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Etching mechanism of $(Ba,Sr)TiO_3$ films in high density $Cl_2/BCl_3/Ar$ plasma

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$(Ba,Sr)TiO_3$ (BST) thin films have attracted great interest as new dielectric materials of capacitors for ultralarge-scale integrated dynamic random access memories such as 1 or 4 Gbit. In this study, inductively coupled $BCl_3/Cl_2/Ar$ plasmas was used to etch BST. The $Cl_2/(Cl_2+Ar)$ was fixed at 0.2, and the BST thin films were etched by adding BCl_3. The characteristics of the plasmas were estimated using optical emission spectroscopy (OES). The change of Cl, B radical density was measured by OES as a function of BCl_3 percentage in Cl_2/Ar. The cross section of BST thin films and residue remaining after the etch was investigated by scanning electron microscopy. The chemical reactions between BST and Cl_2 and the surface of BST films etched with different $BCl_3/Cl_2/Ar$ gas mixing ratios were investigated using x-ray photoelectron spectroscopy. © *2000 American Vacuum Society.* [S0734-2101(00)14504-X]

I. INTRODUCTION

The semiconductor industry has maintained its growth by achieving a 25%–30%/yr cost reduction throughout its history. To keep the cost as low as possible, it is advantageous to use the highest density dynamic random access memory (DRAM) cell technology available to minimize the size of the embedded DRAM chip. It is anticipated that the shrinking of feature size will continue as predicted; but smaller DRAM (1, 4 Gbit) will remain mainstream at the reduced geometry until some other technology, possibly in connection with an architectural breakthrough, will enable larger standalone DRAM. The shrinking bit cell area with each generation leaves three approaches for maintaining constant capacitance per bit: (1) reducing the thickness of the dielectric, (2) increasing the area by forming three-dimensional capacitor structures, and (3) increasing the dielectric constant through new high-permittivity materials. Ta_2O_5 is often considered as an intermediate solution, with extendibility to the 4 Gbit generation, before the high K dielectric $(Ba,Sr)TiO_3$ (BST) material will be needed to build DRAM capacitors. Some companies intended to migrate from oxide/nitride dielectrics directly to BST at the 1 or 4 Gbit generation.[1]

BST thin film is an attractive material for application in high-density (Gbit) DRAMs because of the high relative dielectric constant and small variation in dielectric properties with frequency.[2–4] An anisotropic etching of BST thin films is very important in ferroelectric devices to support a small feature size and pattern transfer. In this study, BST thin films were etched with inductively coupled plasma (ICP) by $BCl_3/Cl_2/Ar$. The characteristics of the plasmas were estimated using optical emission spectroscopy (OES). For the study of chemical reaction on the etched surface, the surface of BST films etched with different $Cl_2/BCl_3/Ar$ gas mixing ratios were investigated using x-ray photoelectron spectroscopy (XPS). The cross sections of the BST films were observed by scanning electron microscopy (SEM).

II. EXPERIMENTAL DETAILS

The 5 in. Si substrates used for this study were doped with B (0.85–1.15 Ω cm), oriented (100), and chemically etched for 60 s using 1% HF:H_2O prior to chemical vapor deposition (CVD) growth. The substrates were coated with a 6000-Å -thick layer of SiO_2 grown by low-pressure CVD (SiH_4+O_2, 420 °C, 240 mTorr). To enhance the adhesion of Pt on the oxide layer, a 1000-Å -thick Ti film was deposited prior to Pt deposition. Deposition of Pt films was performed using a Varian 3180 dc sputtering system equipped with a 7 in. conical magnetron-sputtering source. The final thickness of the sputtered Pt film was $\sim$2000–3000 Å and was $\sim$95% uniform across the surface of the 5 in. wafers. BST thin films were deposited by an rf Anelva SPF-201B sputter system using a 5 in. $(Ba_{0.5},Sr_{0.5})TiO_3$ ceramics single target. Deposition was performed at 5 mTorr pressure with 80% Ar and 20% O_2 gas composition. The substrate temperature was maintained at 500 °C during BST film deposition, the rf source power was 90 W, the base pressure was 2×10^{-7} Torr, and the distance from the source to the substrate was $\sim$3.2 in. The final thickness of BST films was $\sim$2000–3000 Å. BST thin films have a dielectric constant of about 300 and a leakage current of about 10^{-8} A/cm^2.

Plasma etching of BST films was investigated by using an ICP system. A planar ICP etching unit having a four-turn square copper coil on the top of the chamber separated by a 24-mm-thick quartz window was used in this experiment. A rf power of 13.56 MHz was applied to the coil to induce ICP. Another 13.56 MHz of rf power was applied to the substrate to induce bias voltage to the wafer. Wafers were placed on a bottom electrode. $Cl_2/(Cl_2+Ar)$ was fixed at 0.2, and the
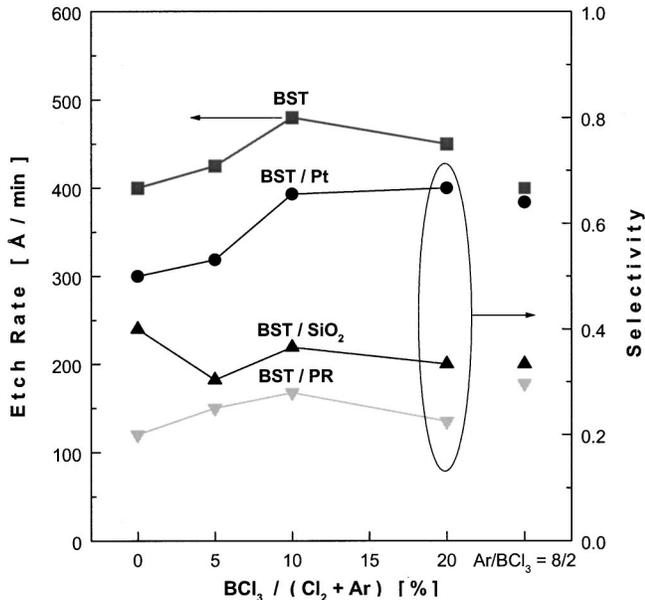
FIG. 1. Etch rate of BST and selectivity of BST to Pt, SiO$_2$, and PR with the addition of BCl$_3$ to Cl$_2$/Ar (coil rf power: 600 W, dc-bias voltage: -250 V, chamber pressure: 10 mTorr).

FIG. 2. Relative optical signal intensity with the addition of BCl$_3$ to Cl$_2$/Ar (coil rf power: 600 W, dc-bias voltage: -250 V, chamber pressure: 10 mTorr).

BST thin films were etched by adding BCl$_3$. The selectivity of BST to the mask material for BST etching and to the bottom electrode (Pt) were investigated. At this time, the Cl$_2$/Ar gas flow was 30 sccm, and rf power/dc-bias was 600 W/-250 V.

The etched samples were exposed to the atmospheric environment for approximately 24 h prior to XPS. Compositional analysis of the BST surface was investigated using ESCALAB 220-IXL. The XPS Al ($K\alpha$) source provides chromatic x rays at 1486.6 eV. Narrow scan spectra of all interested regions were recorded with 20 eV (or 40 eV) pass energy in order to qualify the surface composition and identify the chemical binding state.

III. RESULTS AND DISCUSSION

BST thin films were etched as a function of BCl$_3$/(Cl$_2$+Ar). Figure 1 shows the etch rate of BST thin films and selectivity of BST to Pt, SiO$_2$, and photoresist (PR) at varying concentrations of BCl$_3$ gas. Cl$_2$/(Cl$_2$+Ar) was fixed at 0.2 in this experiment to give an optimal Cl$_2$/Ar gas mixing ratio.[2] The Cl$_2$/Ar flow rate was 30 sccm, rf power/dc bias were 600 W/-250 V, and chamber pressure was 10 mTorr. As 5% (1.5 sccm) and 10% (3 sccm) BCl$_3$ were added to the Cl$_2$/Ar, the etch rate of BST thin films increased; but when 20% (6 sccm) BCl$_3$ was added to the Cl$_2$/Ar, the etch rate of BST thin films decreased. The highest BST etch rate was 480 Å /min at 10% (3 sccm) BCl$_3$ added to Cl$_2$/Ar (30 sccm). It is confirmed from previous research that not only ion bombardment effects, but also chemical reaction between BST and Cl radicals, assists in etching BST thin films.[2] As the additive gas (BCl$_3$) increases, the etch rate of Pt decreases, and then the selectivity of BST to Pt increases. The etch rates of SiO$_2$ and PR were
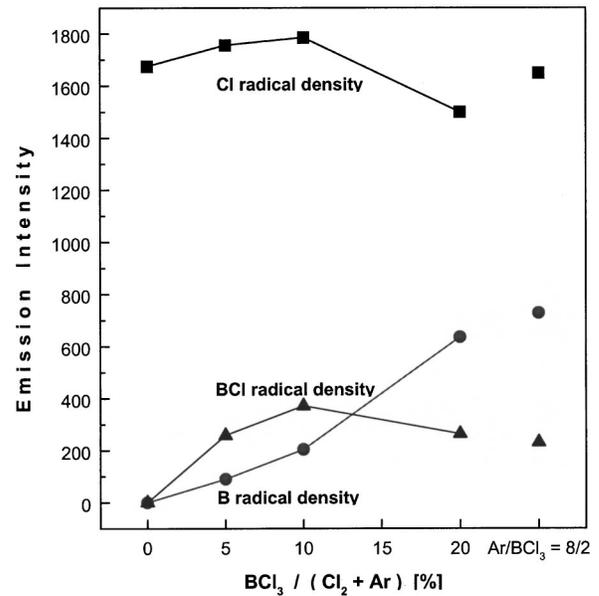
not greatly changed, because the Cl radical does not effect the etching of SiO$_2$ and PR, and the concentration of Ar was high in this experiment.

To understand the effects of the gas combination on the BST, Pt, SiO$_2$, and PR etch rate, OES was used, and the results are shown in Fig. 2. Using OES, estimates of Cl radical peak intensity, BCl radical peak intensity, and B radical peak intensity were obtained. As shown in Fig. 2, the addition of 5% (1.5 sccm) and 10% (3 sccm) BCl$_3$ to Cl$_2$/Ar (6/24 sccm) increased the Cl radical density. The Ar ion assisted the dissociation into Cl radicals. The addition of more than $\sim$10% BCl$_3$ to Cl$_2$/Ar decreased the Cl radical density. The addition of BCl$_3$ to Cl$_2$/Ar increased the B radical density. The BCl$_3$ molecule can be dissociated into B radical, B$^+$ ion, Cl radical and Cl$^+$ ion. However, the BCl$_3$ molecule can be dissociated into B radical or B$^+$ ion easier than Cl radical or Cl$^+$ ion. Therefore, the addition of $\sim$10% BCl$_3$ to Cl$_2$/Ar (BCl$_3$:3 sccm, Cl$_2$:6 sccm, Ar:24 sccm) decreases the Cl radical because the Ar ion assisted insufficiently in dissociating into Cl radicals and there is recombination between Cl species and B species. The etch rate of

TABLE I. Atomic percentage of BST surface etched with BCl$_3$/(Cl$_2$+Ar) gas mixing ratio (coil rf power: 600 W, dc-bias voltage: 250 V, chamber pressure: 10 mTorr).

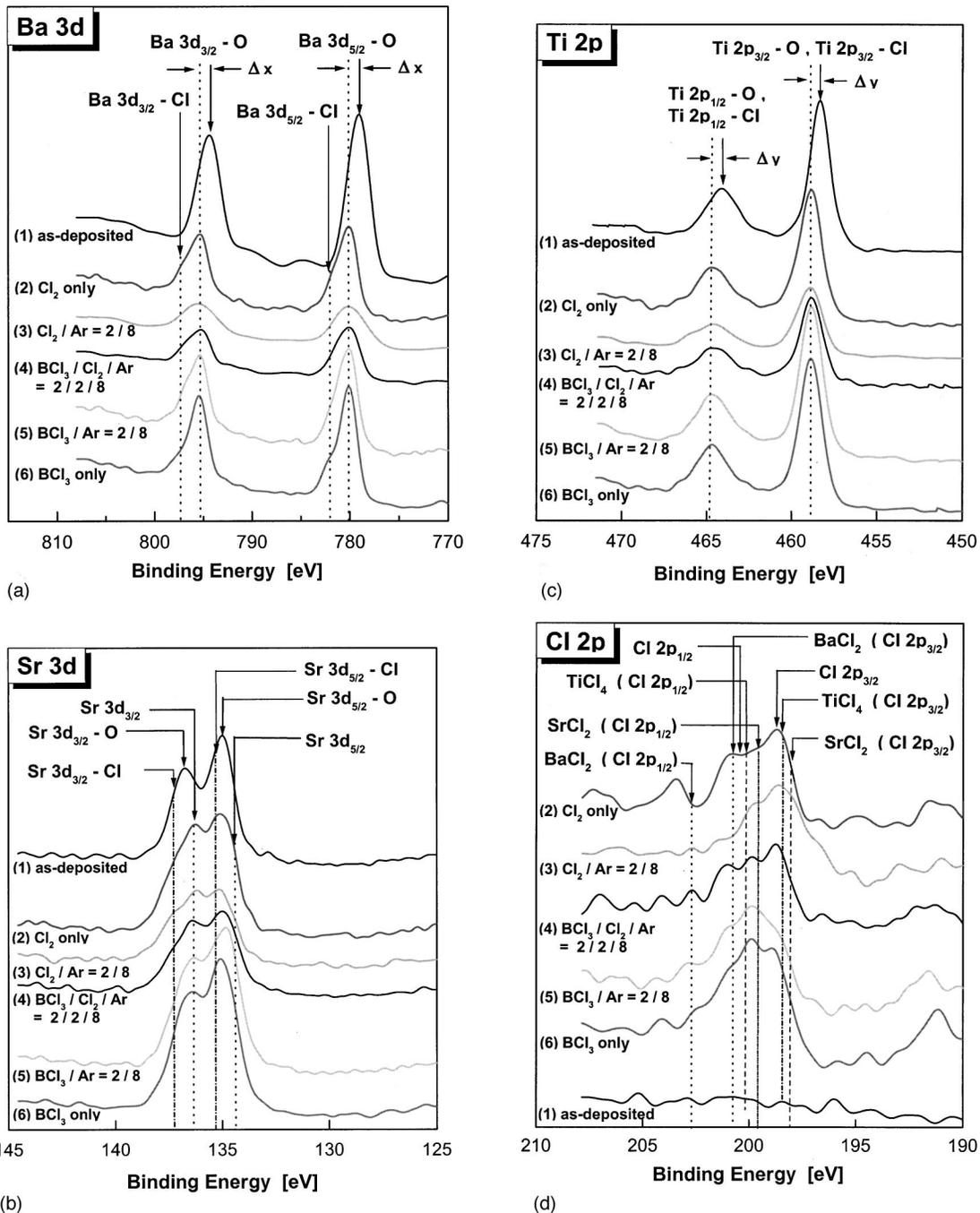| Etch gas	Ba	Sr	Ti	O	Cl	B
As-deposited	7.8	10.2	16.8	65.2	0	0
Cl$_2$ only	7.3	10.5	9.5	68.5	4.2	0
Cl$_2$/Ar=2/8	4.0	7.6	9.0	76.2	3.2	0
BCl$_3$/Cl$_2$/Ar=2/2/8	3.7	7.7	9.6	68.4	3.1	7.5
BCl$_3$/Ar=2/8	4.6	9.5	12.5	66.1	2.6	4.7
BCl$_3$ only	4.8	9.7	11.9	66.8	3.9	2.9

FIG. 3. (a) Ba 3d, (b) Sr 3d, (c) Ti 2p, (d) Cl 2p XPS narrow scan spectra of BST surface etched under $BCl_3/(Cl_2+Ar)$ gas mixing ratio (coil rf power: 600 W, dc-bias voltage: −250 V, chamber pressure: 10 mTorr).

BST thin films increases as the Cl radical density increases due to the chemical reaction between Ba, Sr, Ti, O, and Cl. After adding 20% BCl_3 to Cl_2/Ar, the etch rate of BST thin films decreases somewhat because the Cl radical density decreases; but total ion current density may not decrease. The ion current density of BCl_3 plasma is higher than that of Cl_2 plasma, and the Cl radical density of Cl_2 plasma is higher than that of BCl_3 plasma.

Because the BST films consist of three components (BaO, SrO, TiO_2) in the BST solid solution, it is meaningful to compare relative compositions of the etch component in BST

film surfaces with the addition of the BCl_3 to Cl_2/Ar. To investigate the roles of Cl, BCl, and B radicals, the relative atomic percentage of the etched BST surface was estimated.

Table I shows the relative atomic percentage of the etched BST surface with the addition of BCl_3 to Cl_2/Ar. The relative atomic percentage of Ba, Sr on the BST etched with BCl_3 is lower than that of Ba, Sr on the BST etched with Cl_2. The ion current density of BCl_3 plasma is higher than that of Cl_2 plasma. With the small (10%) addition of BCl_3 to Cl_2/Ar, ion (B^+ ion and BCl^+ ion) current density increases,

which increases the sputtering effect. The relative atomic percentage of Ti on the BST etched with Cl_2 is lower than that of Ti on the BST etched with BCl_3 because the Cl radical density of Cl_2 plasma is higher than that of BCl_3 plasma. This result can be confirmed by previous research.[2] We know that there is a chemical reaction between Ba and Cl, and ion enhancement etching is necessary to break the Ba–O bond and to remove $BaCl_2$. Sr is removed by physical sputtering, and the effect of chemical etching by Cl is very low. There is a chemical reaction between Ti and Cl, and $TiCl_4$ is removed with ease.

A chemical reaction between Ba, Sr, Ti, O and Cl, B was investigated by XPS narrow scan spectra. The variation of Ba, Sr, Ti, O, Cl peaks of etched BST surfaces is shown in Fig. 3 for various gas (BCl_3/Cl_2/Ar) mixing ratios. Figure 3(a) shows that the Ba $3d$ spectra can be resolved as BaO and $BaCl_2$. The Ba $3d_{5/2}$ peaks at 779 and 782 eV binding energies correspond to BaO and $BaCl_2$. The Ba $3d_{3/2}$ peaks at 794.3 and 797.3 eV binding energies correspond to BaO and $BaCl_2$. Spectra (2) and (6) in Fig. 3(a) show that the intensities of BaO and $BaCl_2$ peak higher than the intensities of others. This can be explained because there is little physical bombardment of Ar ion. Figure 3(b) shows that the Sr $3d$ spectra can be resolved into Sr and SrO. The peaks at 134.5 and 136.3 eV binding energies correspond to Sr $3d_{5/2}$ and Sr $3d_{3/2}$ of element Sr, and the peaks of Sr $3d_{5/2}$–O and Sr $3d_{3/2}$–O were observed at 135 and 136.8 eV binding energy. As shown in Fig. 3(b), the intensity of Sr $3d_{3/2}$ peak in spectra (2)–(6) is higher than in spectra (1). This can be explained as follows: Ba–Ti–O and Sr–Ti–O bonds were broken on the BST surface during the etch, and Ba and Ti atoms could be removed with ease, but Sr atoms were hard to remove. The increasing peak intensity at 134.5 eV was not caused by the increasing peak intensity of Sr $3d_{5/2}$–O, but by adding the Sr $3d_{5/2}$–Cl peak and the increased Sr $3d_{5/2}$ peak. The width of the peak broadens around 137.2 eV because there are Sr $3d_{3/2}$–Cl peaks. Therefore, there are chemical reactions between Sr and Cl. Figure 3(c) shows Ti $2p$ spectra. The TiO_2 peak shifts to high binding energy by as much as Δy ($=0.6\ eV$). Nevertheless, $TiCl_4$ ($TiCl_x$) was not found because both TiO_2 and $TiCl_4$ come into view at 458.5–458.7 eV.[5] Therefore, only one peak is viewed. Figure 3(d) shows Cl $2p$ spectra. It appears that spectra (2)–(5) in Fig. 3(d), respectively, can be resolved into four chemical components as Cl–Cl, $TiCl_4$, $BaCl_2$, and $SrCl_2$. The peaks at 198.7 and 200.4 eV binding energies correspond to Cl $2p_{3/2}$ and Cl $2p_{1/2}$. The peaks at 200.7, 198.4, and 198 eV binding energies correspond to $BaCl_2$, $TiCl_4$, and $SrCl_2$ (Cl $2p_{3/2}$). In the case of Cl $2p_{1/2}$, the peaks were the same as Cl $2p_{3/2}$. Chemical reactions between BST and B radicals are hard to find, but a small addition of BCl_3 gas increased Cl radical density and ion current density, and then the etch rate of BST thin films increased.

Figure 4 shows the cross-sectional scanning emission microscopy of the etched BST with addition of 5% BCl_3 into Cl_2/Ar. For the application of Gbit DRAM, the etch slope
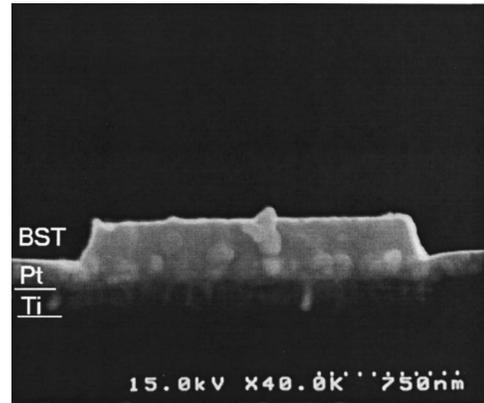

FIG. 4. Cross-sectional SEM micrograph of BST film etched by BCl_3/Cl_2/Ar=1/2/8 (coil rf power: 600 W, dc-bias voltage: −250 V, chamber pressure: 10 mTorr).

must be more than 80°. In future research, we need to improve the etch profile.

IV. CONCLUSION

BST thin films were etched with inductively coupled BCl_3/(Cl_2+Ar) plasma. The maximum etch rate of BST thin films was 480 Å /min under BCl_3/Cl_2/Ar=1/2/8 (3/6/24 sccm), 600 W/ 250 V, and 10 mTorr. The etch slope is about 65°–70°. To use BST thin films as a cell capacitor for Gbit DRAM, it is necessary to study the etching process for vertical etching slopes greater than 80° that are residue free.

After the small (5%, 10%) addition of BCl_3 to Cl_2/Ar, ion (B^+ and BCl^+ ions) current density increases, which increases the sputtering effect. With the addition of BCl_3 to Cl_2/Ar, the density of Cl radical increases, and the etch rate of BST thin films increases.

To study the etching mechanism of BST thin films using inductively coupled BCl_3/Cl_2/Ar plasma, surface reaction of the etched BST films was investigated by XPS analysis. There is a chemical reaction between Ba and Cl, and ion enhancement etching is necessary to break the Ba–O bond and to remove $BaCl_x$. There is a chemical reaction between Sr and Cl, but Sr–Cl remained on the BST thin films during the etch. It is necessary to study how Sr can be removed effectively. There is a chemical reaction between Ti and Cl, and $TiCl_x$ is removed with ease.

ACKNOWLEDGMENT

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