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# Study on surface reaction of (Ba, Sr)TiO<sub>3</sub> thin films by high density plasma etching

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Ferroelectric devices are extremely useful for dynamic random access memories applications because of their high dielectric constant. Using ferroelectric device structure, manufacturing cell capacitance of highly integrated memory device is possible. The small feature size requires anisotropic etching. Since the research of (Ba, Sr)TiO<sub>3</sub> thin film etching is seriously lacking, we studied the surface reaction of (Ba, Sr)TiO<sub>3</sub> thin films by using high density plasma etching. In this study, (Ba, Sr)TiO<sub>3</sub> thin films were etched with Cl<sub>2</sub>/Ar gas combination in an inductively coupled plasma. This was done by varying the etching parameters such as radio frequency power, direct current bias, and chamber pressure. The maximum etch rate of the BST films was 560 Å/min under Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.2, 600 W/250 V, and 5 mTorr. The selectivity of BST to Pt and SiO<sub>2</sub> was 0.52, 0.43, respectively. The surface reaction of the etched (Ba, Sr)TiO<sub>3</sub> thin films was investigated with x-ray photoelectron spectroscopy (XPS) using narrow scan spectra. Ba is removed by chemical reaction such as BaCl<sub>2</sub> and physical sputtering. Ar ion bombardment is more effective than chemical reaction between Sr and Cl to remove Sr. Ti is removed by chemical reaction such as TiCl<sub>4</sub> with ease. The results of secondary ion mass spectrometer analysis were compared with the results of XPS analysis and the results were the same. © 1999 American Vacuum Society. [S0734-2101(99)19804-X]

## I. INTRODUCTION

The memory capacity of the dynamic random access memories (DRAMs), a major application of very large scale integrated circuit and the technology driving semiconductor devices, has quadrupled every three years.<sup>1</sup> To increase device integration, we must solve not only the engineering problem, such as fine patterning, microtransistor operation, and wiring life, but also the problem of capacitance. The storage unit of a DRAM (cell) consists of a storage capacitor and a switching transistor; a minimum amount of electric charge is needed to maintain device operation while the cell area is being reduced by miniaturization. To ensure sufficient accumulated electric charge within a smaller capacitor area, capacitor dielectric film thickness has been reduced, and the dielectric constant has to be increased. Three-dimensional electrodes can be used to increase surface area. However, this adds a complication. The electrode structure causes a significant difference in height between the cell array and the peripheral, making it difficult for lithographic patterning and increasing production costs. In addition, the reduction of dielectric film thickness reaches the physical limit, and leakage current increases as the thickness of dielectric film decreases.

Thin films with high dielectric constant (high *K*) have attracted great attention for their practical use as capacitors for Gbit DRAMs. Among the proposed ferroelectric materials with high dielectric constant, (Ba, Sr)TiO<sub>3</sub> (BST) has fea-

tures which stand out. BST has a high dielectric constant at the high frequency regime for writing to DRAMs.<sup>2,3</sup> BST in thin film form is in a paraelectric phase without spontaneous polarization at device operating temperature. Therefore, there is no possibility that reversals of spontaneous polarization will cause fatigue,<sup>2,4</sup> which is a problem of ferroelectric memories. BST films can be deposited by plasma vapor deposition or chemical vapor deposition (CVD).

BST is considered the leading candidate as the capacitor dielectric for Gbit DRAMs. An anisotropic etching of BST thin films is very important in ferroelectric devices to support a small feature size and pattern transfer. But, there was virtually no solid research of BST etching.

In this study, BST thin films were etched with inductively coupled plasma (ICP) by varying the etching parameters such as Cl<sub>2</sub>/Ar gas mixing ratio, radio frequency (rf) power, direct current (dc) bias voltage, and chamber pressure. For the study of chemical reaction on the etched surface, films etched with different Cl<sub>2</sub>/Ar gas mixing ratio were investigated using x-ray photoelectron spectroscopy (XPS) and a secondary ion mass spectrometer (SIMS).

## 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<sub>2</sub>O. The substrates were then coated with a 6000-Å-thick layer of SiO<sub>2</sub> grown by low-pressure CVD (SiH<sub>4</sub>+O<sub>2</sub>, 420 °C, 240 mTorr). To enhance the adhesion of Pt on the oxide layer, a 750-Å-thick Ti film was

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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 Pt sputtering target was specified at 99.999% purity. Sputtering was performed in research-grade Ar at a pressure of 8 mTorr, and the distance from the source to the substrate was  $\sim 3.3$  in. Typical sputtering power was 9.6 kW. These conditions resulted in a nominal deposition rate of  $\sim 10\,000$  Å/min. During deposition, the substrate was grounded and the substrate temperature was held at 200 °C using the gas conduction heating. The final thickness of the sputtered Pt film was  $\sim 2000$ – $3000$  Å, and has a wafer nonuniformity of 5%. Film thickness was measured using a Tencor Model  $\alpha$ -step 200 surface profiler. BST thin films were deposited by rf Anelva SPF-201B sputter system using a 5 in. (Ba, Sr)TiO<sub>3</sub> ceramics single target. Deposition was performed at 5 mTorr pressure with 80% Ar and 20% O<sub>2</sub> gas composition. The substrate temperature was maintained at 450 °C during BST films deposition, rf source power was 80 W, base pressure was  $2 \times 10^{-7}$  Torr, and the distance from the source to the substrate was  $\sim 3.2$  in. The final thickness of BST films was  $\sim 2800$ – $3000$  Å. BST thin films have the dielectric constant of about 100, and leakage current of about  $10^{-8}$  A/cm<sup>2</sup>.

Plasma etching of BST films was investigated by using the ICP system. Planar ICP etching equipment was used in this experiment. It has a four-turn square copper coil on the top of the chamber separated by a 24-mm-thick quartz window. 13.56 MHz of rf power was applied to the coil to induce inductively coupled plasma. Another 13.56 MHz of rf power signal was applied to the bottom electrode to control the bias voltage to the wafer. The wafer was placed on a bottom electrode. The composition of etching gas (Cl<sub>2</sub>/Ar) was varied to find the characteristics of BST etching. The selectivity of BST compared to the mask material for BST etching was investigated with varying Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) mixing ratio. For these experiments, the total gas flow was 30 sccm, and top rf power/bottom dc bias was 600 W/250 V. In addition, plasma etching of BST films was studied by varying the etching parameter including coil rf power (400–700 W), dc bias voltage to substrate (150–300 V), and gas pressure (5–20 mTorr) with the fixed Cl<sub>2</sub>/Ar gas mixing ratio.

The etched samples were exposed to the atmospheric environment for approximately 24 h prior to XPS and SIMS analysis. Compositional analysis of the BST surface was investigated using ESCALAB 220-IXL and CAMECA IMS6F. 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. SIMS measured the molecular weight of particles released from the surface of a material by bombardment of ions. The Cs<sup>+</sup> ion beam of 1.11 kV and 10.68–10.92 nA was used by SIMS source.

### III. RESULTS AND DISCUSSION

For the characterization of BST thin films in an ICP system, the plasma etching of BST, Pt, and SiO<sub>2</sub> thin films was

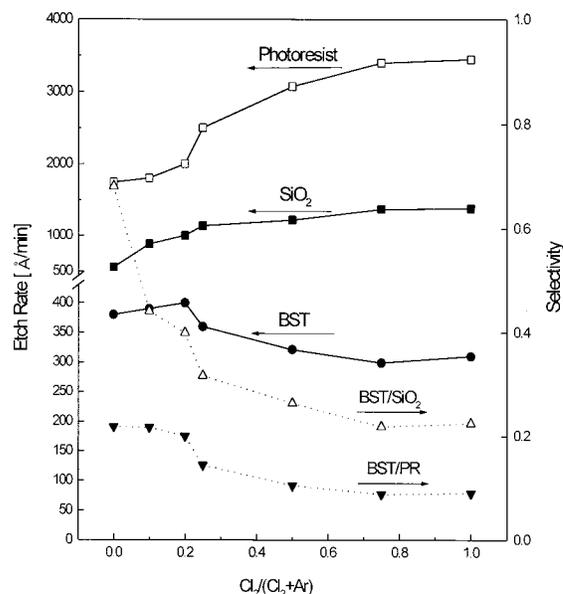


Fig. 1. Effect of the concentration of an etch gas on the etch rate of BST, SiO<sub>2</sub>, and photoresist. (Total flow rate: 30 sccm, coil rf power: 600 W dc bias voltage: 250 V, chamber pressure: 10 mTorr.)

systematically investigated as a function of coil rf power, dc bias voltage, and the chamber pressure. Figure 1 represents the etch rate of BST, SiO<sub>2</sub> and photoresist (PR) and the selectivity of BST to SiO<sub>2</sub> and BST to PR as a function of Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) mixing ratio. The total flow rate was 30 sccm, rf power/dc bias were 600 W/250 V, and chamber pressure was 10 mTorr. As the gas mixing ratio increases, the etch rate of BST decreases while the etch rate of SiO<sub>2</sub>, and PR increases. These results confirm that sputtering by Ar ions is more effective for BST film than SiO<sub>2</sub> or PR. The highest BST etch rate is 400 Å/min at Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.2. It is confirmed that the increased etch rate at Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.2 is the result of the enhanced chemical reaction between BST and Cl radicals and an ion bombardment effect. However for SiO<sub>2</sub> or PR, chemical etching is more effective than physical sputtering. Hence, as the amount of reactive gas (Cl<sub>2</sub>) increases, selectivity of BST to SiO<sub>2</sub> or PR decreases. Selectivity of BST to SiO<sub>2</sub> is 0.4 at Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.2, but selectivity of BST to PR is only 0.2 at Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.2. SiO<sub>2</sub> is better than PR as the mask material for BST etching. Considering the etch rate of BST, all subsequent experiments for the etching of BST films were carried out with the etch gas of 20% Cl<sub>2</sub> in Cl<sub>2</sub>/Ar.

Figure 2 shows the effect of coil rf power on the etch rate of BST, Pt, and SiO<sub>2</sub> under 20% Cl<sub>2</sub> in Cl<sub>2</sub>(Cl<sub>2</sub>+Ar). As the coil rf power increases from 400 to 700 W, the etch rate of Pt and SiO<sub>2</sub> films increases from 420 to 1070 Å/min and from 560 to 1070 Å/min, respectively. And the etch rate of BST films increases from 230 to 450 Å/min. Meanwhile the selectivity of BST to Pt seems to be constant at  $\sim 0.45$ , and the selectivity of BST to SiO<sub>2</sub> seems to be constant at  $\sim 0.4$ . With increasing coil rf power, the plasma density increases so that the increased reactive free radicals and ions enhance the etch rates of BST, Pt, and SiO<sub>2</sub>.

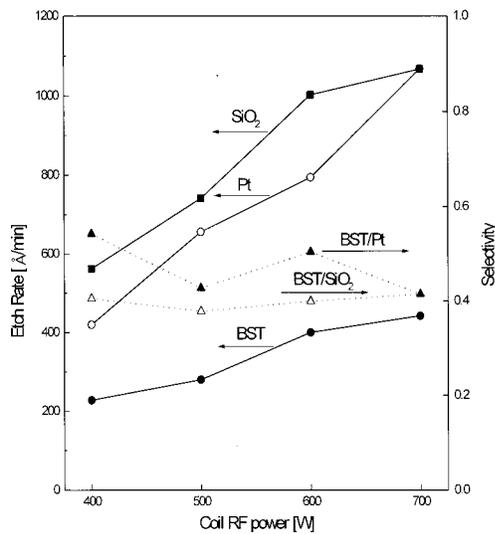


FIG. 2. Etch rate of BST, Pt, SiO<sub>2</sub> as a function of coil rf power. (Total flow rate: 30 sccm, Ar/Cl<sub>2</sub>=80/20[%] dc bias voltage: 250 V, chamber pressure: 10 mTorr.)

The etch rate of BST, Pt, and SiO<sub>2</sub>, and the selectivity of BST to Pt and SiO<sub>2</sub>, are shown in Fig. 3 as a function of dc bias voltage. As the dc bias voltage increases from 150 to 300 V, the etch rate of BST, Pt, and SiO<sub>2</sub>, increases from 240, 470, and 700 to 530, 1000, and 1010 Å/min, respectively. Meanwhile the selectivity of BST to SiO<sub>2</sub>, increased from 0.34 to 0.53. The selectivity of BST to Pt was constant at about 0.52. As the dc bias voltage was increased, the ion bombarding energy increased. This resulted in an increase of the selectivity of BST to SiO<sub>2</sub>, this is because the ion bombardment is more effective to etch BST films. On the other hand the selectivity of BST to Pt seems to be constant, since the ion bombardment effect is similar to BST and Pt etching.

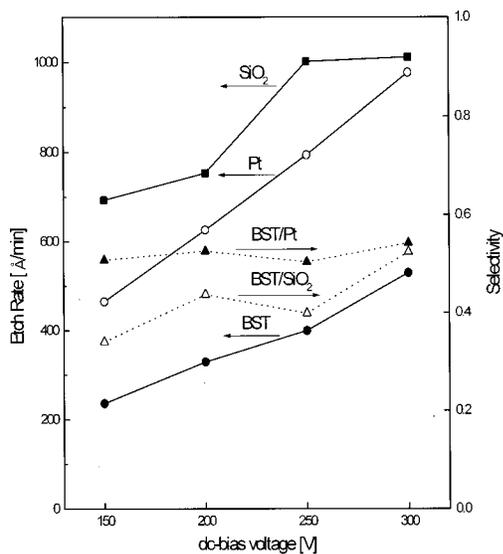


FIG. 3. Etch rate of BST, Pt, SiO<sub>2</sub> as a function of dc bias voltage. (Total flow rate: 30 sccm, Ar/Cl<sub>2</sub>=80/20[%] coil rf power: 600 W, chamber pressure: 10 mTorr.)

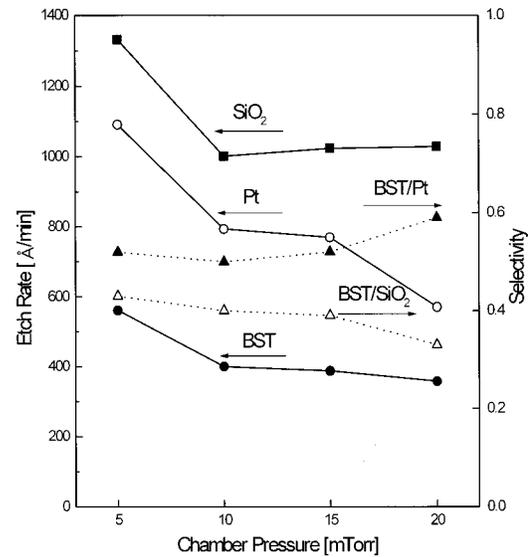


FIG. 4. Etch rate of BST, Pt, SiO<sub>2</sub> as a function of chamber pressure. (Total flow rate: 30 sccm, Ar/Cl<sub>2</sub>=80/20[%] coil rf power: 600 W, dc bias voltage: 250 V.)

The effect of chamber pressure on etch rate is shown in Fig. 4. As the chamber pressure decreases from 20 to 5 mTorr, the etch rate of BST and Pt rapidly increases from 360 and 570 to 560 and 1100 Å/min, respectively. While as the chamber pressure increases, the etch rate of SiO<sub>2</sub> decreases from 1300 to 1010 Å/min and then becomes constant. As the chamber pressure increases, the selectivity of BST to Pt seems to be constant at ~0.55, but the selectivity of BST to SiO<sub>2</sub> decreases from 0.43 to 0.33. Since the mean-free paths of species are inversely proportional to pressure, the rise in potential translates into a higher energy ion flux to the substrate surfaces. That is, low pressures favor higher ion bombardment energies. The BST etching process, however, becomes ineffective (slow etching) in spite of the increase of plasma density (radical density) as the gas pressure increases. This trend also supports the evidence that ion bom-

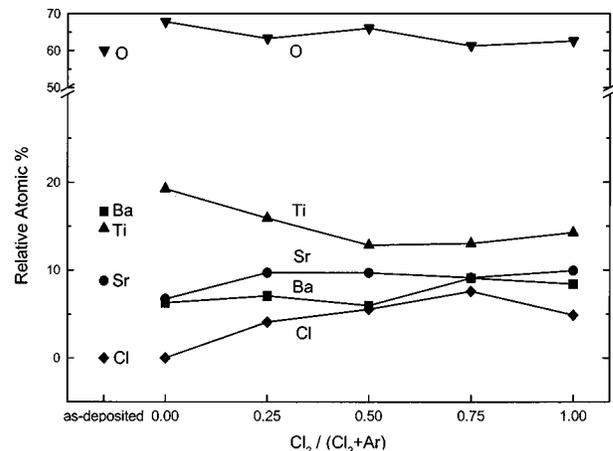


FIG. 5. Atomic percentage of BST surface etched with Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) gas mixing ratio.

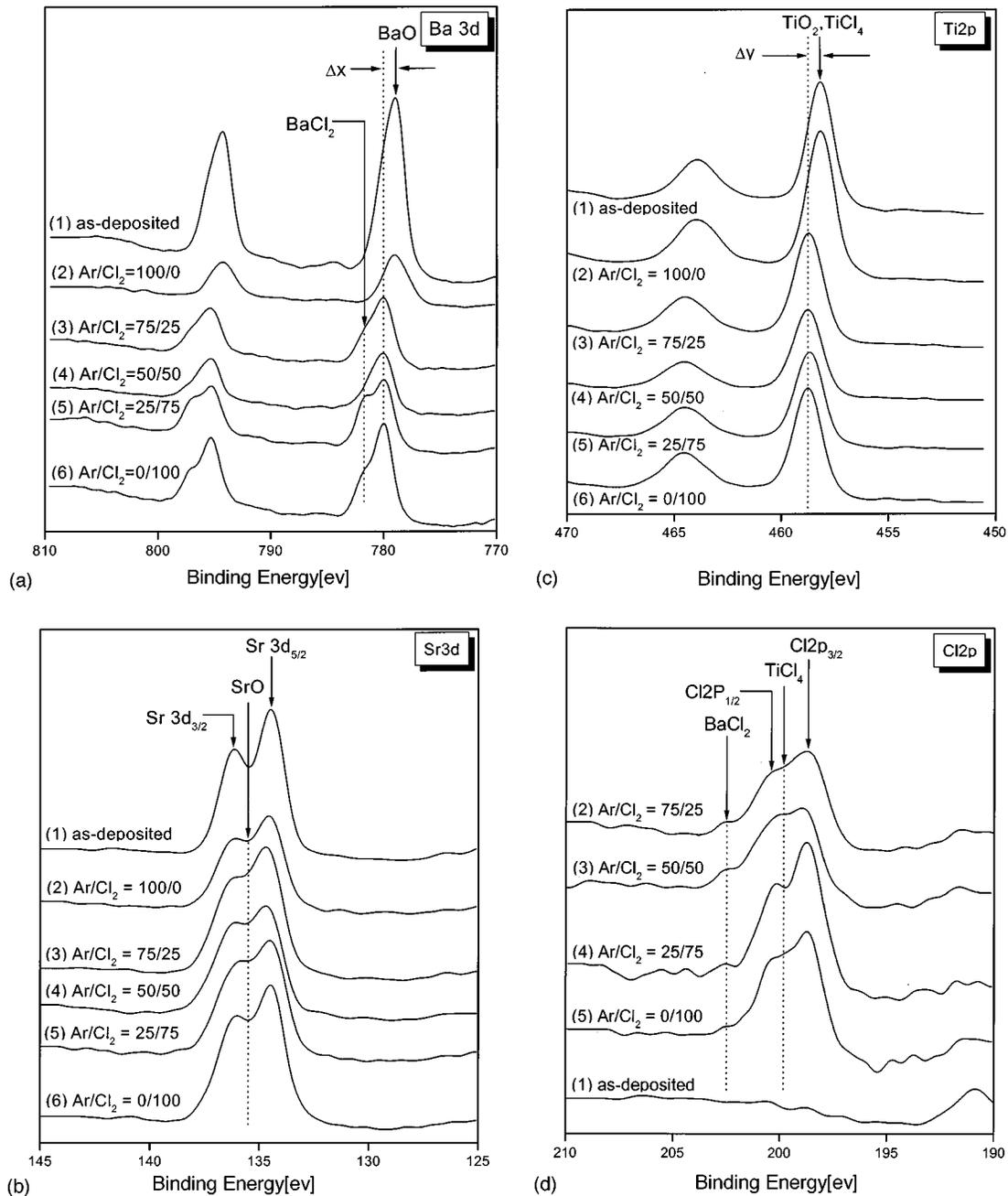


FIG. 6. (a) Ba 3d, (b) Sr 3d, (c) Ti 2p, (d) Cl 2p XPS narrow scan spectra of BST surface etched under Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) gas mixing ratio.

bardment is more effective than chemical plasma etching for BST etching process.

Since the BST film consists of three components (BaO, SrO, TiO<sub>2</sub>) in the BST solid solution, it is meaningful to compare the relative compositions of the etch component in BST films surface as a function of gas [Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar)] mixing ratio. For that reason, the relative atomic percentages of the etched BST surface were investigated. As can be seen in Fig. 1, sputtering by Ar ions is more effective to BST etching. We expect that there is a chemical reaction between BST and Cl radicals. So we examined the chemical reaction between BST and Cl radicals, and the analysis of XPS narrow scan was also performed.

Figure 5 represents the atomic percentages of the etched BST surface with Cl<sub>2</sub>/Ar gas mixing ratio. In Fig. 5, notice the relative atomic percentage of the Ba of BST films etched with Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.5 is the least. The relative atomic percentage of the Ba of BST films etched with high Ar content is less than that of etched BST films under high Cl<sub>2</sub> content. This means that BaO in BST is attacked by Ar ions and Ba–O (or Ba–Ti–O) bond is broken, it then formed into BaCl<sub>x</sub>. But the vapor pressure of BaCl<sub>x</sub> is low, so ion enhanced etching is necessary to remove BaCl<sub>x</sub>. The relative atomic percentage, of the Sr of etched BST with only Ar, is the least. This means that for removing Sr, sputtering by Ar ions is more effective than chemical etching by Cl radicals. It

seems to be difficult to form SrCl<sub>x</sub>, and the vapor pressure of SrCl<sub>x</sub> is low. As the gas Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) mixing ratio increases, the relative atomic percentage of Ti of etched BST sample decreases, since TiCl<sub>4</sub> (or TiCl<sub>x</sub>) can be formed and TiCl<sub>4</sub> is removed with ease. The relative atomic percentage of O in BST film includes the quantities of oxygen contamination, which is caused by air exposure of samples prior to XPS analysis. The resulting percentage appeared higher than actual. To etch the BST films, the bonds of Ba–O, Sr–O, Ti–O (or Ba–Ti–O, Sr–Ti–O) are broken and chemical reaction between Ba, Sr, Ti, and Cl is necessary.

To study how Ba, Sr, Ti combine with Cl radical, the XPS narrow scan was performed. The variation of Ba, Sr, Ti, Cl peaks of etched BST surfaces is shown in Fig. 6 for various gas mixing ratios. Figure 6(a) shows that the Ba3*d* spectra can be resolved into BaO and BaCl<sub>2</sub>. The peaks at 779 and 781.7 eV binding energies correspond to BaO and BaCl<sub>2</sub>. Figure 6(a) shows spectra (3)–(6) shift to the high binding energy by as much as Δ*x* (= 1 eV) because of the chemical reaction. Spectra (5) and (6) in Fig. 6(a) show that the intensities of BaO, BaCl<sub>2</sub> peak higher than others [except (1)]. This can be explained because the BaCl<sub>2</sub> is removed a little by physical bombardment as the concentration of Ar gas decreases. It is evident from Fig. 6(a) that there is a chemical reaction between Ba and Cl. Figure 6(b) shows that the Sr3*d* spectra can be resolved into Sr and SrO. The peaks at 134.45 and 136.15 eV binding energies correspond to Sr<sub>5/2</sub> and Sr<sub>3/2</sub> of element Sr and the peak of SrO was observed at 135.5 eV binding energy. Chemical reaction between Sr and Cl is hard to find because of the lack of chemical shift. The width of peak broadens a little around 133 and 137.7 eV, but it is still hard to distinguish. Therefore, although there is a peak of SrCl bonds on the surface of etched BST films, the peaks of Sr–Cl bonds are hardly found. There is a little chemical reaction between Sr and Cl during the BST films etching. In Fig. 6(b) spectra (2)–(5), the intensities of SrO peaks increase; this is because Sr atoms are removed by the Ar ion bombardment. The Ti2*p* spectra are shown in Fig. 6(c). The TiO<sub>2</sub> peak shifts to high binding energy by as much as Δ*y* (= 0.6 eV). Nevertheless TiCl<sub>4</sub> (TiCl<sub>x</sub>) was not found, because both TiO<sub>2</sub> and TiCl<sub>4</sub> come into view at 458.5–458.7 eV.<sup>5</sup> Therefore, only one peak is viewed. The intensities of the TiO<sub>2</sub> (or TiCl<sub>4</sub>) peaks decrease as the amount of Cl<sub>2</sub> increases. However the intensity of TiO<sub>2</sub> in Fig. 6(c), spectrum (6) is higher than that of TiO<sub>2</sub> in Fig. 6(c), spectrum (5) because there is no ion enhancement effect by Ar. This confirms that chemically reactive etching is greatly effective for Ti removing on the BST films. The Cl2*p* narrow scan spectra are shown in Fig. 6(d). The Cl2*p* without chemical reaction in the narrow scan spectrum can be resolved into two sharp peaks which are Cl2*p*<sub>3/2</sub> and Cl2*p*<sub>1/2</sub>. However, there are new peaks on the etched BST samples. It appears that spectra (2)–(5), respectively, can be resolved into three chemical components as Cl–Cl, TiCl<sub>4</sub>, and BaCl<sub>2</sub>. The peaks at 198.7 and 200.4 eV binding energies correspond to Cl2*p*<sub>3/2</sub> and Cl2*p*<sub>1/2</sub>. The peaks at 202.5 and 199.85 eV binding energies correspond to BaCl<sub>2</sub> and TiCl<sub>4</sub>. As a com-

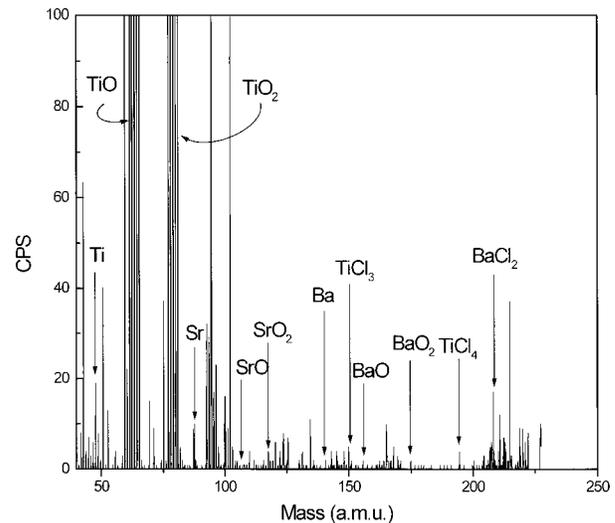


Fig. 7. Mass analysis of BST surface etched with Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.5 by SIMS.

parison with XPS analysis, the surface of etched BST films with Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.5 was analyzed by SIMS. As shown in Fig. 7, the existence of BaCl<sub>2</sub>, TiCl<sub>4</sub> (TiCl<sub>x</sub>) was proven.<sup>6</sup> Even though SrCl<sub>x</sub> exists, it is not found because, only a very small amount of SrCl<sub>x</sub> exists on the surface of etched BST.

#### IV. CONCLUSION

Reactive ion etching of BST thin films was studied by using Cl<sub>2</sub>/Ar in ICP. The etch rate of BST thin films is the highest at Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.2, high rf power, high dc bias voltage, and low pressure. The maximum etch rate of BST films was 560 Å/min under Cl<sub>2</sub>/(Cl<sub>2</sub>+Ar) of 0.2, 600 W/250 V, and 5 mTorr. The selectivity of BST to Pt and SiO<sub>2</sub> was 0.52 and 0.43, respectively.

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<sub>2</sub>. Sr is removed by physical sputtering, and the effect of chemical etching by Cl is very low. To remove Sr more effectively, another reactive gas such as fluorine may be used. There is a chemical reaction between Ti and Cl<sub>2</sub> and TiCl<sub>4</sub> is removed with ease. SIMS analysis confirmed the existence of BaCl<sub>2</sub> and TiCl<sub>4</sub>.

Since the BST film consists of three components (BaO, SrO, TiO<sub>2</sub>) of the BST solid solution, all components must be etched to obtain a high etch rate. Therefore, a mixture of Cl and F broad chemistry is needed to achieve a high etch rate.

#### ACKNOWLEDGMENT

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