STT MRAM patterning challenges

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STT MRAM patterning challenges

Werner Boullart¹, Dunja Radisic¹, Vasile Paraschiv², Sven Cornelissen¹, Mauricio Manfrini¹, Koichi Yatsuda³, Eiichi Nishimura⁴, Tetsuya Ohishi⁴, Shigeru Tahara⁴

¹Imec, Belgium; ²Etch Tech Solutions, Romania; ³Tokyo Electron Ltd., Japan, ⁴Tokyo Electron Miyagi Ltd., Japan

ABSTRACT

In this paper we report on the patterning challenges for the integration of Spin-Transfer Torque Magneto-Resistive-Random-Access Memory (STT MRAM). An overview of the different patterning approaches that have been evaluated in the past decade is presented. Plasma based etching, wet etching, but also none subtractive patterning approaches are covered. The paper also reports on the patterning strategies, currently under investigation at imec.

1. Introduction

Due to its unique set of properties, magnetic tunnel junction based spin-transfer torque magnetoresistive random-access memory (STT MRAM) is being considered as the potential universal memory solution. MRAM devices provide nonvolatility, high writing endurance required for flash memory, fast writing speeds similar to static random access memory (SRAM), and once scaling (density) solutions are provided it also will become a solution for dynamic random access memory (DRAM) scaling. STT MRAM is not yet ready for production today. For sure one of the key challenges yet to overcome to enable its application as a universal memory is providing patterning solutions for magnetic tunnel junctions (MTJ) stack etching.

First generation MTJ stacks used Al₂O₃ as a tunnel barrier, because of superior TMR values today’s research focuses on MTJ stacks based on a MgO tunnel barrier. Furthermore two flavors of stacks respectively in plane and perpendicular, are studied for integration in devices. For future technology nodes however the perpendicular stack is the “working horse”. The exact MTJ stack composition is also determined by the application, and corresponding cell dimensions that are targeted. For stand-alone memory target cell dimensions are 2x nm, or even lower. In order to still achieve sufficient magnetization additional PMA-enhancement layers are inserted. A materials roadmap for respectively embedded and stand-alone STT MRAM is depicted below [Figure 1].
1 PATTERNING CHALLENGES

STT MRAM devices trigger the introduction of ferromagnetic materials such as Co, Fe, Ni, Pd, Mn, Pt in MTJ stacks. These materials are known not to yield volatile etch products in conventional plasma etch chemistries at standard operating conditions. Because of this, the redeposition of low-volatility by-products on the side-walls of etched features is likely to happen. This redeposition will yield tapered profiles, highly undesired because it is a potential showstopper for high density, aggressive pitch arrays. Moreover these side-wall redepositions will likely cause shorts between the free and the pinned layer.

Other challenges to be taken into account include: material compatibility and thermal stability. The interaction of the etch plasma with the materials and interfaces in MTJ stacks should not induce any degradation of the magnetic properties of the MTJ stacks. In order to enhance the volatility of the etch product, plasma etching at elevated temperatures is considered\(^1\). Elevated temperatures however should not compromise the thermal stability; STTRAM materials are reported to degrade at temperatures exceeding 250C-350C degrees\(^2\).

2. SUBSTRACTIVE PATTERNING

2.1. Ion Beam Etching

Ion beam etching (IBE) was first used to etch magnetic materials and MTJ stacks. The Ar ion beam can be made energetic enough to etch thin films under conditions of temperature and pressure where the vapor pressure of the material to be removed is negligible. Key drawback of this technique is that the etched material is sputtered and tends to stick to the first surface it encounters, such as the etched feature and mask. Side-wall polymers so-called “fences” are formed.
These redeposited materials easily will cause shorts across the tunnel barrier. Over-milling and/or changing the beam incidence angle, have been applied with success to remove the fences from arrays of widely-spaced MTJ’s. Alternatively, ion beam etching is combined with reactive ion etching. Applying this approach, M. Gajek et al\(^3\) obtained 20nm small MTJ cells. Successful applying grazing angle beam for cleaning side-wall residues however is limited by shadowing effects from adjacent cells. Therefore the question remains whether this technique can be successfully applied to clean high density memory arrays. Also the low etch/sputter rates of IBE is a potential showstopper for its adoption in high-wafer throughput environment.

![Figure 2](http://spiedigitallibrary.org/)

2.2. Cl and Br Based Plasma Etch Chemistries

In the past decade several studies using Cl\(_2\), Cl\(_2\)/Ar, BCl\(_3\) for etching MTJ stacks haven been performed. S.R. Min et al. using Cl\(_2\)/Ar plasma reported etched MTJ stacks with clean side-walls\(^4\). However, the key problem encountered is the material degradation, Cl\(_x\) species absorbed on the side-walls inducing corrosion of the CoFeB layer\(^5\).

From a bench mark of continuous wave (CW) and Time Modulated (TM) Cl\(_2\) plasma’s for etching PtMn\(^6\), CoFe\(^7\) and NiFe\(^8\) two interesting observations were reported: 1] a substantial increase of the etch rate of all three layers with TM plasma’s, and 2] a much smaller concentration of residual Cl\(_x\) on the etched surfaces. The latter is attributed to the negatively charged Cl\(_2^-\) ions that can reach the etch surface during plasma off time. Another interesting observation reported is the reduced hard mask erosion in time modulated plasma’s. Because of the lower mask erosion also the side-wall residue deposition is suppressed.

E.H. Kim et al.\(^9\) studied the etching of MTJ stacks in HBr/Ar plasma’s. They report a beneficial effect of adding HBr to Ar plasma’s, resulting in more anisotropic profiles. The latter is attributed to the deposition of H-based passivation film which reduces the physical sputtering from Ar-only plasma’s.

2.3. CH\(_3\)OH/Ar Based Plasma’s

As an alternative to halogen plasma’s, CH\(_3\)OH/Ar have been studied by several groups for MTJ stack patterning\(^10,11\). Key observation for this plasma is that much straighter profiles are obtained. The latter is attributed to a strongly enhanced selectivity towards the hard mask, resulting in a much reduced contribution of sputtered hard mask material to the side-walls redeposition. Also a 2 nm thick C-layer was found at the etch front. This protective layer possibly suppresses the back sputtering of the MTJ stack materials. This carbon rich layer possibly can also provide the carbon species for yielding volatile organometallic compounds. However, the lower etch rates measured in CH\(_3\)OH/Ar plasma’s compared to pure Ar plasma do not really support the presence of a chemical etching component in these plasma’s.

Another benefit from CH\(_3\)OH/Ar plasma’s is that no corrosion is observed.
2.4. CO/NH$_3$ and PF$_3$ Based Plasma’s

More recent for the etching MTJ stacks gases such as CO or PF$_3$ that might form metal-ligand complexes with the metals in the MTJ stacks have received large attention. These organometallic complexes are known to have high vapor pressure at standard operating pressures and temperatures. The formation of organometallic carbonyl complexes is driven by the EAN rule, electron pair donating ligands like carbonyl provide electrons to the transition metal to reach the noble gas electron configuration.

<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>Cl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Co$_2$(CO)$_8$ : 52°C</td>
<td>CoCl$_2$ : 1049°C</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(CO)$_5$ : 103°C</td>
<td>FeCl$_2$ : 1025°C</td>
</tr>
<tr>
<td>B</td>
<td>B$_2$H$_6$ : -92.6°C</td>
<td>BCl$_3$ : 12.5°C</td>
</tr>
<tr>
<td>Ti</td>
<td>TiCl$_4$ : 136°C</td>
<td></td>
</tr>
</tbody>
</table>

[Table 1] Boiling points of reaction products of Co/Fe/B and Ti with Cl$_2$ and CO$^{12}$

In pure CO plasma’s low etch rates are reported$^6$, not really supporting a significant chemical etching. Adding NH$_3$ to the etch plasma significantly increases, up to three times, the etch rates. This increase is explained by suppression of CO decomposition. Another positive observation reported about CO/NH$_3$ based plasma etching is that corrosion is not observed. Also is it reported that the stoechiometry of the CoFeB layer is not affected during etching.

The plausible explanation for the low etch rates observed is that for achieving significant chemical etching, the right (high) pressure and (high) temperature conditions are required to enable the formation of the organometallic complexes. Moreover these conditions are different for the respective transition metals. At the low pressures used in ICP reactors the reaction does not take place, is too slow to result in a sizeable etch rate. Another concern regarding plasma etching reactors is that they are very reactive media. High energetic ions, photons can support desorption of the organometallic compounds but they can also destroy these metal-ligand complexes prior to reaching full coordination.

Anticipating the transition metal-ligand complex formation capabilities of PF$_3$, similar to CO, we performed post side walls removal experiments in a high density after glow reactor at temperatures up to 250°C. At elevated temperatures > 150°C a CD reduction indicating SW removal, was observed.

[Figure 3] Side-walls residue cleaning in PF$_3$ high density after-glow plasma.

2.5. Gas Cluster Ion Beam based etching

Given the low volatility of the etch products, patterning at elevated temperatures provides a path to overcome this problem. In order to mitigate the issue of inducing not desired material degradation an alternative solution would be to provide the required thermal energy locally. This can be achieved through gas cluster ion beams (GCIB). With this technique the substrate to be patterned is exposed to bombardment with gas clusters of a few hundred up to several thousands of gaseous atoms or molecules. At the moment of impact, the energy released per atom is very low < 10 eV,
creating low damage surface, or shallow penetration of the active species into the substrate. Although the energy/atom is low the energy density near the surface is very high and the heat released at the point of impact is very high, hence providing the energy for enhancing the chemical reactions, and/or material evaporation. In 2012 A. Yamaguchi et al. reported with success GCIB based patterning the MTJ elements like CoFe, Pt,Ru and Ta.

3. NONE SUBTrACTIVE PATTERNING / FREE LAYERS CONVERSION

Given the challenges associated with subtractive patterning, alternative schemes relying on material conversion are being explored. Key idea is the transformation of the MTJ layers into a layer that becomes an insulator and no longer exhibit magnetoresistance properties. Preferred is the conversion into an insulating material which no longer needs to be removed. Typically the top magnetic layers on top of the magnetic tunneling barrier are converted. The bottom magnetic layers and the “converted” free layer are etched in a subsequent RIE process with larger critical dimension. The latter approach, because of the presence of an insulation layer, also circumvents the problem of shorts across the magnetic barrier due to RIE etch residue redeposition.

[Figure 4] None subtractive patterning of MTJ stacks based on material conversion

Oxidation of the magnetic layers into dielectrics has been reported by different groups. Applying this approach 140x140 nm² nano-size MTJs with a TMR of 31% were successfully fabricated.

4. WET ETCH SOLUTIONS

The difficulties encountered in dry etching of the MTJ layers triggered the screening of the wet etching or etch residue removal using wet chemistries.

Also here challenges are big. The latter because the complex stacks, comprising materials that on one hand are known to be very stable in wet chemistries: Pt, Pd, ... or extremely sensitive to material modification in wet chemistries. Particularly challenging is the compatibility with MgO tunnel barrier material. MgO is known to be very hygroscopic, reacting with the moisture of the ambient forming Mg(OH)₂.

Successful chemical etching of Ni₈₁Fe₁₉ permalloy using aqueous solutions of different α,Ω-dicarboxilic acids (n=1-7) with different additives with good selectivity to the Al₂O₃ tunnel barrier has been reported by J. O’Sullivan et al. Complete layer dissolution was verified by vibrating sample magnetometry and XPS. Even if the wet process was an isotropic one the device characterization has shown promising results. Compatibility with the tunnel barrier materials...
Al₂O₃ and MgO was achieved by adding the alkyl sulfonates inhibitors respectively organophosphorus acids inhibitors. Successful removal of side-walls residues and damaged layers after RIE based etching using amine based solutions evidenced by TMR recovery have been reported by J. N. Kim et al."17 We evaluated mixtures of organic solvents with HF or other complexing agents for the removal of the metallic residues originating from etching Ta/CoFeB/MgO/CoFeB patterning stopping into PtMn. TEM images taking before and after wet treatment are shown below. From the TEM images it is clear that residues deposited on the side walls have been partly removed. No attack of the MgO tunnel barrier could be detected.

[Figure 5] Etched Ta/CoFeB/MgO/CoFeB stacks prior and after wet cleaning in non aqueous solutions. No attack of the MgO tunnel barrier was detected.

5. ENGINEERING TOWARDS PATTERNING SOLUTIONS

A straightforward patterning solution is not available today. However, a successful patterning is also depending on factors such as materials optimization, stack optimizations, hard mask selection, smart patterning sequences.

MTJ stack research, to develop stacks that withstand higher temperature budgets is targeted to make the stacks compliant to the thermal cycles required for integrating it in CMOS back end-of-line (BEOL)."18 From a patterning perspective such stacks are also desirable because they will obviously open up the path for an enhanced chemical etching, hence reducing etch products redeposition, enabling straighter profiles. Recently M. Gotwald et al."19 report ultra-thin Co/Pd multilayers for perpendicular stacks with a thermal stability up to 425°C. These ultra-thin layers, [Co(0.2)/Pd(0.2)]₆, are also very attractive from a patterning perspective. Thinner layers that require shorter etch times, will lead to reduced side-walls redeposition. Furthermore such thinner stacks will allow for side-walls removal by tilted IBE in denser arrays.

The fact that for MTJ stack etching, physical sputtering is the dominant component of all the reported plasma etching chemistries directly translates into poor hard mask selectivity. High masks erosion in a sputtering dominated process will contribute to the side-walls redeposition. Therefore, proper hard mask selection can contribute in suppressing the side-wall redeposition. Table 2 reports on the different hard mask (HM) etch rates measured in CH₄/H₂/Ar chemistries used for MTJ stack etching.

<table>
<thead>
<tr>
<th>HM material</th>
<th>TiW</th>
<th>TiN</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etch rate (240s) / nm</td>
<td>13</td>
<td>19</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 2: HM consumption in CH₄/H₂/Ar plasma
Suppressing the HM erosion can also be achieved by selecting plasma etching chemistries that result in the deposition of a protective layer onto the hard mask. E. H. Kim et al.\textsuperscript{10} reported a drastic increase of the hard mask selectivity upon increasing the CH\textsubscript{3}OH content in an Ar/CH\textsubscript{3}OH. This reduced sputtering of the hard mask and materials also opens the window for side-walls residue removal during the over etch.

Shorts across the tunnel barrier at any time will kill the STT MRAM device. This problem can be circumvented by a staged etch approach whereby, after etching the top stack consisting of cap-layer/free-layer stopping onto the tunnel barrier, this partially etched stacked is encapsulated with an insulating layer. Resuming the etching, first clearing the dielectric cap layer from between adjacent cells, and subsequently completing the etching of the pinned layer and bottom electrode layers does no longer necessitate a side-wall deposition free etch chemistry. Etch by products – eventually metallic in nature – will be deposited onto the encapsulating dielectric. Hence, shorts across the tunnel barrier can be avoided. This patterning approach is illustrated in figure 6.

![Diagram of STT MRAM patterning scheme](image)

[Figure 6] Schematic representation of a STT MRAM patterning scheme relying on partial etching of top the layers stopping into tunnel barrier, followed by subsequent encapsulation, and final etching of the bottom layers.

![TEM image of planar MTJ stack](image)

[Figure 7] SST MRAM cell patterned using intermittent encapsulation scheme.

A TEM image of an in planar MTJ stack etched with such an approach are shown in picture 7. Further optimization of the patterning of the top layers to obtain straight profile to allow for high quality spacer encapsulations is required. Another side remark is that this patterning scheme inherently puts a limit to the maximum cell density that can be achieved.

6. MTJ CELL DEGRADATION FROM PLASMA PATTERNING

RIE based plasma’s provide the means for anisotropic patterning, and hence has been one of the driving forces for the CMOS scaling revolution from the past decades. At the same time the plasma’s used for making devices are also known as one of the key sources inducing damage to electronic devices: gate dielectric break down, channel mobility
In plasma’s device damage can originate from chemical interaction (radicals, ions), photon interactions (plasma’s are known to emit high energetic VUV light), and charges (hot electrons, high energetic ions). Surfaces subjected to these processes can be chemically and electrically modified. Another concern is diffusion of these reactive species along the multiple interfaces. Damage induced by the plasma etching process is reflected in MR ratio reduction and H_{off} shift.

Regarding chemical induced damage, Cl radicals from Ar/Cl₂ plasma’s have been reported to induce corrosion⁵. The latter triggered the exploration of alternative plasma chemistries. This corrosion is initiated upon interaction with moisture after retrieving the wafers from the etch reactors. Therefore, a possible way to circumvent could be removal of residual Clₓ through dedicated post etch plasma clean, in that respect H-plasma’s are considered as a possible alternative. Clₓ can be converted into HCl and hence evacuated from the plasma reactors. Also oxygen plasma’s used for photo resist ashing after dielectric/metalllic hard mask opening have been identified as causes for degradation²⁰.

Regarding damage induced by charges (ions, electrons), especially the tapered profiles are a concern, because the MTJ cell layers are directly subjected to ion bombardment. In his work Cornelissen reported a perimeter dependent degradation of magnetization of the CoFeB layer etched by ion beam milling²¹. In order to reduce this damage low energy ion beam milling is pursued, especially for the side-walls residue cleaning step for which grazing angle ion beams are used. K. Kinoshita et al¹¹ bench marked different etch plasmas at constant ion energies. From this work it was found that also the chemical composition of the plasma is contributing to the damage. Moreover the effects on respectively MR and H_{off} could be opposite. In the case of CH₃OH plasma it was reported that the formation of C-rich film on top of the MgO barrier was beneficial suppress ion induced damage. T. Mukai et al⁷ compared continuous wave and time modulated plasma’s in relation to plasma induced degradation. They found that the damage is strongly reduced in TM plasma’s. The latter is attributed to strong reduction of high energy VUV photon radiation. Also the plasma off time is promoting etch product desorption, hence reducing the chances for material modification through interaction with reaction by-products.

7. CONCLUSION

Providing patterning solutions for sure is one of the key challenges to enable the manufacturing of high density SST MRAM arrays for future device nodes. It is clear that a straightforward solution does not exist today. Optimization of etch plasma’s, exploration of new plasma chemistries, materials research, smart patterning solutions, it will take a lot of small advances to allow for large scale production of STT MRAM based integrated devices for future technology nodes.

References


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