Improved Etch Characteristics of Magnetic Tunneling Junction Materials by Using Helium

Sungwoo Park, Sungkyu Shim, Jeagun Park, and Geunyoung Yeom

Abstract

As next generation memory devices replace volatile dynamic random access memory (DRAM) devices, many research groups in the semiconductor industry are investigating new nonvolatile memory devices like spin transfer torque magnetic random access memory (STT-MRAM), resistive random access memory (ReRAM), phase change random access memory (PRAM), etc. Among these, STT-MRAM has many advantages such as high speed of read/write cycles, low power consumption of the device, and high density memory cells in addition to the nonvolatility of information. However, it is difficult to etch magnetic materials chemically and to etch small features such as a 20 nm thick magnetic tunneling junction (MTJ) because of sidewall redeposition and plasma induced etch damage. In addition, the sidewall re-deposition causes an electrical short and a tapered profile. Ar ion milling (or Ar ion beam etch (IBE)) has been used to etch MTJ materials. The advantage of the Ar ion milling is that the process induces very little or no chemical damage to the MTJ materials. To improve the etch profile and to remove the sidewall redeposition, a side-milling process (etching by tilting) has been applied. This can induce a shadow effect caused by adjacent cells in the case of high density MRAM with an aggressive pitch array, and which results in an electrical short failure due to the conductive redeposition at the edge of the pattern sidewall.

Etching of MTJ materials using halogen-based etch gases such as Ar/Cl2 chemistry in ICP reactive ion etching (ICP-RIE) systems has been reported to induce chemical damage on the MTJ material surface during the etching and form a thin oxide layer on the patterned sidewall of MTJ materials, which reduces the performance of the device, even though the oxide layer can be partially removed using a H2 plasma. To avoid corrosion, ICP-RIE using C-O-based gases involves lower etch selectivities over mask materials, which reduces the performance of the device, even though the oxide layer can be partially removed using a H2 plasma. To avoid oxidation of the MTJ features, the MTJ etched using CO/NH3 gases showed the lowest saturation magnetization (Ms) measured by a vibrating-sample magnetometer (VSM) possible due to the sidewall oxidation of MTJ while the Ms values of the MTJ etched using He and Ar are similar. It is found that, by etching the MTJ materials using He ICP with the ion energy near the hardmask sputter threshold energy, highly anisotropic etch profiles could be obtained without forming the sidewall redeposited materials and without significant degradation of magnetic properties.

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Experimental

All experiments were conducted using a commercially available radio frequency ICP etch system (STI PLC). Separate 13.56 MHz RF power generators were applied to both the ICP source and the bias electrode. The schematic diagram of the ICP etch system is shown in Fig. 1. For all experiments, the process conditions were kept at 700 W ICP power, 7 mTorr operating pressure, and 50 sccm gas flow rate. In the case of CO/NH3, the gas mixture containing 12.5 sccm CO and 37.5 sccm NH3 was used.

Blank unit thin film samples such as CoPt, MgO, CoFeB, and W that consist MTJ were etched with He, Ar, and CO/NH3 gases using an ICP etch system and the etch rates and selectivities of the MTJ materials over W were calculated. Patterned MTJ samples were etched using He, Ar, and CO/NH3 gas to observe the etch profiles and magnetic degradation. The patterned MTJ sample was composed of CoFeB(10nm)/MgO(1nm)/CoPt(10nm) on Ta/SiO2/silicon wafer with a hard mask consisting of patterned W (100 nm)/Ti (3 nm)/Ru (10 nm). The half pitch of the pattern was 55 nm.

The etch depths were measured using a step profilometer and field emission scanning electron microscopy (FE-SEM). Separate 13.56 MHz RF power generators were applied to both the ICP source and the bias electrode. The schematic diagram of the ICP etch system is shown in Fig. 1. For all experiments, the process conditions were kept at 700 W ICP power, 7 mTorr operating pressure, and 50 sccm gas flow rate. In the case of CO/NH3, the gas mixture containing 12.5 sccm CO and 37.5 sccm NH3 was used.
Schematic of the ICP reactive ion etch system used in the experiment.

Figure 1. Schematic of the ICP reactive ion etch system used in the experiment.

measure M-H property of MTJ features are located and this MTJ pattern in the 1 cm × 2 cm coupon is repeated in the wafer, so, we cut the same MTJ pattern and used for the VSM measurement to obtain M-H properties more reliably.

SRIM simulation was conducted to investigate the sputter yield \( <S> = \frac{(\text{sputtered atom})}{(\text{incident sputter ion})} \) of CoFeB and the sputter etch selectivity over W during sputter etching using He and Ar ion, and to investigate the similarity between the simulation results and the actual etch data. Co and Fe have a combined mole fraction of 0.8 in CoFeB (4:4:2) used in this study. Therefore, the sputter yields of Co and Fe were similar as 0.036; and these values were similar to the sputter yield of B in CoFeB. Similar results were obtained for 250 eV He/47 eV Ar and for 350 eV He/52 eV Ar. The increase of He ion energy (150, 250, 350 eV) increased the CoFeB sputter yield values, but the sputter yield ratio of CoFeB/W for Ar from \( \sim 6.7 \) at 35 eV to \( \sim 0.9 \) at 47 eV, and to \( \sim 0.7 \) at 52 eV. The higher sputter yield ratio of CoFeB/W for He compared to Ar was related to the lower energy transfer rate (T) to W from He compared to Ar because the elastic energy transfer between the two atoms can be expected from the following formula:

\[
T = \frac{4 \times Mm}{(M + m)^2}E
\]

where, \( M \) is the mass of the target atom, \( m \) is the mass of the incident atom, and \( E \) is the energy of the incident atom. The energy transfer rates of Co/Fe and W by He, Ne, Ar, and Xe were compared using Eq. 1 and the results on the energy transfer rate and their ratios of (Co/Fe)/W are shown in Fig. 2. As shown in the figure, the use of higher mass incident atom increased the energy transfer rate for both Co/Fe and W, which results in the increase of sputter yield, but the energy transfer rate ratio of (Co/Fe)/W was decreased with increasing the gas atomic mass indicating the decreased sputter yield ratio. To maximize the sputter etch selectivity between MTJ material and W hardmask and to decrease damage, it is found that a sputter etch gas with lower atomic weight which results in higher energy transfer rate ratio of CoFeB/W is required.

Table I. SRIM input parameters for W and CoFeB (4:4:2). \( \rho \) is the bulk material density, \( E_D \) is the bulk atom displacement energy, \( E_L \) is the lattice energy, and \( U_0 \) is the surface atom binding energy. Each value was obtained from the reference and other values were used to deduce sputter yield and sputtered atom characteristics.

<table>
<thead>
<tr>
<th>Type of SRIM calculation</th>
<th>( \rho ) (g/cm(^3))</th>
<th>( U_0 ) (eV)</th>
<th>( E_D ) (eV)</th>
<th>( E_L ) (eV)</th>
<th>Ion incident energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>19.35</td>
<td>3</td>
<td>6.88</td>
<td>He: 150/250</td>
<td>35/47/52</td>
</tr>
<tr>
<td>CoFeB (4:4:2)</td>
<td>7.80</td>
<td>3</td>
<td>4.43</td>
<td>He: 150/250</td>
<td>35/47/52</td>
</tr>
</tbody>
</table>

Table II. Sputtering yields of Co, Fe, and B in amorphous CoFeB and W investigated by SRIM simulation program.

<table>
<thead>
<tr>
<th>Incident Energy (eV)</th>
<th>( S ) of W</th>
<th>( S ) of Co in CoFeB</th>
<th>( S ) of Fe in CoFeB</th>
<th>( S ) of B in CoFeB</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.000</td>
<td>0.036</td>
<td>0.036</td>
<td>0.010</td>
</tr>
<tr>
<td>Ar</td>
<td>0.006</td>
<td>0.037</td>
<td>0.036</td>
<td>0.005</td>
</tr>
<tr>
<td>He</td>
<td>0.002</td>
<td>0.062</td>
<td>0.063</td>
<td>0.016</td>
</tr>
<tr>
<td>Ar</td>
<td>0.076</td>
<td>0.066</td>
<td>0.063</td>
<td>0.010</td>
</tr>
<tr>
<td>He</td>
<td>0.025</td>
<td>0.076</td>
<td>0.076</td>
<td>0.018</td>
</tr>
<tr>
<td>Ar</td>
<td>0.100</td>
<td>0.075</td>
<td>0.075</td>
<td>0.011</td>
</tr>
</tbody>
</table>
Based on the simulation results, blanket thin films related to MTJs were etched and the results were compared with the simulation results. Figure 3a shows the etch rates of materials related to MTJs such as MgO, CoPt, and CoFeB with W used as a hardmask material. Figure 3b shows the etch selectivities of the materials over W for etching using the ICP etcher with a bias voltage of −150 V for He and −35 V for Ar. To compare with previous etch results on magnetic materials, the etching of the materials at the bias voltage of −400 V with CO/NH$_3$ (1:3) was also investigated.

For the etching experiment, the same condition of 13.56 MHz source power of 700 W flow rate of 50 sccm, operating pressure of 7 mTorr, and room temperature were used for all materials. As shown in Fig. 3a, at −150 V of He and −35 V of Ar, the etch rates of CoFeB were similar at 5.14 and 5.06 nm/min, respectively; therefore, the simulation results of sputter yields in Table II could be confirmed experimentally. The etch rates of MgO and CoPt at −150 V of He and −35 V of Ar were also similar each other. For the etch selectivity measured by the experiment, as shown in Fig. 3b, the etch selectivity of CoFeB/W for −150 V He (4.39) was higher than that for −35 V Ar (0.93) similar to the simulation results in Table II and also in Fig. 3c even though the sputter yield ratios of CoFeB/W for simulation results were much higher than experimental results by showing ~600 for 150 V He and ~6.7 for 35 V Ar as mentioned above. The differences between the etch selectivity obtained by experiment and sputter yield ratio obtained by simulation appear to be related to the non-consideration of plasma potential, the energy distribution in the ion energy bombarding the substrate, and the gas impurity effect that could not be considered in the simulation. Especially, the lower etch selectivity obtained by the experiment is believe to be more related to a wide energy distribution of He ion incident to the materials surface. By using the He ions with a narrower energy distribution, higher etch selectivity of MTJ over the mask materials, therefore, more anisotropic etch profile of MTJ feature could be achieved. In general, it is known that the use of lower ion mass and lower rf bias power frequency tend to increase ion energy distribution incident to the substrate. By using a very high frequency (>30 MHz) rf bias power instead of a lower frequency (13.56 MHz) rf bias power as a next step, it is believed that a narrower He ion energy distribution, therefore, more selective MTJ etching can be obtained for the aggressive scaling of these MTJ features. However, even for now, the etch selectivities of CoFeB over W were still higher for −150 V He compared to −35 V Ar at the similar etch rates of MTJ materials. In the case of CO/NH$_3$ at −400 V, as shown in Figs. 3a and 3b, the etch rates of MgO, CoFeB, and CoPt were higher than that etched with −150 V He while the etch selectivities over W were a little lower than those etched with −150 V He. In the etching of magnetic materials related to MTJs by inert gases such as He and Ar, one of the serious problems is the sidewall redeposition of magnetic materials on the etched MTJ features due to the non-volatility of the sputter etched materials. Using the SRIM simulation, the energy and angular distribution of the sputtered magnetic atoms by the sputter etching using He and Ar were investigated. Figures 4 and 5 show the simulation results of the energy and angular distribution of sputtered Co in CoFeB and the angular probability density function (PDF) of sputtered Co by He and Ar, respectively. The black arrow indicates the direction of incident atom. The angular probability density function (PDF) of sputtered Co (Fig. 4b, Fig. 5b) reconfigured from Figs. 4a and Fig. 5a, respectively. The incident energies for the simulation were 150 eV for He and 35 eV for Ar. The simulation results of Fe were similar to those of Co, therefore, only the results of Co are shown in Fig. 4 and Fig. 5. As shown in Figs. 4 and 5 the sputtered Co atoms tend to have higher energy and higher ejection angle for 150 eV He than 35 eV Ar. The average ejection angles for 150 eV He and 35 eV Ar were 72.86° and 68.78° from the surface, respectively; therefore, the Co atoms were sputtered with higher angles by 150 eV He than 35 eV Ar. The etch profiles are generally affected by the etch selectivities of W mask over MTJ materials and redeposition of material on the sidewall of the etched features. The different sputter angles of magnetic materials during the sputter etching with He and Ar obtained in the simulation of Figs. 4 and 5 can be related to the degree of redeposition of magnetic materials during the etching of
Figure 4. Energy and angular distribution of sputtered Co in CoFeB with He (a) and angular probability density function of sputtered Co atom with He (b). The incident energies of the simulation are 150 eV for He.

Figure 5. Energy and angular distribution of sputtered Co in CoFeB with Ar (a) and angular probability density function of sputtered Co atom with Ar (b). The incident energies of the simulation are 35 eV for Ar.
Figure 6. SEM etch profiles of the nanoscale patterned MTJ stack features composed of CoPt (10 nm)/MgO (1 nm)/CoFeB (10 nm) on Ta/SiO$_2$/silicon wafer. Patterned W (100 nm)/Ti (3 nm)/Ru (10 nm) was used. Also, to achieve similar etch depth, the etch time was varied for each condition.

nanoscale MTJ features, therefore, it may also affect the etch profiles and electrical short of MTJs.

Using the patterned MTJ sample, etch profiles were observed by field emission scanning electron microscopy (FE-SEM; Hitachi, S-4700) after the etching using He ($-150$ V/$-250$ V/$-350$ V), Ar ($-35$ V/$-47$ V/$-52$ V), and CO/NH$_3$ ($-200$ V/$-300$ V/$-400$ V) are shown in Fig. 6. For each etch condition, different etch times were used to maintain the same MTJ etch depth. Other etch conditions are the same as those used to etch the blank unit thin films. With Ar, the etch profile was not highly anisotropic due to the poor etch resistance of W over Ar and the severe redeposition of W on the surfaces of the MTJ materials, which was predicted in the SRIM simulation and the blank unit thin film etch test. The composition of CO/NH$_3$ (1:3) and the bias voltage ranging from $-200$ to $-400$ V were selected from the previous studies, that show the anisotropic etch profiles with CO/NH$_3$ gas mixtures. As shown in Fig. 6, even though the etch depths are similar, the increase of bias voltage degraded the etch profile for all etch gases, due to the decreased etch selectivity of the magnetic materials over W as obtained by the SRIM results. The etch characteristics were similar to those by He ICP, even though the etch profiles of CO/NH$_3$ were slightly worse than those etched using He ICP. As shown in Fig. 7, the sidewall angles of the MTJ stacks were $81^\circ$ for He, $75^\circ$ for Ar and $79^\circ$ for CO/NH$_3$. Therefore, the most anisotropic MTJ etch profiles could be observed by etching using He as expected from the previous results.

To observe the possible redeposited material and residue on the etched MTJ features, the MTJ features etched using $-150$ V He, $-35$ V Ar, and $-400$ V CO/NH$_3$ (shown in Fig. 6) were observed using transmission electron microscopy (TEM, ARM-200F). The results are shown in Figs. 8a and 8b for He and CO/NH$_3$, respectively. Due to the rough sidewall and the least anisotropic etch profile, no TEM images were taken for the MTJ features etched using Ar. As shown in Fig. 8, a more anisotropic etch profile could be observed for the MTJ feature etched by He. However, no sidewall redeposited material or residue could be clearly observed for the MTJ features etched with He or CO/NH$_3$, possibly due to the extreme thin thickness of the remaining residue material. Even though no noticeable sidewall redeposition or residue could be observed on the etched MTJ features, the MTJ features can be degraded by forming a very thin damaged layer or impurity layer, etc. during the etching.

Figure 7. Magnified SEM images of the nanoscale patterned MTJ stack features for $-150$ V He, $-35$ V Ar, and $-400$ V CO/NH$_3$ in Fig. 6.
was 61.1% of that etched with Ar. The oxygen in the gas chemistry tends to form a thin oxide layer on the patterned sidewall of MTJ materials, which reduces the performance of the device. Therefore, even though no sidewall redeposited material, residue, or damage could be observed in Fig. 7, the MTJ features etched by CO/NH$_3$ appeared to be chemically damaged by forming a sidewall oxide on the surface. However, in the case of the MTJ feature etched with He, the $M_s$ was about 92.3% of that with Ar was observed. A little smaller Ms for He compared to Ar could be related to the surface damage of MTJ due to deeper penetration of He by the high energy of the He-ions compared to Ar during the etching. (SRIM simulation showed that the penetration depth for 150 eV He into CoFe can be $\sim$10 nm while that for 35 eV Ar is $\sim$2.5 nm when ion is incident to the materials vertically) However, it is believed that, by having more anisotropic etching of MTJ, a less physical damage to the MTJ sidewall surface by He ion is expected by less penetration of He ion to the sidewall of the features.

Conclusions

The advantages of etching magnetic materials related to MTJs of STT-MRAM using He ions with the energy close to the hardmask sputter threshold energy as an alternative to Ar and other gas mixtures such as CO/NH$_3$ were investigated. Due to the higher etch selectivity of the magnetic material over W for He compared to Ar at similar etch rates of the magnetic materials, the etching of patterned MTJ with W hardmask using He exhibited a much better etch profile and less hardmask erosion than that using Ar, especially at an He ion energy close to the hardmask sputter threshold energy. The use of the CO/NH$_3$ gas mixture in the etching MTJ exhibited etch characteristics comparable to He. However, the CO/NH$_3$ gas mixture appeared to induce more magnetic degradation than the inert gases such as He and Ar due to the sidewall oxidation of the etched MTJ features. Therefore, it is believed that the etching of MTJ using He with the ion energy near the hardmask sputter threshold energy could be beneficial in obtaining highly anisotropic etch profiles without the formation of the sidewall redeposited materials and without significant electrical degradation of magnetic properties.

Acknowledgments

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References