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Etch residue removal of CoFeB using CO/NH₃ reactive ion beam for spin transfer torque-magnetic random access memory device

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Using a reactive ion beam etching (RIBE) system, the possibility of removing the sidewall residues remaining on etched nanoscale CoFeB features and the W hard mask after using a conventional inductively coupled plasma etching system was investigated. Upon increasing the ion energy of the Ar beam, a similar sputter yield increase was found for both CoFeB side wall residues and the W hard mask. Hence, increasing the ion beam energy to improve etch residue removal efficiency at the same time induces a degradation of the CoFeB profile because of the W hard mask erosion. However, when CO/NH₃ was used as the RIBE gas mixture, at ion energy in the range of 90–110 eV, the effective residue removal from CoFeB etched features without etching the W hard mask. When the ion energy of the CO/NH₃ RIBE exceeds 140 eV, again similar sputter yields are found for both CoFeB side wall residues and the W hard mask.

I. INTRODUCTION

Spin transfer torque magnetic random access memory (STT-MRAM) is one of the most promising candidates for the next generation memory devices due to its high density and nonvolatile storage, fast switching speed, infinite rewrite, high endurance, and low operating voltage relative to conventional memory devices.1–6

To commercialize the STT-MRAM devices, the magnetic tunneling junction (MTJ) cell size must be reduced to sub-30 nm scale. The dry etch process is a critical issue for the fabrication of nanoscale STT-MRAM devices due to difficulty in forming volatile compounds between the MTJ materials, such as CoFeB, CoPt, MgO, NiFe, and the etch gases. The etching of the MTJ materials has been investigated by using conventional reactive ion etching (RIE) with noncorrosive gases, such as CO/NH₃, CH₃OH, etc., to increase the volatility of the etch products without corroding the nanoscale features.7–10 The results generally showed relatively low etch rates, low etch selectivity over the hard mask material, and etch residue on the etched pattern sidewall. Therefore, instead of the RIE, the Ar ion beam etching or Ar ion sputter etching has been generally used for etching of the MTJ materials. However, this method also has problems such as the heavy redeposition of etch residue on the etched CoFeB surface, decreased etch selectivity over the hard mask, and nonvolatile etch residues on the etched CoFeB surface were decreased as compared to etching using continuous wave plasmas. Even though these techniques have improved the etch characteristics of the MTJ materials, some of the etch residues still remain on the surface and the sidewall of the etched features.20,21

In this study, after the etching of the CoFeB cells with W hard mask using a conventional ICP system, as a method to remove the sidewall residue remaining after the main etching, reactive ion beam etching (RIBE) is applied, and the effect of CO/NH₃ etch gas and the RIBE parameters on the removal of the sidewall residue is investigated.

II. EXPERIMENT

In this study, nanoscale patterned CoFeB (composition ratio = 4:4:2) samples etched using a CO/NH₃ gas mixture in an ICP (STS PLC, UK) were used. The main etching of the CoFeB was performed at 5 mTorr with a gas mixture of CO (12.5 sccm)/NH₃ (37.5 sccm) by applying 500 W (13.56 MHz) of ICP power and −300 V (13.56 MHz) of dc bias voltage for 3 min. The etching was carried out at room temperature. During the main etching, 20 nm thick nanoscale CoFeB features masked with W (100 nm W/20 nm Ti/5 nm Ru) on Ta/SiO₂/Si wafer were formed. Figure 1(a) shows a cartoon of the formation of sidewall residue during main etching of the CoFeB with W hard mask, and Fig. 1(b) shows the scanning electron microscopic (SEM) images of...
the CoFeB samples with sidewall residue used in the experiment. The width of the etched CoFeB feature masked with W (that is, W/Ti/Ru) was 67 nm, and the height of the CoFeB feature with the remaining W mask was 141 nm.

After the main etch process of the patterned CoFeB sample in the ICP system, the possibility in removing etch residue on the sidewall of the etched CoFeB features was investigated using a home-made RIBE system with a CO/NH$_3$ (1:3) gas mixture as the reactive gas. The RIBE system used in the experiment was composed of an ICP ion source with three grids. The schematic diagram of the reactive ion beam etching system used in the experiment is shown in Fig. 2. RF power of 13.56 MHz was applied to the ICP source, and a positive voltage from +30 to +100 V was applied to the first grid for the acceleration of the ions, a negative voltage of −300 V was applied to the second grid to focus the beam, and the third grid was grounded. To study the effect of the reactive gas mixture, the system was operated as an Ar ion beam system by using Ar instead of CO/NH$_3$.

The etch profile of the patterned CoFeB features with W hard mask on a Ta/SiO$_2$/silicon wafer was observed using a field emission scanning electron microscope (Hitachi S-4700) and a transmission electron microscope (TEM, JEOL JEM ARM 200F). The chemical binding characteristics and the change in the surface morphology of the unpatterned CoFeB film surface after main etching and after RIBE were investigated by x-ray photoelectron spectroscopy (XPS, ESCA2000, VG Microtech Inc.) using a Mg $K\alpha$ twin-anode source and a high resolution atomic force microscopy (SPA-300HV), respectively. The ion energy bombarding the CoFeB surface for the different first grid voltages during the ion beam etching was estimated using a home-made ion energy analyzer.

III. RESULTS AND DISCUSSION

Before using the CO/NH$_3$ reactive ion beam, an Ar ion beam was used and its sidewall residue removal characteristics were investigated. Figure 3 shows the SEM images of the CoFeB features observed after the etching as a function of the first grid voltage of the Ar ion beam system from +35 to +75 V. The ion source was operated with 300 W of ICP power, −300 V of the second grid voltage, and the third grid was grounded for 30 min at 100 sccm Ar flow. As shown in Fig. 3, the use of the Ar ion beam after CoFeB main etching degraded the etch profile without selectively etching the...

![Fig. 1.](image1) (Color online) (a) Illustration showing the formation of the sidewall residue during the main etching of CoFeB with W hard mask (100 nm W/5 nm Ti/5 nm Ru) on Ta/SiO$_2$/Si wafer and (b) SEM images of the CoFeB samples with sidewall residue obtained after CO/NH$_3$ ICP etching of CoFeB features with W mask.

![Fig. 2.](image2) (Color online) Schematic diagram of the RIBE system used in the experiment. The RIBE system used in the experiment was composed of an ICP ion gun with three grids. RF power of 13.56 MHz was applied to the ICP source, and a positive voltage from +30 to +100 V was applied to the first grid for the acceleration of the ions, a negative voltage of −300 V to the second grid to focus the beam, and the third grid was grounded.
sidewall residue, and a degraded etch profile was observed at the higher first grid voltage, therefore, at the higher Ar ion beam energy (the bottom width of the CoFeB feature was increased from 60 nm at +35 V to 73 nm at +75 V while decreasing the height of the CoFeB feature from 136 nm at +35 V to 122 nm at +75 V). The degradation of CoFeB etch profile was related to the nonselective sputter etching of CoFeB and W hard mask by using the Ar ion.

The second set of experiments involved the usage of CO/NH\textsubscript{3} reactive ion beam for studying the sidewall residue removal efficiency; the effect of the beam parameters on the etch profile was investigated. The SEM images obtained after RIBE are shown in Fig. 4. A gas mixture of 20 sccm of CO and 60 sccm of NH\textsubscript{3} was fed to the ICP source of the RIBE system, and the first grid voltage was varied from +30 to +100 V. The CoFeB features were exposed to the reactive ion beam for 50 min, and the other beam conditions were the same as those used for the Ar ion beam (that is, 300 W of ICP source power, −300 V of second grid voltage, and a grounded third grid). As shown, the increase in the first grid voltage up to +70 V did not significantly change the height of the CoFeB feature with the W mask, but the etch profile was improved with the increase in the first grid voltage by decreasing the CoFeB feature width from 67 nm (after main etching) to 55 nm (after RIBE with +70 V of first grid voltage) while keeping the CoFeB feature height at about 136 ~ 139 nm, indicating the possibility of removing the sidewall residue on the CoFeB feature more selectively at the higher first grid voltage without etching the W mask. However, when the first grid voltage was increased to +100 V, the decrease in the CoFeB feature height (from 136 nm at +70 V to 113 nm at +100 V) with the increase in the CoFeB feature width (55 nm at +70 V to 60 nm at +100 V) was observed to be similar to the results obtained for the Ar ion beam possibly due to the nonselective etching of W in addition to CoFeB. The improved CoFeB etch profile observed for RIBE with the first grid voltage up to +70 V is believed to be related to the formation of more volatile chemical compounds with the CoFeB residue deposited on the sidewall of the etched feature and the more selective removal of the residue compared to W and pristine CoFeB due to the looser atomic binding of the sidewall residue.

While keeping the first grid voltage at +70 V, the process time was varied from 15 to 100 min and the SEM images of the CoFeB features were observed as a function of the process time after RIBE are shown in Fig. 5. Other process conditions are maintained the same as those in Fig. 4. The increase in the process time to up to 100 min improved the etch profile and decreased the feature width (the CoFeB feature width changed from 62 nm at 15 min, to 61 nm at 30 min, 55 nm at 50 min, and 54 nm at 100 min), indicating a decrease in the sidewall residue as the process time increased. Moreover, during the process time up to 100 min, no significant change was observed in the feature height, possibly due to selective etching of the CoFeB residue only without etching of W at the first grid voltage of +70 V.

The residue species and thickness remaining on blanket CoFeB samples etched using the main etch condition in
FIG. 4. (Color online) SEM images for the CoFeB features etched with the W hard mask (W/Ti/Ru) observed after etching using the CO/NH$_3$ reactive ion beam as a function of the first grid voltage. The first grid voltage was (a) $+30$ V, (b) $+50$ V, (c) $+70$ V, and (d) $+100$ V. The ion source was operated with 300 W of ICP power, $-300$ V of the second grid voltage, and the grounded third grid for 50 min while a gas mixture of 20 sccm of CO and 60 sccm of NH$_3$ flowed to the ICP source.

FIG. 5. (Color online) SEM inspection images from CoFeB samples processed with different RIBE process times. While keeping the first grid voltage at $+70$ V, the process time was varied from 15 to 100 min. The residue removal time was (a) 15 min, (b) 30 min, (c) 50 min, and (d) 100 min. Other process conditions are maintained the same as those in Fig. 4.
Fig. 1(b) and those on the CoFeB samples exposed to the RIBE using theetch conditions in Figs. 5(c) and 5(d) after main etching were investigated using XPS to examine the possibility of a more selective removal of the etch residue than with pristine CoFeB material using RIBE. The XPS narrow scan data of Co 2p, Fe 2p, and B 1s on the CoFeB surfaces after the main etching, after the RIBE of the main etched CoFeB for 50 min, and after 100 min are shown in Figs. 6(a)–6(c), respectively. The CoFeB surfaces were depth profiled using an Ar ion gun in the XPS system with an ion energy of 2 kV and an ion current of 3 μA (the raster size was 3 × 3 mm), and the XPS narrow scan data were measured again every 90 s of depth profiling to 360 s. The binding energies of Co 2p, Fe 2p, and B 1s of the pristine CoFeB were observed at 778.3 and 793.2 eV for Co 2p, 707 and 720.2 eV for Fe 2p, and 188 eV for B 1s. However, as shown in Fig. 6, after the etching, additional peaks at 781 and 797.1 eV for Co 2p, 710 and 723.5 eV for Fe 2p, and 192 eV for B 1s possibly related to oxides such as Co(OH)x, or Co3O4, Fe3O4, and B2O3 were observed. For the samples that received a CO/NH3 RIBE treatment for, respectively, 50 and 100 min, from the XPS depth profiling, it was found that the thickness of the oxide layer was strongly reduced during the RIBE treatment. The XPS signals collected at depth profiling times greater than 180 s no longer reveal the presence of oxides.

The change in the relative atomic composition of Co, Fe, B, O, N, and C on the etched CoFeB surfaces with increasing the depth profiling time in Fig. 6 is shown in Figs. 7(a)–7(c) for the conditions in Figs. 6(a)–6(c), respectively. Oxygen percentages on the etched CoFeB surfaces are redrawn in Fig. 7(d) to compare the remaining oxygen percentages before and after the RIBE treatments. As shown, for all etched CoFeB samples, the surface was mostly composed of carbon and oxygen, and the percentages of carbon and oxygen were decreased with increasing depth profiling time while the percentages of Co, Fe, and B were increased with increasing the
depth profiling time. No noticeable nitrogen percentage was observed on the etched CoFeB surfaces. However, the CoFeB samples etched by RIBE for 50 and 100 min showed the saturation of Co, Fe, and B at about the sputtering time at about 270 and 180 s while the main etched CoFeB was not saturated until 360 s. Therefore, the thickness of the residue on the CoFeB surfaces was the lowest for the CoFeB exposed to the reactive ion beam for 100 min, and that was the highest for the main etched CoFeB. This indicates the decrease in the residue on the main etched CoFeB with increasing the RIBE time. Even though these results do not provide the exact evidence on the removal of the sidewall residue on the main etched CoFeB features by RIBE because blank CoFeB samples were used in the experiment, the results provide the possibility in removing the sidewall residue on the main etched CoFeB features using RIBE.

The surface roughness of the blank CoFeB sample etched with the main etch conditions in Fig. 1(b) and those exposed to RIBE after main etching with the conditions in Fig. 5 were measured by AFM, and the results are shown in Fig. 8. As a reference, the surface roughness measured for pristine CoFeB was included. As shown, before etching, the pristine CoFeB showed the RMS surface roughness of about 0.57 nm, and after main etching using CO/NH₃ ICP, the surface roughness was increased to 2.41 nm. However, as shown in the figure, with increasing the RIBE time to 50 min, the surface roughness was decreased to 1.02 nm, and the further increase of RIBE time to 100 min did not noticeably change the surface roughness. The increase in the surface roughness on the blank CoFeB surface is believed to be partially related to the non-uniform residue redeposited on the CoFeB surface during etching. Therefore, the decrease in the surface roughness with

![Fig. 7](image1.png)

**Fig. 7.** (Color online) Relative atomic percentages of the etched blank CoFeB measured by XPS depth profiling as a function of the depth profiling time for the conditions in Figs. 6(a)–6(d) oxygen percentages only after main etching and RIBE of main etched CoFeB for 50, and 100 min.

![Fig. 8](image2.png)

**Fig. 8.** (Color online) AFM surface roughness of the blank CoFeB sample etched with the main etch condition in Fig. 1(b) and those exposed to RIBE after main etching with the conditions in Fig. 5. The surface roughness measured for pristine CoFeB was included as a reference.
increasing the RIBE time is believed to be also related to the decrease of the residue on the etched CoFeB surface by the RIBE. Therefore, it is believed that, by the RIBE using CO/NH₃, the residue remaining after the main etching of CoFeB can be effectively removed.

For the CoFeB features in Figs. 1(b) and 5(c), the bottom areas of the CoFeB feature were further examined using TEM, and the results are shown in Figs. 9(a)–9(c) for the CoFeB masked with W(Ti/Ru), after main etching using the conditions in Fig. 1(b) and after RIBE with the conditions in Fig. 5(c). As shown in Fig. 9(a), before the main etching, the CoFeB was masked with W (W/Ti/Ru) and about 20 nm width CoFeB was exposed for the etching. After the main etching, as shown in Fig. 9(b), the CoFeB was etched; however, the bottom was not clear due to the etch residue remaining on the sidewall of the CoFeB features (the CoFeB in the open area was completely etched). However, as shown in Fig. 9(c), after the RIBE of the main etched CoFeB for 50 min, the residue on the sidewall of the CoFeB in Fig. 9(b) was mostly cleared due to selective etching of the residue remaining on the sidewall of the CoFeB features.

Finally, the actual ion energy of the RIBE system bombarding the CoFeB surface was estimated for different first grid voltages, and the results are shown in Fig. 10. The reactive ion beam was operated with a CO/NH₃ gas ratio of 1:3, 300 W of ICP power, −300 V to the second grid, and a grounded third grid. As the first grid voltage was increased from +30, +50, +70, to +100 V, the ion energy, which is the sudden drop voltage in the figure, was increased from ~67, ~90, ~110, to ~140 eV. Therefore, the actual ion energy was about ~40 eV higher than the first grid potential possibly due to the plasma potential of about 40 V developed in the ICP chamber with the CO/NH₃ plasma.

IV. CONCLUSIONS

A method for removing the sidewall residue was investigated during etching of CoFeB, which is one of the magnetic materials used for the next generation high-capacity nonvolatile STT-RAM devices. CO/NH₃ RIBE was used, and its effect on removing the sidewall residue on the etched nanoscale CoFeB features with W mask was investigated. When an Ar ion beam was used, due to insufficient etch selectivity between the CoFeB residue and W, the CoFeB etch profile...
was degraded with increasing the Ar ion beam energy; however, when CO/NH3 reactive ion beam was used, with increasing ion energy of the reactive ion beam up to 110 eV (*+70 V of first grid voltage*), the etch profile was improved possibly due to the formation of more volatile chemical compounds with CoFeB residue deposited on the sidewall of the etched feature and a more selective removal of the residue compared to W and pristine CoFeB due to the looser atomic binding of the sidewall residue. The increase in etch time using the 110 eV of CO/NH3 reactive ion beam improved etch profile, therefore, removed the etch residue selectively without etching of W. However, the increase in the ion energy higher than 140 eV (first grid voltage of *+100 V*) again degraded the etch profile possibly due to the nonselective etching of W and pristine CoFeB material together with the sidewall residue due to a higher ion bombardment energy.

This experiment indirectly exhibits the increased volatility of chemical compounds formed between CoFeB and CO/NH3 reactive ions, and it is believed that CO/NH3 reactive ion beam can be applied to the selective removal of sidewall residue formed on the MTJ material during the STT-MRAM device fabrication. Especially, in our study, the time to remove the etch residue using RIBE was longer than 50 min due to the low ion beam flux of the home-made RIBE system. Therefore, the use of a high flux RIBE system is believed to be able to effectively remove the etch residue within a reasonable time.

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