Inductively coupled plasma reactive ion etching of IrMn magnetic thin films using a CH$_4$/O$_2$/Ar gas

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A B S T R A C T
In this study, the etch characteristics of IrMn magnetic thin films patterned with TiN hard mask were investigated using an inductively coupled plasma reactive ion etching in CH$_4$/Ar and CH$_4$/O$_2$/Ar gas mixes. As the CH$_4$ concentration increased in the CH$_4$/Ar gas, the etch rates of IrMn and TiN films simultaneously decreased, while the etch selectivity increased and etch profiles improved without any redeposition. The addition of O$_2$ to the CH$_4$/Ar gas led to an increase in the etch selectivity and a higher degree of anisotropy in etch profile. The dc-bias voltage and gas pressure were varied to examine and optimize the etching process of IrMn films. Low gas pressure and high dc-bias voltage improved the etch profiles. Surface analysis of etched films by X-ray photoelectron spectroscopy was performed to identify the existence of compounds during etching.

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1. Introduction

Since the beginning of the information-oriented society, the amount of information that each individual needs continues to rapidly increasing along with the advent of various smart devices. In order to meet these demands, there is a need to develop the next generation memory devices with high density and high speed [1,2]. Currently, dynamic random access memory (DRAM) was developed with high density using cutting edge nanotechnology, which involves materials with dimensions between 30 and 50 nm. Despite the great performance of DRAMs, DRAMs have volatile properties and the data is erased when the power is turned off. Magnetic random access memory (MRAM) has also been highlighted as the next generation universal memory. MRAM is composed of a complementary metal oxide semiconductor field effect transistor and a magnetic tunnel junction (MTJ). MTJ stacks which correspond to capacitors in DRAM are the key component of MRAM. It consists of a variety of magnetic thin films, which have the property of tunneling magnetoresistance [2–4].

To achieve high density MRAM, the development of a process to etch the MTJ stacks is a prerequisite. The MTJ stacks are composed of magnetic layers such as IrMn, CoFeB and FePt thin films. At the early stage of etching the magnetic thin films, ion milling, which is a physical sputtering method, has been used because the magnetic thin films hardly react with chemically active species in a plasma. However, ion milling has several disadvantages, including heavy redeposition on the sidewall of the patterns and etching damage to the magnetic properties [5–7].

Many etching studies using an inductively coupled plasma reactive ion etching (ICPRIE) have been previously attempted in Cl$_2$, BCl$_3$, HBr gases to address these limitations, [7–9]. These methods have improved the etch profile but issues associated with corrosion, which cause surface corrosion due to remnant corrosive species on the film surface, still need to be addressed. Recently, NH$_3$/CO and CH$_3$OH gases have been applied to etch magnetic films and they showed some progress with good etch profiles [10–12].

In this study, the etch characteristics of IrMn thin films, a key layer in MTJ stacks, were investigated using an ICPRIE in CH$_4$/Ar gas, which are non-corrosive and non-toxic gases. In addition, the etching results and etch mechanism were explored by adding O$_2$ gas into the CH$_4$/Ar gas.

2. Experimental details

Two types of etch samples were prepared to investigate the etch rates, etch selectivities and etch profiles. One type was single layers of IrMn and TiN films with a thickness of 100 nm, respectively. These layers were deposited on Si substrates by dc magnetron sputtering using the 3-in diameter targets at pressures ranging from 7.8 to 9.1×10$^{-5}$ Pa. The samples were then patterned by conventional lithography using an AZ1512 photoresist that was 1.2 μm thick. The other type of sample was composed of two layers, IrMn and TiN thin films. The TiN hard masks were deposited on top of the IrMn thin films that were on Si substrates. The TiN films were then patterned by lithography, followed by ICPRIE in a C$_2$F$_6$/Cl$_2$/Ar gas mix. The patterns of the photoresist layers consisted of lines and spaces that were 1, 5, 10, 50, and 100 nm wide. Finally, the photoresist films from the lithography process were stripped by wet stripping.
and O₂ ashing after etching. The patterned TiN films were left on the IrMn thin films.

The IrMn and TiN films were etched using ICPRIE equipment (A-Tech, Republic of Korea). The ICP coil for generating a high density plasma was located on the top of the main chamber and connected to a 13.56 MHz rf power supply. The dc-bias voltage was induced by the other rf power at 13.56 MHz accelerated ions and radicals to the surface of substrates in the plasma. The main chamber was evacuated down to a pressure of $1.07 \times 10^{-4}$ Pa using a turbo molecular pump. The temperature of the susceptor was constantly maintained using chilled fluid at 12–15 °C and the substrate was cooled by cold helium gas filled between the substrate and susceptor.

In this study, the etch characteristics of IrMn thin films were investigated using an ICPRIE in CH$_4$/Ar and CH$_4$/O$_2$/Ar gas mixes. The etch rates and etch profiles of IrMn thin films were examined by varying the CH$_4$ and O$_2$ concentrations in CH$_4$/Ar and CH$_4$/O$_2$/Ar gas mixes and the dc-bias voltage and gas pressure. The surface profiler (Tencor P-1) and field emission scanning electron microscopy (FESEM; 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 X-ray source of Alkα and X-ray beam energy of 12 kV was employed to assess the etch mechanism of IrMn thin films by detecting the presence of chemical compounds on the etched surfaces of the films. Optical emission spectroscopy (OES) was also used to measure the levels of active species in the plasma.

3. Results and discussion

To determine the optimal concentration of CH$_4$ in the CH$_4$/Ar gas mix, IrMn magnetic thin films patterned with photoresist masks were etched using various concentrations of the CH$_4$ gas. A coil rf power of 800 W, dc bias voltage of 300 V and gas pressure of 0.67 Pa were chosen as the standard etching conditions. Fig. 1 shows the etch rates of IrMn and TiN thin films at various CH$_4$ concentrations in the CH$_4$/Ar gas mix. The etch rates of IrMn thin films remarkably decreased from 1850 Å/min in pure Ar to 220 Å/min in 80% CH$_4$/Ar. The etch rates of TiN hard masks also decreased from 250 Å/min in pure Ar to 30 Å/min in 80% CH$_4$/Ar gas. The etch selectivity of the IrMn thin films to the TiN hard masks slightly increased with an increase in CH$_4$ concentration. The decrease in etch rates with an increase in CH$_4$ concentration was attributed to a decrease in the energetic Ar ions due to a reduction of Ar gas, which physically etches the film surface.

The etch selectivity increased when the CH$_4$ concentration was increased up to 60% and then slightly decreased as more CH$_4$ gas was added to Ar. This occurred because the decrease in the etch rate of TiN hard mask was larger than that of the IrMn films. In addition, the formation of polymer films containing C and H in high CH$_4$ concentrations exceeding 60% resulted in a decrease in the etch rate of the films because these formed polymers interrupted ion bombardment and/or any chemical reactions between the radicals and the film surface.

FESEM micrographs of the etched samples in various CH$_4$ concentrations are presented in Fig. 2. Thick redeposition on the sidewall of IrMn thin film etched in pure Ar was observed (Fig. 2 (a)). This
occurred because physical sputtering by Ar ions, which was the etch mechanism, often results in redeposition on the sidewall of the etched films. The level of redeposition was decreased by adding CH4 gas to Ar gas, as shown in Fig. 2(b)–(d). When the CH4 concentration was increased from 20% to 60%, redeposition completely disappeared, leading to a steep etch slope of the sidewall of the films. These positive results were due to the assistance of chemical reaction between the chemically active species in the plasma and the film surface. The increase in etch selectivity of the IrMn films with increasing CH4 gas was also considered to be partially responsible for the improved etch profile. However, when the CH4 concentration in the CH4/Ar gas mix was higher than 60%, redeposited materials or etch residues on both the sidewall and the film surface were observed. It is believed that the formation of polymer films containing C and H in high CH4 concentrations was responsible for this effect.

Although etching using high concentrations of CH4 in the CH4/Ar gas mix improved the etch profile, a higher degree of anisotropy in the etch profile without redeposition or etch residues is still required. In order to achieve this goal, a CH4 gas concentration of 60% was selected as a standard concentration based on the results described above and oxygen gas was added to further improve the etch profile.

![Fig. 3. Etch rate of IrMn and TiN thin films and etch selectivity of IrMn to Ti films (a) and FESEM of IrMn thin films etched in the presence of various O2 concentrations. (b) 0% O2, (c) 6.7% O2, (d) 10% O2, (e) 13.3% O2; Etch conditions: 60% CH4/Ar, coil rf power of 800 W, dc-bias voltage of 300 V and gas pressure of 0.67 Pa.](image)

![Fig. 4. OES analysis of 60% CH4/Ar plasma in the presence of varying concentrations of O2.](image)
Fig. 3 showed the etch rates of IrMn and TiN thin films and FESEM micrographs in various CH4/O2/Ar gas mixes. The selectivity of the IrMn thin film to TiN hard mask increased by greater than a factor of two when O2 gas was added to CH4 gas (Fig. 3 (a)). The etch profile of IrMn films masked with TiN improved when the O2 concentration was increased up to 13.3%, while the etch rate of IrMn films decreased with an increase in the O2 concentration. The increase in the etch selectivity was caused by big decrease in etch rate of TiN films which were due to the formation of TiOx under the addition of O2 gas. On the other hand, the etch rate of IrMn films also decreased but the oxidized metals had relatively high sputtering yield. As a result, the decrease in etch rate of TiN hard masks was bigger than that of IrMn films.

The OES for 60% CH4/O2/Ar gas mixes was performed to examine changes in the [O], [Ar] and [H] components in the plasma when the O2% concentration was increased from 6.7% to 13.3% (Fig. 4). When the O2% concentration was increased from 6.7% to 13.3%, the [O] intensity and [O]/[Ar] ratio gradually increased as expected. In addition, the [H] intensity also increased with an increase in O2 concentration. This effect was attributed to the increase in [H] due to the bonding between C and O. As a result, the increase in [O] led to an increase in the etch selectivity of IrMn/TiN films, which resulted in a high etch slope [13,14].

To examine the effects of the etch parameters on the etch rate, etch selectivity and etch profile, the ICP rf power, dc-bias voltage to substrate and gas pressure were varied at a gas mixture composition of 60% CH4/6.7% O2/Ar. When ICP rf power was increased from 600 W to 1000 W, the etch rates of films slightly increased (data not shown). Fig. 5 shows the change in the etch rate and etch selectivity of the films under varying dc-bias voltage and gas pressure. As the dc-bias voltage increased from 200 V to 400 V, the etch rate of IrMn films greatly increased and the etch selectivity improved, leading to a higher etch slope of IrMn films etched at a 400 V dc-bias voltage (Fig. 6(b)). At a high dc-bias of 400 V, the bombardment energy of the ions was greatly enhanced so that the etch rate of IrMn rapidly increased compared to that of TiN films, resulting in an increase in the etch selectivity. Generally, metal films show higher sputtering yield
than ceramic films so that the etch rate of IrMn films at high dc bias was significantly higher than that of TiN films.

Fig. 5(b) shows the change in the etch rate and etch selectivity at different gas pressures. The etch rates and etch selectivity monotonously decreased when the gas pressure was increased from 0.133 Pa to 1.33 Pa. The etch profile of IrMn films etched at 0.133 Pa showed a higher etch slope that than etched at 1.33 Pa. This result can be explained in terms of the mean free path of particles in the plasma. The ions and radicals at lower pressure have longer mean free path than those at high pressure. This leads to an increase in the vertical bombardment of ions on the film surface and/or a more effective approach to the film without the occurrence of scattering events, which result in a high degree of anisotropy of the etched films.

XPS analysis was employed to examine the surfaces of the etched IrMn films in CH4/O2/Ar plasma in order to understand the etch mechanism of IrMn thin films in the CH4/O2/Ar gas mix. The IrMn thin films, which were not masked with a photoresist, were used for XPS analysis. Pre-sputtering was carried out to remove any contaminants formed through exposure to the atmosphere. IrMn thin films etched in various concentrations of gases (20% and 60% CH4/Ar and 60% CH4/6.7% O2/Ar) were subjected to XPS analysis. Fig. 7(a) shows the narrow scan of the Ir 4f peaks of the etched IrMn films. The peak before etching indicates the chemical state of metal iridium element, which has a peak at a binding energy of 60.1 eV. When the IrMn films were etched in CH4/Ar gas, the Ir 4f peaks were slightly shifted (approximately 60.1 to 60.3 eV). These shifts are thought to be within the range of the peak indicating the metallic iridium [15]. The peak of the films etched at 60% CH4/6.7% O2/Ar gas mix was slightly shifted to a higher binding energy of 60.8 eV, which corresponded to the formation of IrO2 or the binding (O2/Ar) between Ir and molecular O [15].

Fig. 7(b) shows the narrow scans of the Mn 2p peaks for the etched IrMn films in various concentrations of CH4/Ar and CH4/O2/Ar gas mixtures. The Mn 2p peak before-etching clearly indicates the formation of MnOx (640–641 eV) as well as metallic Mn (638–639 eV). When the IrMn films were etched in CH4/Ar gas, a more distinct Mn peak was observed without the formation of any other compounds of Mn. However, the binding energy of the Mn 2p peak after etching in CH4/O2/Ar gas mix increased up to 640–641 eV, which demonstrates that MnOx compounds formed on the film surface [15].

The narrow scans of the O 1s peak are shown in Fig. 7(c). The O 1s peak before-etching was a pure O 1s peak has and had a binding energy of 531 eV. However, when the IrMn films were etched in CH4/O2/Ar as well as CH4/Ar, the O 1s peak was separated into two distinct peaks: one peak of 531 eV, which represents O and the other peak at 529–530 eV, which corresponds to metal oxide. In this case, metal oxide was considered to be MnOx rather than IrOx because the existence of MnOx was already confirmed in Fig. 7(b). Based on the above XPS analysis, the etching of IrMn films in CH4/O2/Ar gas mix may proceed with the assistance of O2 gas, by forming metal oxide during etching. This may have contributed to the high degree of anisotropy in the etch profile in the CH4/O2/Ar gas mix [15].

4. Conclusions

The etching of IrMn magnetic thin films patterned with TiN hard masks was carried out in the high density plasma of CH4/Ar and CH4/O2/Ar gas mixses. As the CH4 concentration increased, the etch rates of the films decreased and the etch profiles improved without redeposition and etch residue. When the CH4 concentration was higher than 80%, polymers were generated on film surfaces due to the high density of hydrocarbons.

The 60% CH4 concentration was selected to assess the effects of O2 gas on the etch characteristics of IrMn films. As the O2 concentration increased, the etch rates slightly decreased and the etch selectivity increased and slight improvement in the etch profiles were observed. By varying the etch parameters such as dc-bias voltage to substrate and gas pressure, the etch rate and etch selectivity were shown to increase when the dc-bias voltage was high and the gas pressure was low. From the OES data, the addition of O2 into CH4/Ar gas was shown to increase the [H]/[Ar] ratio as well as the [O]/[Ar] ratio, which increased the etch selectivity and improved the etch profile. XPS analysis was employed to understand the etch mechanism of IrMn films in CH4/O2/Ar. This analysis revealed that the formation of IrOx and MnOx compounds occurred during etching. Therefore, the etching of IrMn films in CH4/O2/Ar gas mix is believed to proceed through sputter etching with the help of some chemical reactions.

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