromethane sulfonic acid solution, the low solubility of the $CH_3(CH_2)_{15}SO_3^-Na^+$ (SHS) can make the etchant solution more difficult to use, e.g., it takes overnight to dissolve in aqueous solution at room temperature. As will be discussed in greater detail below, Applicant has discovered that more soluble alkane sulfonic acid salts, that are generally less effective than the longer alkyl chain derivatives, can be made more

effective to prevent tunnel layer dissolution through the use of at least one cation additive within the etchant composition.

Exemplary alkylsulfonates along with its corresponding critical micelle point are provided in Table 1 below.

Table 1.

N a m e	C h e m i c a l F o r m u l a	C r i t i c a l M i c e l l e P o i n t
Sodium 1-decanesulfonate	$\text{CH}_3(\text{CH}_2)_9 \text{SO}_3^- \text{Na}^+$	$4.5 \times 10^{-2} \text{ M (25}^\circ\text{C)}$
Sodium 1-dodecanesulfonate	$\text{CH}_3 (\text{CH}_2)_{11} \text{SO}_3^- \text{Na}^+$	$1.2 \times 10^{-2} \text{ M (40}^\circ\text{C)}$
Sodium 1-tetradecanesulfonate	$\text{CH}_3(\text{CH}_2)_{13} \text{SO}_3^- \text{Na}^+$	$2.5 \times 10^{-3} \text{ M (40}^\circ\text{C)}$
Sodium 1-hexadecanesulfonate	$\text{CH}_3 (\text{CH}_2)_{15} \text{SO}_3^- \text{Na}^+$	$7.0 \times 10^{-4} \text{ M (50}^\circ\text{C)}$

These surface active inhibitors are characterized by a) having a hydrophobic tail (normally called the lyophobic group) which possess little attraction for bulk aqueous solution, and b) functional groups called lyophilic groups (hydrophilic) which have a strong attraction for the bulk aqueous phase. The lyophobic group causes distortion of the aqueous solution structure, and increases the overall free energy of the system, and results in less work being required to transport such a molecule to a surface or interface. Driven by factors such as poor solubility the surface active molecule tends to adsorb or concentrate at such locations, or it may undergo other processes to lower the energy of the system, such as micelle formation. Micelle formation is a process in which individual molecules in solution aggregate into clusters, averaging 25 – 200 molecules, and which are sometimes spherically shaped. This occurs in such a way that the hydrophobic parts of the molecules are closely associated with one another, and are largely protected from extensive contact with the bulk of the aqueous phase. The micelle formation phenomena tend to occur at a well-defined concentration of the surface active compound; the concentrations for the sulfonates of interest to the present work are listed in Table 1. The concentrations of all inhibitor solutions used in the present study were generally about 5 – 10 times smaller than the CMC value.

Figure 2 shows a typical S-shaped adsorption isotherm for a surface active material. The isotherm has distinct regions labeled 1, 2, 3, which may be associated with different stages in the surfactant adsorption process as described in the figure caption. Region 1 primarily involves replacement of any counter-ions adsorbed on the surface by similarly-charged surface active ions; no significant net change in surface charge (or surface potential) occurs in this stage. Region 2 involves adsorption of surface active ions onto oppositely-charged surface sites not occupied by counter-ions; the net surface charge decreases in this stage. As progress in adsorption of surface active species leads to complete neutralization of the surface, the surface will go through its point of zero charge (pzc); in the latter state all the surface charged species will have been paired by adsorbed surface active ions (i.e., region 3).

The driving force for the ability of surface active species (i.e. surfactants) to displace similarly charged simple inorganic ions from the surfaces of solids by an ion exchange mechanism is believed to be due in part to van der Waals dispersion forces. These latter forces increase with increase in molecular weight of the adsorbate, or adsorbing species; hence the well known phenomenon of increase in surface activity with hydrophobic chain length for surfactants. The hydrophobic tails of the surfactant molecules are generally perpendicular, inclined at an angle to the surface, or in some instances, may lie flat on the surface.

The at least one cation additive is selected from the group consisting of Al^{+3} , Fe^{+3} , and combinations comprising at least one of the foregoing cations. Other examples include Gd^{+3} , Cr^{+3} , Ce^{+3} , Ga^{+3} , La^{+3} , and Sm^{+3} . The at least one cation additive is introduced into the etchant composition as a soluble salt, wherein the anion portion is not intended to be limited to any particular anion so long as the anion is substantially inert to the MRAM structure as well as the etchant composition. By way of example, the Al^{+3} cation can be introduced with a $\text{Al}(\text{CF}_3\text{SO}_3)_3$ solution and the Fe cation can be introduced with a $\text{Fe}_3(\text{NO}_3)_3$ solution.

The mechanism of metal ion adsorption on hydrous (hydrated) oxide surfaces involves an ion exchange process in which the adsorbing metal ions replace bound protons as shown in

the following simplified reaction scheme:



In practice the Fe^{+3} ion will exist in solution as the hexaquo ion or a hydrolyzed variant if the solution pH is not low enough; similarly H_2O molecules tend to occupy available coordination positions on the surface adsorbed metal ion. The released protons may undergo readsorption on the alumina surface through either ion pair formation or protonation of aluminol (AlOH) groups as shown above or remain in solution. In this manner, positive charge density is increased on the tunneling barrier AlO_x surface through metal cation adsorption, and thus more sites are generated for anionic surfactant adsorption. This charge-based, largely ion-pairing based adsorption mechanism is likely to be more applicable to lower molecular weight surfactants, for which van der Waals forces are less important as a driving force for adsorption. As such, the addition of the at least one cation additive to the etchant composition provides a means to be able to use the shorter-chain (albeit less effective inhibitors by themselves), and thus, more soluble alkane sulfonate surfactants.

The etchant solution typically comprises the surfactant inhibitor at a concentration of at least about 5×10^{-6} molar, with a preferred concentration being dependent on the solubility of the surfactant inhibitor. For example, the preferred concentration for sodium tetradecanesulfonate is from about 2×10^{-5} to about 10^{-4} molar. The perfluoroalkyl sulfonic acid is at a concentration of from about 10^{-3} molar to about 1.0 molar, with a concentration from about 5×10^{-3} molar to about 5×10^{-2} molar being more preferred. The at least one cation additive is at a concentration of about 5×10^{-4} to about 5×10^{-2} molar.

While not wanting to be bound by theory, it is believed that the ferromagnetic freelayers (e.g., magnetic layer 14) undergo dissolution in trifluoromethane sulfonic acid solution via oxidation of the metal and its dissolution as hydrated metal ions (e.g. $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$, possibly with partial hydrolysis, or deprotonation of H_2O molecules, if the solution pH is high enough) as the anodic reaction(s), enabled by the reduction of protons, along with the reduction of dissolved O_2 gas when the latter is present, as the cathodic reaction(s). On removal of the MRAM MTJ freelayer by etching in acidic solution, rapid development of AlO_x tunneling barrier surface charge occurs due to hydration of the surface and protonation

of surface oxide ions. A possible method of slowing the rate of dissolution of AlO_x at the conclusion of freelay etching is to utilize the net positive charge present on the AlO_x surface for adsorption of the alkyl sulfonate anionic inhibitors as described above to protect potentially active sites from dissolution. Sulfonates were chosen rather than the analogous sulfates due to the greater resistance to hydrolysis of the sulfonate class.

The etching step is typically carried out at a temperature of about 15°C . to about 50°C . for a period of time from about 0.5 to about 15 minutes, depending on the source and type of parts, the condition of the free top layer surface, and the thickness of the top magnetic layer 18. More preferably, the etching step is carried out at a temperature of about 20°C to about 35°C .

The following examples are presented for illustrative purposes only, and are not intended to limit the scope of the invention.

EXAMPLE 1.

In this example, open circuit potential behavior was studied for a film stack including a silicon substrate, $1000\text{\AA}$ of SiO_2 , $50\text{\AA}$ of tantalum, $50\text{\AA}$ of Co-Fe; $9\text{\AA}$ of AlO_x in etching solutions containing $2 \times 10^{-2}\text{ M}$ trifluoromethane sulfonic acid with and without various additives. The etching solutions included (a) $2 \times 10^{-2}\text{ M}$ trifluoromethane sulfonic acid by itself; (b) $2 \times 10^{-2}\text{ M}$ trifluoromethane sulfonic acid and $1 \times 10^{-3}\text{ M}$ decanesulfonate (DS); (c) $2 \times 10^{-2}\text{ M}$ trifluoromethane sulfonic acid, $1 \times 10^{-3}\text{ M}$ decanesulfonate, and $5 \times 10^{-3}\text{ M}$ $\text{Al}(\text{CF}_3\text{SO}_3)_3$; and (d) $2 \times 10^{-2}\text{ M}$ trifluoromethane sulfonic acid, $1 \times 10^{-3}\text{ M}$ decanesulfonate, and $5 \times 10^{-3}\text{ M}$ $\text{Fe}(\text{NO}_3)_3$. The results are shown in Figure 3, wherein trifluoromethane sulfonic acid is labeled TFMSA, and decanesulfonate is labeled DS.

Advantageously, the use of the highly soluble $\text{CH}_3(\text{CH}_2)_9\text{SO}_3^- \text{Na}^+$ decanesulfonate inhibitor provided improved ease in etchant solution preparation since the etchant solution could be made immediately prior to the etching process. Moreover, the open circuit potential behavior of the model film stack $50\text{\AA}\text{ Ta} \mid 50\text{\AA}\text{ Co-Fe} \mid 9\text{\AA}\text{ Al(Ox)}$ in $2 \times 10^{-2}\text{ M}$ TFMSA solution only showed that the sample AlO_x and Co-Fe layers etched rapidly within a few minutes in pure TFMSA solution. In the presence of DS inhibitor, the etch resistance of the

AlO_x was improved by a factor of about 2 to 3. However, the addition of Al⁺³ and Fe⁺³ cations to the TFMSA + DS solution dramatically increased the stability of the AlO_x, with final etching of the underlying Co-Fe layer occurring after approximately 60 minutes in the case of the Al⁺³ cation additive, and after approximately 160 minutes in the case of the Fe⁺³ cation. Thus, the present disclosure shows it is possible to use the more soluble member of the sulfonate family as an inhibitor for arresting AlO_x tunneling barrier dissolution in the solution used for etching the soft magnetic layer.

This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

CLAIMS

1. A process for selectively patterning a magnetic film structure, comprising:

5 providing a magnetic structure comprising at least one bottom magnetic layer, at least one top magnetic layer, wherein the at least one bottom magnetic layer is separated from the at least one top magnetic layer by a tunnel barrier layer; and

10 selectively etching the top magnetic layer with an etching solution comprising at least one weakly absorbing acid, a surfactant inhibitor soluble in the at least one weakly absorbing acid, and at least one cation additive.

2. The process of claim 1, wherein the tunnel barrier layer is Al_2O_3 .

3. The process of claim 1, wherein the at least one cation additive is Al^{+3} and/or Fe^{+3} .

15 4. The process of claim 1, wherein said at least one top magnetic film layer and said at least one bottom magnetic film layer are the same or different, and are Ni_xFe_y , $\text{Ni}_x\text{Co}_y\text{Fe}_z$, wherein x, y and z are any integers whose sum adds up to 100.

20 5. The process of claim 1, wherein said at least one top magnetic layer is Ni_xFe_y and the at least one bottom magnetic film layer is a stack comprising Ni_xFe_y and Co_xFe_y .

6. The process of claim 1, wherein each one of the at least one top and bottom magnetic layers has a thickness of less than 150 Å.

25 7. The process of claim 1, wherein said surfactant inhibitor employed is an alkylsulfonic acid salt.

8. The process of claim 1, wherein said surfactant inhibitor employed is $\text{CH}_3(\text{CH}_2)_h\text{SO}_3^- \text{Na}^+$, wherein h is an integer from 6 to 14.

30 9. The process of claim 1, wherein the concentration of said surfactant inhibitor is at least about 5×10^{-6} molar.

10. The process of claim 1, wherein etching is at a temperature from about 15° C. to about 50° C. for a time period from about 0.5 to about 15 minutes.

11. The process of claim 1, wherein the at least one weakly adsorbing acid employed is perfluoroalkane sulfonic acid.

12. The process of claim 1, wherein the at least one weakly adsorbing acid employed is trifluoromethane sulfonic acid.

13. The process of claim 1, wherein the concentration of said perfluoroalkane sulfonic acid is from about 10^{-3} molar to about 1.0 molar.

14. The process of claim 1, wherein the concentration of said perfluoroalkane sulfonic acid is from about 5×10^{-3} molar to about 5×10^{-2} molar.

15. The process of Claim 1, wherein the at least one weakly absorbing acid is of a formula $\text{CF}_3(\text{CF}_2)_n\text{SO}_3\text{H}$ or $(\text{CF}_2)_m(\text{SO}_3\text{H})_2$, wherein n can be zero or any integer from 1 to 6, m can be any integer from 1 to 6, and the F atom can be optionally substituted by $-\text{NH}_2$.

16. The process of claim 1, wherein the at least one cation additive is selected from the group consisting of Al^{+3} , Fe^{+3} , Gd^{+3} , Cr^{+3} , Ce^{+3} , Ga^{+3} , La^{+3} , Sm^{+3} and combinations comprising at least one of the foregoing cations

17. A process for selectively patterning a magnetic film structure, comprising:

providing a magnetic structure comprising at least one bottom magnetic layer, at least one top magnetic layer, wherein the at least one bottom magnetic layer is separated from the at least one top magnetic layer by a tunnel barrier layer; and

selectively etching the top magnetic layer with an etching solution comprising at least one perfluoroalkane sulfonic acid, an alkylsulfonate salt soluble in the at least one perfluoroalkane sulfonic acid, and at least one cation additive selected to replace bound protons on a surface of the tunnel barrier layer.

18. The process of Claim 17, wherein the tunnel barrier layer is an aluminum oxide.

19. The process of claim 17, wherein the at least one top magnetic film layer and the at least one bottom magnetic film layer are the same or different, and are Ni_xFe_y , $\text{Ni}_x\text{Co}_y\text{Fe}_z$,
5 wherein x, y and z are any integers whose sum adds up to 100.

20. The process of claim 17, wherein the perfluoroalkane sulfonic acid is of a formula $\text{CF}_3(\text{CF}_2)_n\text{SO}_3\text{H}$ or $(\text{CF}_2)_m(\text{SO}_3\text{H})_2$, wherein n can be zero or any integer from 1 to 6, m can be any integer from 1 to 6, and the F atom can be optionally substituted by $-\text{NH}_2$.
10

21. The process of claim 17, wherein the alkylsulfonate salt soluble in the at least one perfluoroalkane sulfonic acid is of a formula $\text{CH}_3(\text{CH}_2)_h\text{SO}_3^-\text{M}^+$, wherein h is an integer from 6 to 14.

22. The process of claim 17, wherein the at least one cation additive is selected from the group consisting of Al^{+3} , Fe^{+3} , Gd^{+3} , Cr^{+3} , Ce^{+3} , Ga^{+3} , La^{+3} , Sm^{+3} and combinations comprising at least one of the foregoing cations.
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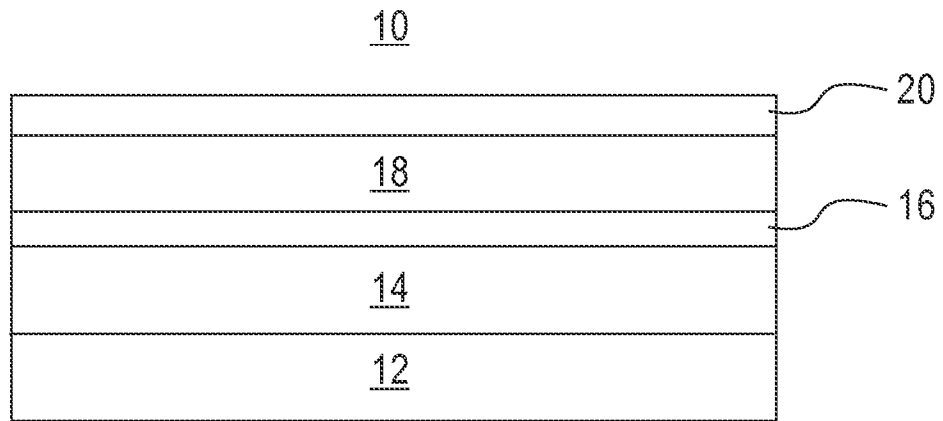


FIG. 1

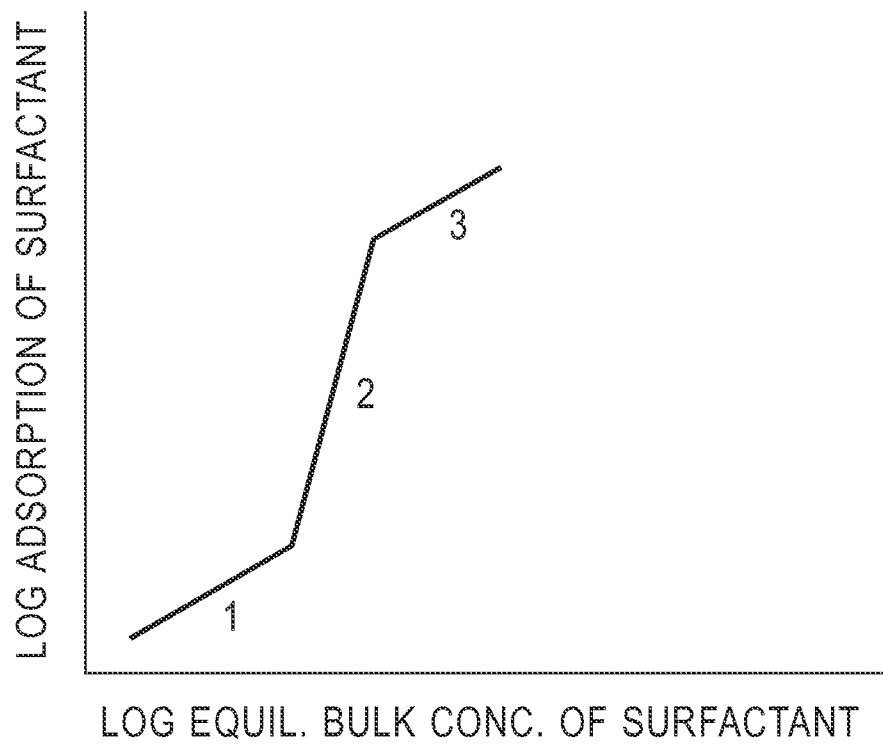
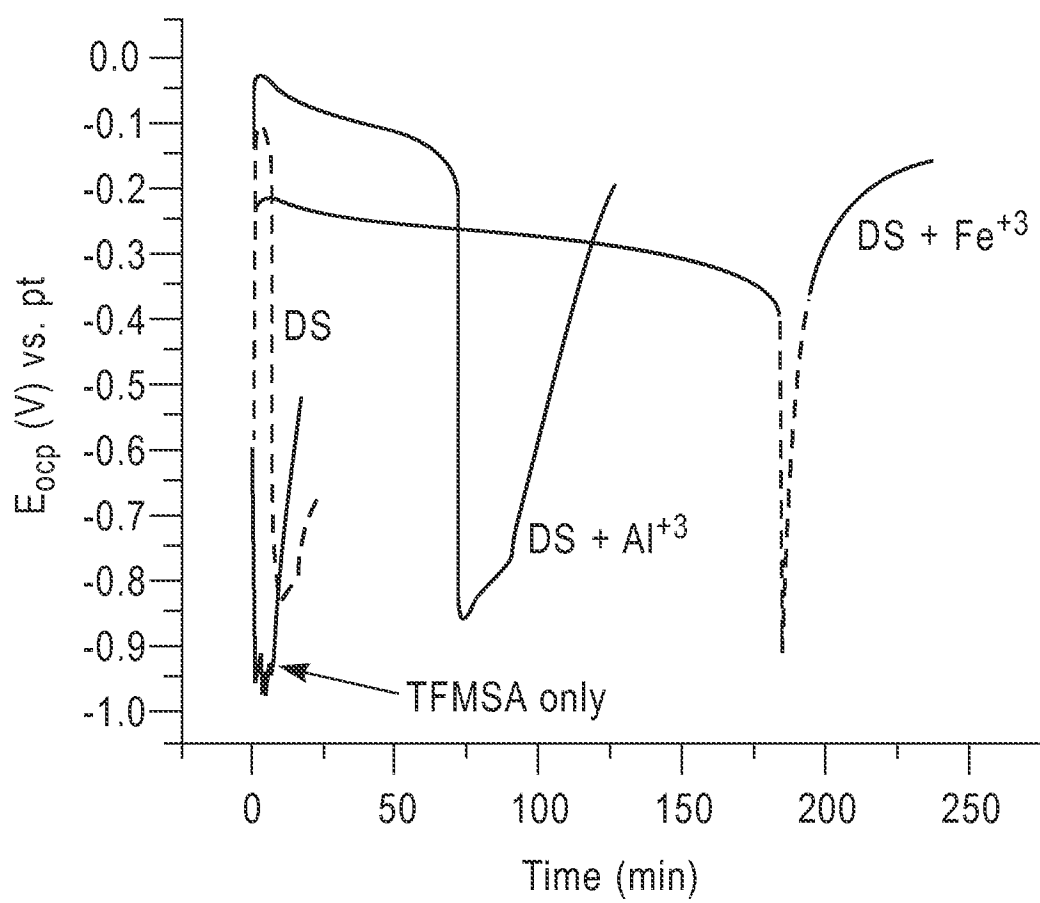


FIG. 2

**FIG. 3**

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/058240

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L21/3213 C23F1/28 C23F1/30

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 H01F C23F

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/012656 A1 (O'SULLIVAN EUGENE J [US] ET AL) 18 January 2007 (2007-01-18) claims -----	1-22

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

☒ See patent family annex.

* Special categories of cited documents :

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- *E* earlier document but published on or after the international filing date
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- *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
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- *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

4 September 2009

Date of mailing of the international search report

14/09/2009

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/058240

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007012656 A1	18-01-2007	NONE	