Etch characteristics of CoFeB magnetic thin films using high density plasma of a H2O/CH4/Ar gas mixture

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Etch characteristics of CoFeB magnetic thin films patterned with TiN hard masks were investigated using inductively coupled plasma reactive ion etching in H2O/Ar and H2O/CH4 gas mixes. As the H2O concentration in the H2O/Ar gas increased, the etch rates of CoFeB and TiN films decreased simultaneously, while the etch selectivity increased and etch profiles improved slightly without any redeposition. The addition of CH4 to the H2O gas resulted in an increase in etch selectivity and a higher degree of anisotropy in the etch profile. X-ray photoelectron spectroscopy was performed to understand the etch mechanism in H2O/CH4 plasma. A good pattern transfer of CoFeB films masked with TiN films was successfully achieved using the H2O/CH4 gas mix.

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1. Introduction

Owing to the demand for the transfer of a variety of information and massive data via various electronic devices, development of the next generation of memory devices with high speed and high density is essential. High density dynamic random access memory (DRAM) is currently developed by using cutting edge technologies that function at nanometer dimensions of 30–50 nm. DRAM has many advantages including high density, fast speed, and low power consumption; however, it has the disadvantage of volatility. Therefore, the development of next generation memory devices to meet these demands is prerequisite [1,2].

Among a variety of emerging and nonvolatile candidate memory devices, magnetic random access memory (MRAM) has drawn a great deal of attention because it has many advantages including high density, fast speed, nonvolatility and radiation hardness. MRAM consists of a complementary metal oxide semiconductor field effect transistor and a magnetic tunnel junction (MTJ). MTJ stacks, which correspond to capacitors in DRAM, are important components of MRAM. These stacks are composed of a variety of magnetic thin films, metals and a tunneling barrier layer [2–4].

To fabricate high density MRAM, it is necessary to develop a method of etching the MTJ stacks. The MTJ stacks consist of a few metal films, MgO as a tunneling barrier layer, and magnetic layers such as CoFeB, PtMn, IrMn and FePt thin films. Initially, etching of the magnetic thin films was carried out by ion milling, which employed a physical sputtering etch mechanism, and by reactive ion etching which used a physical and chemical etch mechanism. Magnetic thin films undergo little reaction with chemically active species in plasma; therefore, ion milling has been the main method used for etching of magnetic thin films. However, ion milling has shown several disadvantages including heavy redeposition on the sidewall of the etched patterns and etch damage to the magnetic properties [5–7]. To overcome these issues, inductively coupled plasma reactive ion etching (ICPRIE) was employed to etch the magnetic thin films. Initially, Cl2, BCl3, and HBr gases were used for etching; however, they did not produce satisfactory etch results because of the slanted sidewall angles of the etched films (called an etch slope hereafter) and thick redeposition on the sidewall of the films [7–9]. Some studies used a CO/NH3 gas mixture to etch the magnetic films [10–12], but this process could not be reproduced and the proposed etch mechanism could not be confirmed. Recently, etch studies using CH3OH to etch magnetic films and MTJ stacks were reported and some progress with good etch profiles was found [13–15].
In this study, the etch characteristics of CoFeB thin films, which are the key layer in MTJ stacks, were investigated using an ICPRIE in H₂O and H₂O/CH₄ plasmas. The effects of H₂O and CH₄ gases on the etch rate, etch selectivity and etch profiles of CoFeB thin films were examined. In addition, the etch mechanism was explored by using XPS along with the etch characteristics.

2. Experimental details

ICPRIE of CoFeB thin films masked with TiN thin films was carried out using H₂O/Ar and H₂O/CH₄ gas mixes. CoFeB and TiN thin films were prepared on Si substrates by dc magnetron sputtering using 3-in diameter targets at pressures ranging from 7.8 to 9.1 × 10⁻⁵ Pa. To study the etch profile, TiN thin films were deposited on CoFeB thin films. These thin films were then patterned by photolithography using a 1.2 μm-thick conventional photoresist. TiN thin films deposited on CoFeB films were etched by reactive ion etching in a Cl₂/C₂F₆/Ar gas after patterning by lithography. The photoresist masks were subsequently removed using a stripping solution and O₂ plasma ashing after the TiN hard mask was etched. The patterned TiN films were left on the CoFeB thin films.

The CoFeB and TiN thin films were etched using ICPRIE equipment (A-Tech, Korea). The ICP coil connected to a 13.56 MHz rf power supply was located on top of the main chamber for generating a high density plasma. The dc-bias voltage induced by another rf power at 13.56 MHz accelerated ions and radicals to the surface of substrates in the plasma. The main chamber was evacuated to a pressure of 1.07 × 10⁻⁴ Pa using a turbo molecular pump. The temperature of the susceptor was constantly maintained at 12–15 °C using chilled fluid and the substrate was cooled by cold helium gas filled between the substrate and susceptor. The schematic of the ICPRIE system was shown in Fig. 1.

In this study, the etch characteristics of CoFeB thin films were investigated using an ICPRIE in H₂O/Ar and H₂O/CH₄ gas mixes. The etch rates, etch selectivities and etch profiles of CoFeB thin films were examined by varying the H₂O and CH₄ concentrations in H₂O/Ar and H₂O/CH₄ gas mixes. The surface profiler (Tencor P-1) and field emission scanning electron microscopy (FESEM; Hitachi S-4300) with an operating voltage of 20 kV were used to measure the etch rate of the films and etch profiles, respectively. X-ray photoelectron spectroscopy (XPS: ThermoScientific K-Alpha) with a source of Al Kα and X-ray beam energy of 1486.6 eV was employed to assess the etch mechanism of CoFeB thin films by detecting the presence of chemical compounds on the etched surfaces of the films.

3. Results and discussion

The main objective of this study was to develop a prospective gas for etching of CoFeB thin films. To prevent corrosion of CoFeB magnetic films by corrosive etch gases such as Cl₂, BCl₃ and HBr, and to reduce the heavy redeposition on the sidewall of the etched films by CH₃OH and CH₄ [16,17], H₂O gas was used for etching. Fig. 2 shows the etch rates of CoFeB and TiN thin films in H₂O/Ar gas containing various H₂O concentrations. The etching was carried out under two different etch conditions; etch condition 1 (etch 1), which was an ICP rf power of 800 W, dc-bias voltage of 300 V, and gas pressure of 0.67 Pa; and etch condition 2 (etch 2), which consisted of an ICP rf power of 900 W, dc-bias to substrate of 300 V and gas pressure of 0.13 Pa. The etch rates of CoFeB and TiN thin films decreased remarkably as the H₂O concentration increased for both etch conditions. The etch rates under etch condition 2 were...
higher than those under etch condition 1. Moreover, the etch rate of CoFeB films showed some change with variations in H2O concentration, while the TiN etch rate showed little change with such variations. The decrease in etch rates with increasing H2O concentration was attributed to reduction of the ion bombardment onto the specimen due to decreased energetic Ar ions and/or hindrance of an instantaneously formed layer containing hydrogen in H2O plasma. These results suggest that etching of CoFeB thin films under H2O/Ar gas does not follow the reactive ion etching mechanism [18]. Fig. 3 shows the etch selectivities of CoFeB films to TiN hard masks under various H2O concentrations for both etch conditions. The etch selectivity is defined by the ratio of CoFeB etch rate to TiN etch rate. The etch selectivity of CoFeB/TiN was higher under etch condition 2 than etch condition 1. In the case of etch condition 1, the etch selectivity of CoFeB/TiN increased initially at 20% H2O but remained almost constant after a further increase to 100% H2O. However, under etch condition 2, the etch selectivity gradually increased with increasing H2O concentration due to the increase in etch rate of CoFeB films.

Fig. 4 shows FESEM micrographs of CoFeB thin films with TiN hard masks after etching under different H2O concentrations. The etch profiles showed very slanted etch slopes with little redeposited materials on the sidewall of the etched films. As the H2O concentration increased, the etch slopes of the CoFeB films improved slightly. This slight improvement with increasing H2O concentration was due to the increased etch selectivity under high H2O concentrations. A high etch slope of TiN masks as well as that of CoFeB films etched in 100% H2O was observed. Although the slow etch rate of CoFeB thin films in H2O plasma can be accepted, the etch profile of CoFeB films needs to be improved before this process can be applied to fabrication of MRAM.

To enhance the etch profile of CoFeB films in H2O plasma, CH4 gas was added to H2O because it could produce the hydroxide and oxide through C and CHx species, as shown in etching of CoFeB films in CH3OH or CH4/O2/Ar gas mixes [16,17]. In addition, Ar was left out of the etch gas to clearly confirm the effect of CH4 on the etch profile of CoFeB films. Fig. 5 presents the etch rate and etch selectivity of CoFeB/TiN in H2O/CH4 gas mix containing various CH4 concentrations. As the CH4 concentration increased from 0% to 90% in H2O/CH4 gas mix, the etch rate of the CoFeB films increased significantly, while the etch rate of the TiN hard mask showed slight increase. Therefore, the etch selectivity of CoFeB/TiN increased from approximately 4 in 100% H2O to 6 in 90% CH4. These findings imply that the chemical reactivity of CoFeB films was better in CH4 plasma than in H2O plasma. FESEM micrographs etched in H2O/CH4 gas mix

![Fig. 4. FESEM micrographs of CoFeB thin films with TiN hard masks, etched in (a) 20% H2O/Ar, (b) 60% H2O/Ar, and (c) 100% H2O/Ar; Etch condition: ICP rf power of 900 W, dc-bias voltage of 400 V, and gas pressure of 0.13 Pa.](image-url)
condition: ICP rf power of 800 W, dc-bias voltage of 300 V, and gas pressure of 0.67 Pa.

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range of 50%–75%.

XPS of CoFeB films etched using different etch gases was con-ducted to examine the etch mechanism. Fig. 7 shows the narrow scans of Co 2p (a), Fe 2p (b), B 1s (c), C 1s (d), and O 1s (e). Each figure compares the narrow scans for three cases: before etching, etching in 100% H2O, and etching in 66.7% CH4/H2O. The narrow scans were deconvoluted to confirm the chemical compounds on the film surface. The binding energies of 779.5, 780.2 and 781.5 eV were determined from the deconvoluted peaks of the narrow scans of the Co 2p3/2 peaks of CoFeB films etched in 100% H2O. These corresponded to CoO (779.7–780.3 eV), Co2O3 (779.5–780.2 eV), and Co(OH)2 (780.7–781.3 eV) [19]. The deconvoluted peaks of the Co 2p3/2 peaks of the films etched in 66.7% CH4/H2O gas mix indicated the binding energies of 779, 779.7, and 781 eV which corresponded to Co(CH3)2 (779.10 eV), Co2O3, and Co(OH)2 respectively.

Fig. 7(b) presents the narrow scans of Fe 2p peaks for three cases. When the CoFeB films were etched in 100% H2O, the Fe 2p3/2 peak shifted to the high binding energy of 710.5 eV. The deconvoluted peaks in the narrow scan showed the binding energies of 709.2 and 710.9 eV, which corresponded to FeO (709.4 eV) and Fe2O3 (710.8–710.9 eV), respectively [19]. A distinct separation in the Fe 2p3/2 peak of the films etched in 66.7% CH4/H2O gas mix was observed. One corresponded to Fe(CH3)2 compounds having a binding energy of 707.7 eV and others corresponded to FeO or Fe2O3 having a binding energy of 710 eV and FeOOH compound having a binding energy of 712.5 eV [19]. For the B 1s peak, the specimen before etching is composed of borides with a binding energy of 187.7 eV (boride: 187.2–189.2 eV) [19]. However, after the films were etched in 100% H2O, the main peak of B 1s was shifted to a binding energy of 191.5 eV. This indicated the existence of B2O3 compound (192 eV) on the film surface [19]. However, the intensities of the peaks of the films etched in 66.7% CH4/H2O were decreased and the peak with the binding energy of approximately 189 eV corresponded to metal borides containing Co and Fe. These findings implied the role of O in 100% H2O and 66.7% CH4/H2O gas mix.

Fig. 7(d) showed the narrow scans of C 1s peaks for CoFeB films. In the case of before etching and 100% H2O, the C 1s peak was observed with the low intensity and it was thought to be the contaminants on the film surface before the analysis. The peaks for before etching and 100% H2O gas were very similar. When the 66.7% CH4 added in the H2O, the intensity of C 1s peak increased significantly and two peaks with the binding energies of 283.5 and 284.5 eV were observed, which corresponded to Fe3C, Co(C5H5)2 and Fe(C5H5)2, respectively [19]. These indicated the existence of Co and Fe compounds containing C and H. This is in good agreement with the results of Co 2p and Fe 2p peaks. In the case of O 1s peak (Fig. 7(e)), the peak in the narrow scan for 100% H2O increased significantly and two deconvoluted peaks corresponded to metal oxide (529.7 eV) and FeOOH (531.1 eV). However, these peaks in the case of 66.7% CH4/H2O gas mix were decreased and small peak corresponding to B2O3 compounds (533 eV) was identified. This was attributed to the decrease of metal oxides due to the reduction of O by the addition of CH4 gas.

Based on the XPS analysis, the CoFeB films were oxidized under 100% H2O gas, forming metal oxides containing Co, Fe and B, respectively. When the CH4 gas was added to H2O, the films could form metal compounds containing C or CH groups. Therefore, the H2O/CH4 gas mix could be a proper etch gas for etching of CoFeB thin films by maximizing the chemical reaction between the etch gas and film. Finally, good pattern transfer of CoFeB thin films

Fig. 6. FESEM micrographs of CoFeB thin films with TiN hard mask on, etched in (a) 50% H2O/50% CH4, (b) 33.3% H2O/66.7% CH4, (c) 25% H2O/75% CH4, (d) 10% H2O/90% CH4. Etch condition: ICP rf power of 800 W, dc-bias voltage of 300 V, and gas pressure of 0.67 Pa.
masked with TiN films could be achieved in the range of 50%–75% CH₄ in the H₂O/CH₄ gas mix.

4. Conclusions

The etching of CoFeB magnetic thin films masked with TiN films was carried out in high density plasma of H₂O/Ar and H₂O/CH₄ gas mixes. As the H₂O concentration in H₂O/Ar increased, the etch rates of the films decreased and the etch selectivity of CoFeB film to the TiN mask increased. The etch profiles of CoFeB films improved slightly without redeposition with increasing H₂O concentration.

As CH₄ gas was added to H₂O, the etch rates of CoFeB and TiN films increased and the etch selectivity of CoFeB to TiN greatly increased due to the high increase in CoFeB etch rate when compared to the TiN etch rate. When the CH₄ concentration in the H₂O/CH₄ gas mix increased, the etch profile improved significantly, which was attributed to the increased etch selectivity and chemical reactions under high CH₄ concentrations.

XPS analysis was employed to elucidate the etch mechanism of CoFeB thin films using H₂O/CH₄ gas mix. The results revealed that metal oxides (CoOₓ, FeOₓ) and/or metal hydroxides (Co(OH)₂ and FeOOH) were formed in H₂O plasma and that the compounds containing carbon and hydrogen (Co(C₅H₅)₂, Fe(C₅H₅)₂) were formed in H₂O/CH₄ plasma. The etching of CoFeB films in the H₂O/CH₄ gas mix is believed to proceed through sputter etching with the effect of some chemical reactions. Good pattern transfer of CoFeB thin films masked with TiN films was achieved using the H₂O/CH₄ gas mix. Therefore, H₂O/CH₄ may be a good candidate for etching of CoFeB thin films.

Fig. 7. XPS narrow scans of the (a) Co 2p, (b) Fe 2p, (c) B 1s (d) C 1s and (e) O 1s peaks for CoFeB thin films etched using different H₂O/CH₄ concentrations. Etch condition: ICP rf power of 800 W, dc-bias voltage of 300 V, and gas pressure of 0.67 Pa.
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