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Among the ferroelectric thin films that have been widely investigated for ferroelectric random access memory (FRAM) applications, the SrBi$_2$Ta$_2$O$_9$ (SBT) thin film is appropriate as a memory capacitor material due to its excellent fatigue endurance. However, very few studies on the etch properties of SBT thin films have been reported, even though dry etching is an area that demands a great deal of attention in the very-large-scale integration of ferroelectric thin-film capacitors for FRAM applications. In this study, SrBi$_2$Ta$_2$O$_9$ thin films were etched using a magnetically enhanced inductively coupled Ar/CHF$_3$ plasma. Etch properties, such as etch rate, selectivity, and profile, were measured for different gas mixing ratios of CHF$_3$/(Ar+CHF$_3$), while the other process conditions were fixed at rf power of 600 W, dc-bias voltage of -150 V, and chamber pressure of 5 mTorr. The maximum etch rate of SBT thin films was 1650 Å/min under CHF$_3$/(Ar+CHF$_3$) of 0.1. Selectivities of SBT to Pt and photoresist masks were 1.35 and 0.94, respectively. The chemical reaction and compositional change of the etched surfaces were investigated by x-ray photoelectron spectroscopy analysis. The Sr and Ta atoms of SBT films react with fluorine; Sr–F and Ta–F are then removed by physical sputtering by Ar ions. The surface of a SBT film etched with CHF$_3$/(Ar+CHF$_3$)=0.1 was analyzed using secondary ion mass spectrometry. Scanning electron microscopy was used to examine etched profiles of SBT thin films. The wall angle of a SBT film etched using CHF$_3$/(Ar+CHF$_3$)=0.1 was approximately 85°. © *2000 American Vacuum Society.* [S0734-2101(00)04404-3]

I. INTRODUCTION

Ferroelectric random access memory (FRAM) devices using polarization reversal and hysteretic characteristics show higher speed, lower power consumption, and more stable data exchange compared with electrically erasable and programmable read-only memory or flash memories.[1,2] Furthermore, as FRAM advances in integration density and performance, it has the potential to extend the range of applications of dynamic random access memory.

One of the main process objectives in the integration of ferroelectric capacitors into memory devices is development of the ability to pattern ferroelectric films and the associated electrode materials by selective removal of one material from another. Wet chemical etching can be used for pattern transfer because it provides the capability to terminate etching precisely at an underlying chemically different layer. However, as the complexity of memories increases, the isotropic nature of wet etching results in a loss of control in critical lateral dimensions and, therefore, is not acceptable in the manufacture of integrated circuits. The required directionality and the faithful pattern transfer can be provided by plasma-assisted etching processes. Etching processes must fulfill a number of requirements: sufficient etch profile control and selectivity to the underlying layers and the mask; adequately high etch rates for acceptable productivity; and no damage to the underlying circuit components. Therefore, high-density plasmas such as inductively coupled plasmas, transformerly coupled plasmas, and electron cyclotron resonance plasmas should be employed.[3,4]

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SrBi$_2$Ta$_2$O$_9$ SBT thin films have especially high potential as data storage capacitor materials because SBT has superior fatigue-free properties and small coercive fields E_c, but SBT thin-film etching is very difficult due to its nonvolatile etch products, etch residue, and low selectivity versus mask and bottom electrode materials.[5,6]

In this study, the dry etching of SBT ferroelectric thin films was studied as a function of CHF$_3$/(Ar+CHF$_3$) gas mixing ratios in a magnet-enhanced inductively coupled plasma (MEICP) system. Chemical effects during SBT etching were investigated using x-ray photoelectron spectroscopy (XPS) to determine the elemental composition of the etched surface. The molecular weight of particles released from the surface was measures by secondary ion mass spectrometry (SIMS) analysis.

II. EXPERIMENTAL DETAILS

The 5 in. Si(100) substrates used for this study were doped with B (0.85–1.15 Ω cm) and chemically etched for 60 s using 1% HF:H$_2$O. The substrates were then coated with a 6000-Å-thick layer of SiO$_2$ grown by low-pressure chemical-vapor deposition (SiH$_4$+O$_2$, 420 °C, 240 mTorr). To enhance the adhesion of Pt on the oxide layer, a 300 Å Ti film was deposited prior to Pt deposition. Deposition of 1000–1500 Å Pt films was performed using a Varian 3180 dc-sputtering system equipped with a 7 in. conical magnetron-sputtering source. Film thickness was measured using a Tencor Model α-step 200 surface profiler. SBT thin films were prepared by metal–organic decomposition spin coating. Strontium 2-ethylhexanoate, bismuth 2-ethyl-hexanoate, and tantalum ethoxide were selected as precurors, and xylene was used as a solvent. Stock solutions with a mole ratio (Sr:Bi:Ta) of 0.8:2.4:2.0 were spin coated on Pt/Ti/SiO$_2$/Si substrates. The thickness of the SBT thin films was 1800–2400 Å after crystallization.

SBT etching was investigated using the MEICP system. To generate inductively coupled plasma, 13.56 MHz rf inductive power was applied to a planar spiral Au-coated Cu coil at the top of the process chamber. Separate 13.56 MHz rf power was also applied to the bottom electrode to generate dc self-bias voltages. The distance between the quartz window and substrate was 7.5 cm and the substrate diameter was about 6 in. The magnet configuration, 10 cm long and equally spaced four pairs of permanent magnets having 2000 G on the surface, were located around the chamber wall by making the long axis of the magnets parallel to the chamber axis as shown in Fig. 1.

SBT etching was performed by varying the CHF$_3$/(Ar+CHF$_3$) gas mixing ratio while rf power, dc-bias voltage, and chamber pressure were fixed at 600 W, −150 V, and 5 mTorr.

Analysis of the etched SBT surface was investigated using ESCALAB 220-IXL and CAMECA IMS6F. The XPS Al $K\alpha$ source provides nonmonochromatic x rays at 1486.6 eV. Narrow scan spectra of all interested regions were recorded with 20 eV pass energy in order to qualitatively determine the surface composition and identify the chemical binding
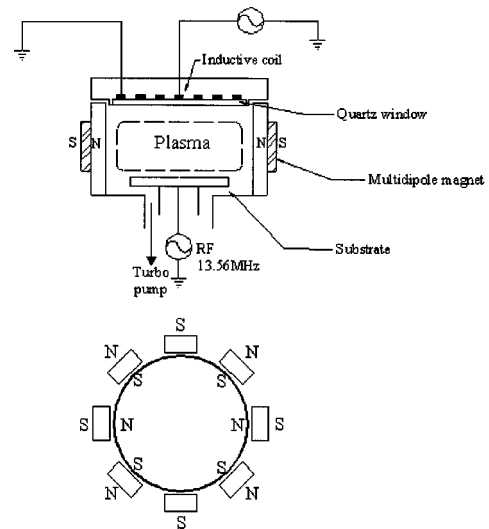

FIG. 1. Schematic of magnet-enhanced inductively coupled plasma (MEICP) system.

state. SIMS measures the molecular weight of particles released from the surface of a material by the bombardment of ions. A Cs ion beam of 1.11 kV and 10.68–10.92 nA was used as the SIMS source.

III. RESULTS AND DISCUSSION

Etching of SBT thin films was investigated as a function of the gas mixing ratio. Figure 2 shows the etch rate of SBT and the selectivities of SBT to Pt, photoresist (PR), and SiO$_2$ as a function of the Ar/CHF$_3$ gas mixing ratio. The maximum etch rate of SBT was 1650 Å/min using CHF$_3$/(Ar+CHF$_3$)=0.1. The etch rate of SBT decreases as the CHF$_3$/(Ar+CHF$_3$) gas mixing ratio increases more than to 0.1. This result suggests that SBT is dominantly etched by Ar bombardment, and that SBT etching is assisted by the
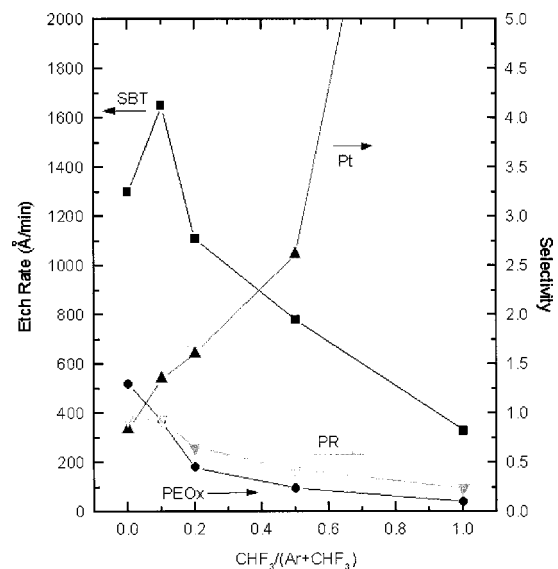

FIG. 2. Etch rate of SBT and selectivity over Pt, PR, and PEO$_x$ (coil rf power: 600 W, dc-bias voltage: −150 V, chamber pressure: 5 mTorr).
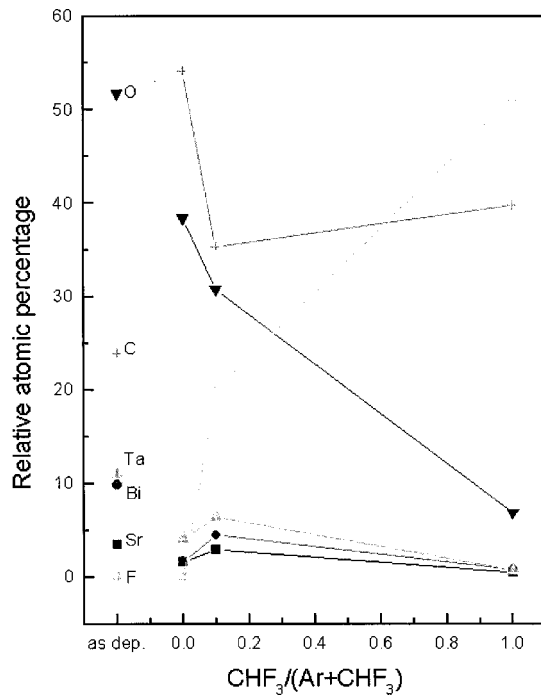
FIG. 3. Relative atomic percents of SBT surface etched with $CHF_3/(Ar+CHF_3)$ gas mixing ratio (coil rf power: 600 W, dc-bias voltage: −150 V, chamber pressure: 5 mTorr).

FIG. 4. Sr $3d$ narrow scan spectra of SBT surface etched with $CHF_3/(Ar+CHF_3)$ gas mixing ratio (coil rf power: 600 W, dc-bias voltage: −150 V, chamber pressure: 5 mTorr).

chemical reaction of CHF_3 gas under the $CHF_3/(Ar+CHF_3)=0.1$ gas condition. Usually, additional reactive gas makes volatile products and enhances the etch rate, but halides of Sr, Bi, and Ta atoms in SBT are nonvolatile due to their low vapor pressures. To explain the enhancement of the etch rate of SBT with a $CHF_3/(Ar+CHF_3)$ gas mixing ratio=0.1, we propose that carbon and hydrogen react with oxygen and fluorine reacts with sputtered metal atoms. The selectivity of SBT to Pt increases as the CHF_3 gas increases since Pt is chemically stable and chemical etching of Pt is lower than that of SBT. Selectivities of SBT to PR and SiO_2 decreases as CHF_3 gas increases since fluorine radicals enhance the chemical etching of PR and SiO_2.

To examine the chemical assistance of CHF_3 in SBT etching, XPS analysis was performed. Fig. 3 shows the relative atomic percentages on the etched surface of a SBT film. As the gas mixing ratio increases, the relative atomic percentage of oxygen decreases and that of fluorine increases. This suggests that oxygen is effectively removed from SBT by CHF_3 gas and that fluorine reacts with metal atoms. The products of the chemical reaction between metal and fluorine can be removed more easily by Ar-ion bombardment. Using a $CHF_3/(Ar+CHF_3)$ gas mixing ratio of more than 0.1, these products are not efficiently removed by the Ar ions and form a passivation layer. In Fig. 3, the relative atomic percentages of Bi, Sr, and Ta in a $CHF_3/(Ar+CHF_3)$ gas mixing ratio = 1 is relatively low compared with a $CHF_3/(Ar+CHF_3)$ gas mixing ratio=0. This suggests that the etched SBT surface is covered with the passivation layer including C, H, and F and, therefore, the x-ray photoelectron intensity of Sr, Bi, and Ta
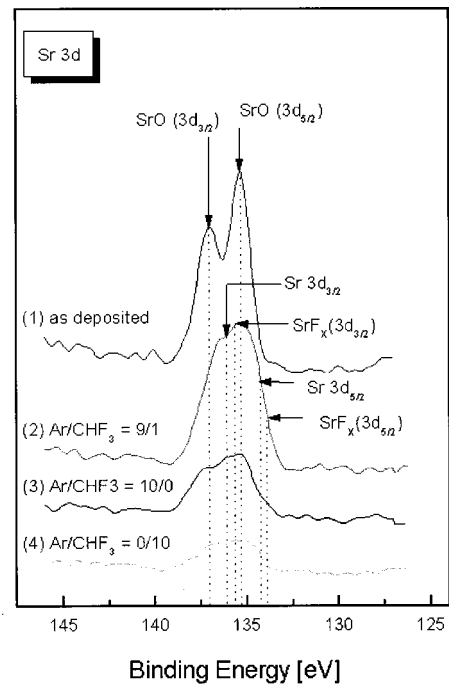
is decreased. This result corresponds with formation of a passivation layer on the etched surface.

For a more precise investigation of the chemical reaction between fluorine and Sr, Bi, and Ta atoms, an XPS narrow scan of the etched surface was performed. Figure 4 shows the Sr $3d$ narrow scan spectra of the SBT surface etched with different $CHF_3/(Ar+CHF_3)$ gas mixing ratios. In Fig. 4(1), the peaks at 135.39 and 137.04 eV correspond to $SrO(3d_{5/2})$ and $SrO(3d_{3/2})$. In Figs. 4(2) and 4(4), the peaks of $SrF_x(3d_{5/2})$ and $SrF_x(3d_{3/2})$ bonds appear at 133.67 and 135.50 eV, as expected. In Fig. 4(3), the peak intensities of Sr $3d_{5/2}$ and Sr $3d_{3/2}$ are increased by Ar-ion bombardment. Therefore, it appears that the chemical bond between Sr and O is broken by Ar^+ bombardment and some Sr reacts with fluorine.

Figure 5 shows the Bi $4f$ narrow scan spectra of a SBT surface etched with different $CHF_3/(Ar+CHF_3)$ gas mixing ratios. In Fig. 5, Bi–F bond and Bi cannot be seen and it seems that Bi reacts with little CHF_3 and Bi is removed predominantly by argon-ion bombardment.

Figure 6 shows the Ta $4f$ narrow scan spectra of a SBT surface etched with different $CHF_3/(Ar+CHF_3)$ gas mixing ratios. In Fig. 6, $Ta(4f_{7/2})$–O and $Ta(4f_{5/2})$–O bonds correspond to binding energies of 28.59 and 30.36 eV. The Ta–O–(Bi or Sr) bonds are expected to appear at 29.88 and 31.75 eV. In the case of Ta $4f$ spectra, the TaF_x peak and several small peaks are expected. The results of Sr $3d$, Bi $4f$, and Ta $4f$ narrow scan spectra correspond with the trend in relative atomic percentage. The XPS narrow scan spectra of Sr $3d$, Bi $4f$, and Ta $4f$ suggest that CHF_3 gas addition is more effective in removing Sr and Ta.
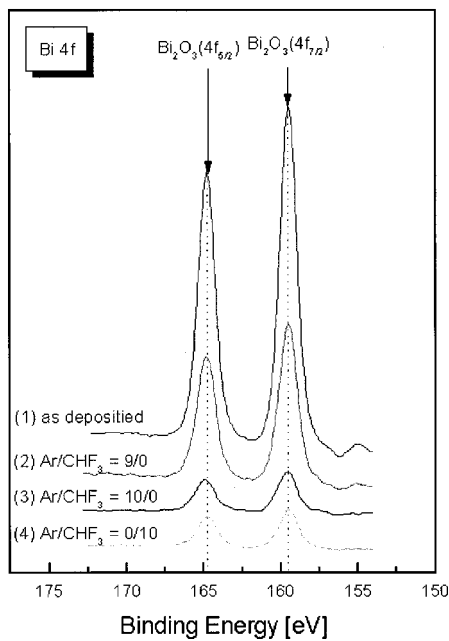
FIG. 5. Bi $4f$ narrow scan spectra of SBT surface etched with CHF$_3$/(Ar+CHF$_3$) gas mixing ratio (coil rf power: 600 W, dc-bias voltage: −150 V, chamber pressure: 5 mTorr).

The surface of etched SBT films was investigated by SIMS analysis for comparison with XPS results. Figure 7 shows secondary ion mass spectra from the SBT surface etched using a CHF$_3$/(Ar+CHF$_3$) gas mixing ratio of 0.1. In Fig. 7, SrF and TaF$_2$ were found; this result is consistent with the XPS analysis.

CHF$_3$ gas reacts with Sr and Ta atoms and makes Sr–F and Ta–F bonds, but it reacts with very little Bi. The addi-
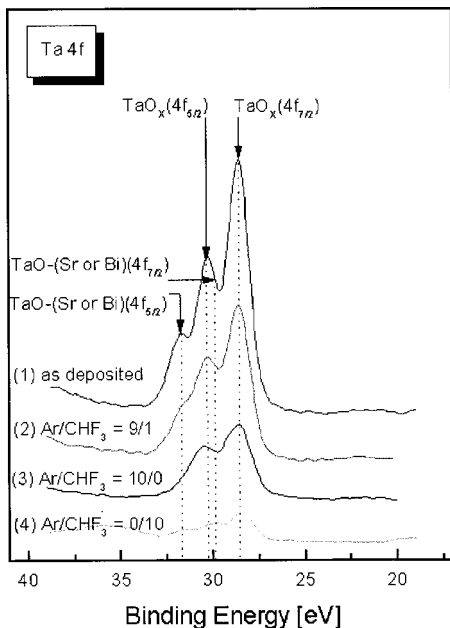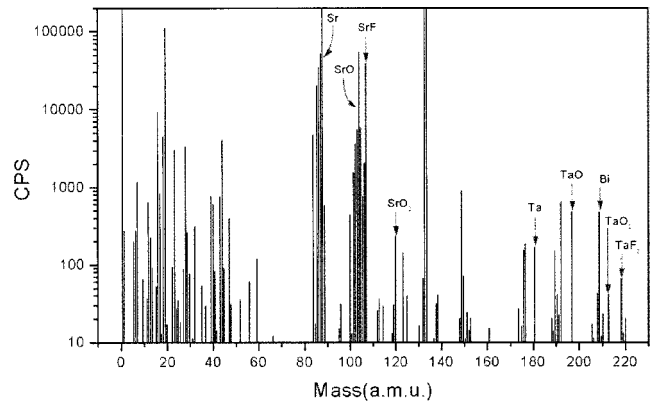

FIG. 7. Mass analysis of SBT surface etched with CHF$_3$/(Ar+CHF$_3$) of 0.1 by secondary ion mass spectrometer (SIMS) (coil rf power: 600 W, dc-bias voltage: −150 V, chamber pressure: 5 mTorr).

tion of 10 % CHF$_3$ enhances the etch rates of SBT thin films, but XPS and SIMS analyses reveal that excessive CHF$_3$ gas causes the formation of a passivation layer.

Figure 8 shows a scanning electron microscopy (SEM) photograph of a SBT film etched using a gas mixing ratio of 0.1. The profile of the etched SBT film is approximately 85°, but etch residue is found at the sidewall.

IV. CONCLUSION

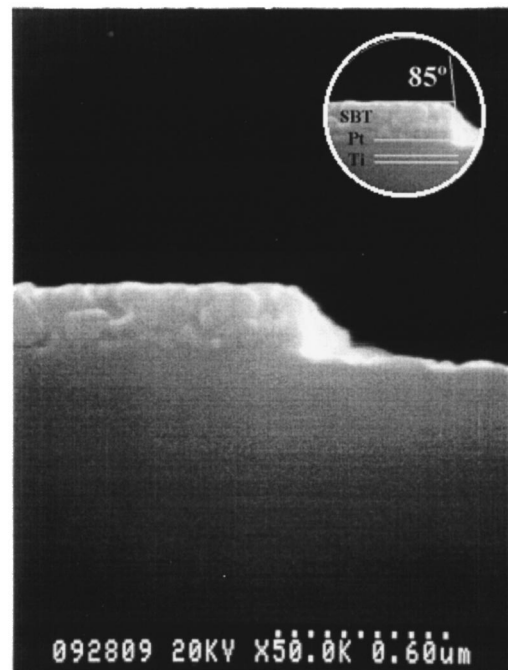Etching of SBT thin films was studied using CHF$_3$/Ar gas chemistry in a MEICP system. The etch rate of SBT in-

FIG. 6. Ta $4f$ narrow scan spectra of SBT surface etched with CHF$_3$/(Ar+CHF$_3$) gas mixing ratio (coil rf power: 600 W, dc-bias voltage: −150 V, chamber pressure: 5 mTorr).

FIG. 8. Cross-sectional SEM photograph of SBT film etched with CHF$_3$/(Ar+CHF$_3$) of 0.1 (coil rf power: 600 W, dc-bias voltage: −150 V, chamber pressure: 5 mTorr).

creased up to a CHF$_3$/(Ar+CHF$_3$) of 0.1 and a maximum etch rate of SBT was 1650 Å/min. Selectivities of SBT to Pt and PR were 1.35 and 0.94, respectively. The sidewall slop of a SBT film etched using a CHF$_3$/(Ar+CHF$_3$) gas mixing ratio of 0.1 was approximately 85°.

The surface composition of the etched SBT films was investigated using XPS analysis. Fluorine reacts with metal atoms such as Sr and Ta and compounds such as Sr–F and Ta–F remain on the surface of etched SBT films. These products can be removed easily by Ar-ion bombardment. With a CHF$_3$/(Ar+CHF$_3$) gas mixing ratio of more than 0.1, these products are not sufficiently sputtered by the Ar ions and form a passivation layer. Chemical reaction between Bi and F was not observed using the Ar/CHF$_3$ gas chemistry. Bi

is removed by physical sputtering and the chemical assistance of F is very low in this element.

The SIMS analysis of a SBT surface etched with CHF$_3$/(Ar+CHF$_3$)=0.1 shows SrF and TaF$_2$ compounds consistent with the XPS analysis.

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