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# Magnetically Damage-free Etching of MTJ Film for Future 0.24-μm-rule MRAMs

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## 1. Introduction

Magnetic tunnel junction (MTJ) stacked films are used to fabricate magnetoresistive random access memories (MRAMs). However, the conventional plasma etching processes used for their production cause serious problems, such as, low etching rates, sidewall deposition and residual corrosions because the volatile products (chloride and fluoride) of magnetic materials cannot be easily formed on their surface. Additionally, as is well known, the magnetic properties are sometimes damaged during the plasma etching processes. To breakthrough these problems, we propose pulse-time-modulated (TM) plasma etching [1-3]. In this paper, we report that we have developed a TM plasma process can achieve high-rate MTJ etching with negative ions, but without sidewall deposition, residual corrosion, or magnetic damage.

## 2. Experiments

We used an electron cyclotron resonance (ECR) plasma etching system with cylindrical permanent magnet arrays for this study (Fig. 1). The microwave power, RF bias, gas, flow rate, and pressure, substrate temperature were 1kW(2.45GHz), 100W (600kHz), $Cl_2$, 50sccm, 2mTorr, and 30°C, respectively. To generate the TM plasma, the microwave power was modulated at a few tens of μsec. During the pulse-off time in the TM plasma, a large amount of negative ions was generated through the dissociative attachment of low energy electrons with $Cl_2$. Then, negative ($Cl^-$) and positive ($Cl_2^+$) ions could be mutually accelerated to the substrate by applying 600 kHz RF bias [1-3]. In contrast, only positive ion ($Cl_2^+$) were accelerated in the CW plasma.

The negative ion density in the TM plasma strongly depended on the pulse-off time. When the pulse-off time was 30μsec in the TM plasma, the negative ion density was the maximum value (Fig. 2). The pulse-off time was varied from 10 to 70 μsec (pulse-on time was fixed at 30 μsec) to investigate the effects of negative ions in MTJ etching. The incident ion energy for the TM plasma was fixed to be the same as that for the CW plasma. The samples used for etching were MTJ stacked films of $SiO_2$-Mask/ Ta/ NiFe/ AlOx/ CoFe/ Ru/ CoFe/ PtMn/ Ta (Fig. 3, 4000/ 200/ 50/ 15/ 30/ 10/ 30/ 200/ 200A). We investigated the etching characteristics in the TM $Cl_2$ plasma, with a comparison of that in the continuous wave (CW) $Cl_2$ plasma.

## 3. Results and Discussion

The magnetic films (CoFe, NiFe) and the $SiO_2$ etching rates as a function of the pulse-off time are shown in Fig. 4. The magnetic film etching rate increased when the pulse-off time was increased from 10 to 30 μsec, while the $SiO_2$ etching rate was kept constant by using the TM plasma. This result suggests that the trends of etching rates for magnetic materials corresponded to the trends of negative ion density in the TM plasma and the $SiO_2$ etching rate strongly depended on the incident ion energy. Figure 5 shows SEM images of the MTJ stacked films directly etched using CW plasma and TM plasma (on/off = 30/ 30 μsec). An anisotropic etching profile could be achieved by using TM plasma without any sidewall deposition and residual corrosions, but with high etching selectivity to the $SiO_2$ mask. In contrast, we observed large tapered profiles with sidewall deposition, residual corrosions, and thinner remaining $SiO_2$ mask when the conventional CW plasma was used.

Figure 6 shows the atomic percentages obtained from the XPS spectrum on the etched surface as a function of the pulse-off time in the TM plasma. The components of residual etching products (Cl, Pt, and Mn) on the surface were drastically reduced by increasing the pulse-off time. This completely corresponded to the trends of negative ion density in the plasma. Specifically, the TM plasma enhanced the surface chemical reactions even for the MTJ films by injecting negative ions from the plasma. As a result, we achieved high performance magnetic film etching by using the TM plasma process.

We compared the magnetic properties of the dot patterned MTJ that we fabricated using the TM plasma and CW plasma etching processes for magnetic damage in the junctions (Fig. 7, 8). We measured the magnetic properties of the dot patterned MTJ from 0.6μm to 0.24μm width with a vibrating sample magnetometer (VSM). Fig. 7 shows the major loop of the MTJ etched using TM plasma and CW plasma process. The dot patterned MTJ fabricated using the TM plasma showed the same magnetization curve as that before etching, while that etched using the CW plasma showed extension of the hysteresis loop at the zero external magnetic field region. This implies that TM plasma can be used to etch without any magnetic damage. Fig. 8 shows the minor loop of the MTJ etched using TM plasma and CW plasma processes as a function of MTJ pattern width. The CW plasma process degraded the magnetic property of MTJ in any pattern width, as compared with that in the TM plasma. In fact, TM plasma etching never caused any magnetic damage to the MTJ characteristics even for the 0.24-μm rule.

In Fig. 9, we provide cross sectional TEM images of the MTJ film structure after the TM plasma etchings and after the CW plasma etchings to aid understanding of the effect of TM plasma in relation to magnetic damage during the MTJ etching. Actually, the CoFe crystal structure was changed to amorphous structure just near the sidewall after CW plasma etching, whereas the crystal structure could be maintained after using TM plasma etching (Fig. 9). We speculate that this damage in the former is due to the residual Cl corrosions with CoFe film on the etched sidewall that occur during the CW $Cl_2$ plasma etching because the residual chloride intruded from the sidewall into the

CoFe/PtMn layer in the case of CW plasma etching.

According to these results and discussion, we found the TM plasma enhanced the surface reaction of MTJ by injection of negative ions, and eliminated magnetic damage by enhancing the evaporation of by-products from the etched sidewall.

## 4. Conclusions

We developed a high-rate and damage-free process for etching of magnetic tunnel junction (MTJ) film by using pulse-time-modulated (TM) chlorine plasma. By using TM plasma, we could eliminate magnetic damage with enhanced evaporation of by-products on the sidewall. The negative ions injected from TM plasma drastically enhanced the chemical reaction on the magnetic film surface and caused no residual Cl corrosion. From these results, we propose TM plasma etching as a promising candidate for fabricating advanced MRAM devices.

## References


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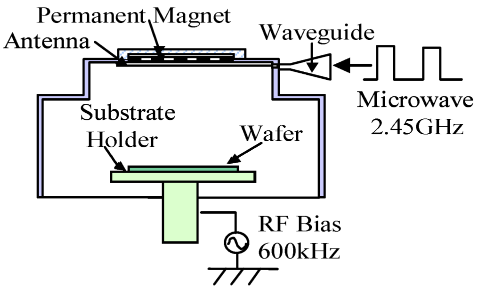

Fig. 1. Schematic illustration of the TM-ECR plasma etching system.

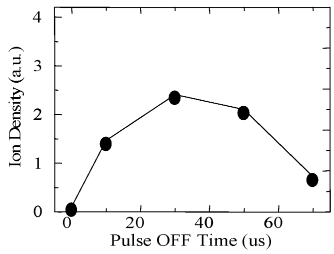

Fig. 2. Negative ion density as functions of pulse off time in the TM plasma using QMS.

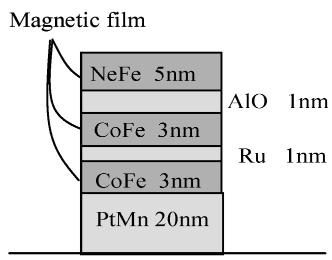

Fig. 3. Schematic illustration of MTJ stacked structure in this experiment.

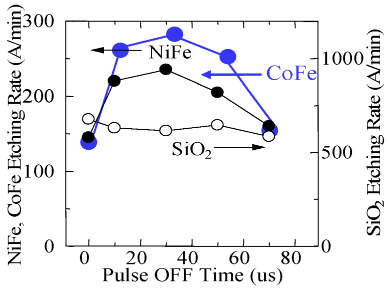

Fig. 4. Magnetic films and $SiO_2$ etching rates as functions of pulse-off time in TM plasma.

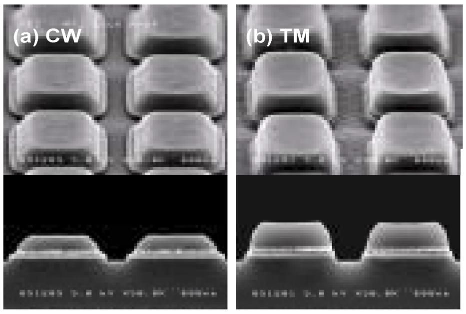

Fig 5. Magnetic tunnel junction film etching profiles using (a) CW plasma and (b) TM plasma.

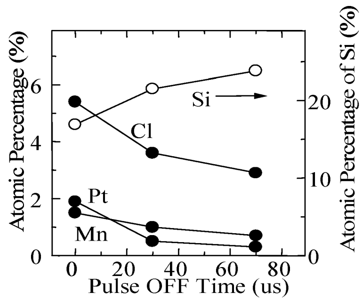

Fig. 6. Atomic percentage obtained from the XPS spectrum as function of pulse off time in the TM plasma.

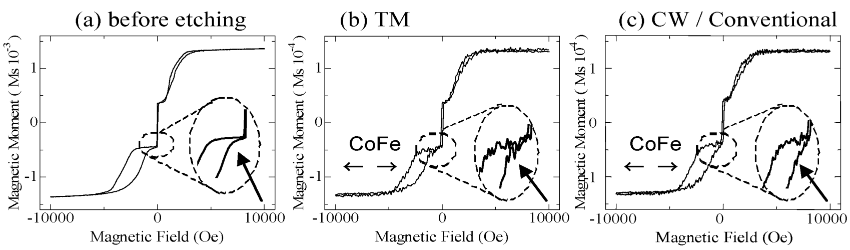

Fig. 7. Major loop of the magnetic tunnel junction film (a) before etching and after etching by using (b) TM plasma, and (c) conventional CW process.

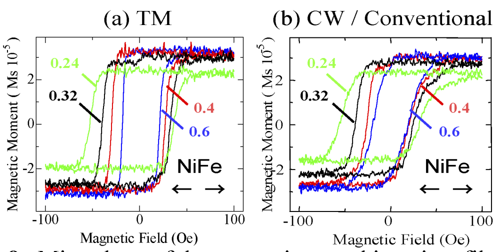

Fig. 8. Minor loop of the magnetic tunnel junction film etched using (a) TM plasma (b) conventional CW process as a function of MTJ pattern width (from 0.24μm to 0.6μm).

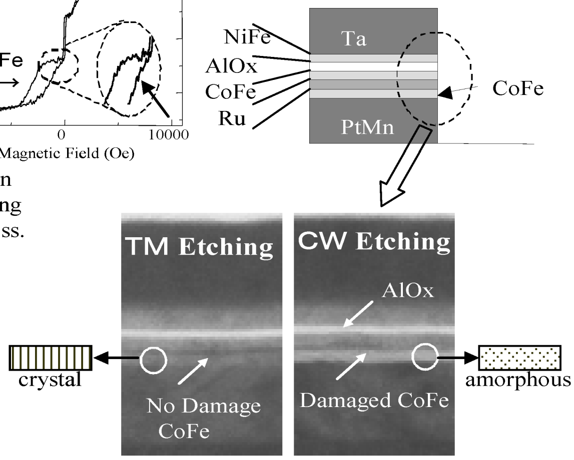

Fig 9. Cross-sectional TEM image of MTJ after (a) TM and (b) CW chlorine plasma etchings.