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Effects of BCl_3 addition on Ar/Cl_2 gas in inductively coupled plasmas for lead zirconate titanate etching

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The lead zirconate titanate ($PbZr_xTi_{1-x}O_3$:PZT) ferroelectric thin films have received great attention for the applications on nonvolatile memory, infrared sensor, electro-optical device, microelectromechanical system device, etc. In order to accomplish the integration of these devices, the etching process for both PZT film and electrode material must be developed. In this study, PZT etching was performed using planar inductively coupled $Ar(20)/Cl_2/BCl_3$ plasma. The etch rate of PZT film was 2450 Å/min at $Ar(20)/BCl_3(80)$ gas mixing ratio and substrate temperature of 80 °C. X-ray photoelectron spectroscopy analysis for film composition was utilized. The chemical bond of PbO is broken by ion bombardment, and the peak of metal Pb in a Pb $4f$ peak begins to appear upon etching, decreasing Pb content faster than Zr and Ti. Also, the relative content of oxygen decreases rapidly. We thought that abundant B and BCl radicals made a volatile oxycompound such as B_xO_y and/or BCl–O bond. To understand the etching mechanism, Langmuir probe and optical emission spectroscopy analysis were utilized for plasma diagnostic. *© 2000 American Vacuum Society.* [S0734-2101(00)00404-8]

I. INTRODUCTION

Since the early 1970s, the rapid development of plasma etching technology was stimulated by its application to the manufacture of microelectronic devices. Dry etching over wet etching has become one of the critical processes for the pattern transfer in silicon integrated circuit devices.[1] As the device feature size shrinks, this requirement is more necessary. Therefore, in silicon devices, the etching characteristics on device performance have been investigated as a real issue to minimize the negative etching effect.[2,3] Lead zirconate titanate (PZT) films have been used extensively in many applications such as nonvolatile memory, actuators, ultrasonic motors, and infrared sensors because of their ferroelectric, piezoelectric, and other electrical properties.[4] In order to accomplish the integration of these devices, the etching process for both PZT film and electrode material must be developed. In particular, much research of PZT ferroelectric films as a dielectric material for storage capacitors of highly integrated memory devices has been carried out since this film has a high dielectric constant and remanent polarization. However, there has been little study about the etching mechanisms of PZT material as a function of substrate temperature. Also, to obtain a high PZT etch rate, not only sputter etching by energetic ion bombardment is required to break the strong chemical bonding of PZT, but also chemical reaction forming volatile etching products is required in PZT etching.[5,6] In this study, dry etching of the PZT film with $Ar/Cl_2/BCl_3$ gas was studied as a variation of substrate temperature by using inductively coupled plasmas (ICPs). The study was performed as a function of etching parameters including substrate temperature and gas mixing ratio. Etching characteristics on ferroelectric PZT films have been investigated in terms of etch rate, etch selectivity, and etch profile. To understand etch mechanism, optical emission spectroscopy (OES) and Langmuir probe analysis were utilized in plasma diagnostic. X-ray photoelectron spectroscopy (XPS) was performed to examine the surface composition.

II. EXPERIMENT

PZT thin films of 3000 Å were prepared on $Pt/Ti/SiO_2/Si$ substrates by sol-gel processes. The sol-gel solution for PZT films was prepared from lead acetate-trihydrate, zirconium *n*-propoxide, and titanium isopropoxide. Acetic acid and *n*-propanol were used as solvents. The solution was spun on substrate at 3500 rpm for 30 s. The coated PZT films were annealed at 650 °C for 1 h to form the PZT perovskite phase. A Pt film of 1000 Å was deposited with direct current (dc) magnetron sputtering [Varian 3180 dc sputtering system] and a Ti layer of 1000 Å was used as an adhesion layer between the Pt and SiO_2 films. The samples were patterned using conventional photoresist with a thickness of 1.2 μm. The ICPs were generated with a 13.56 MHz radio frequency (rf) power which was applied to a planar spiral Cu coil separated

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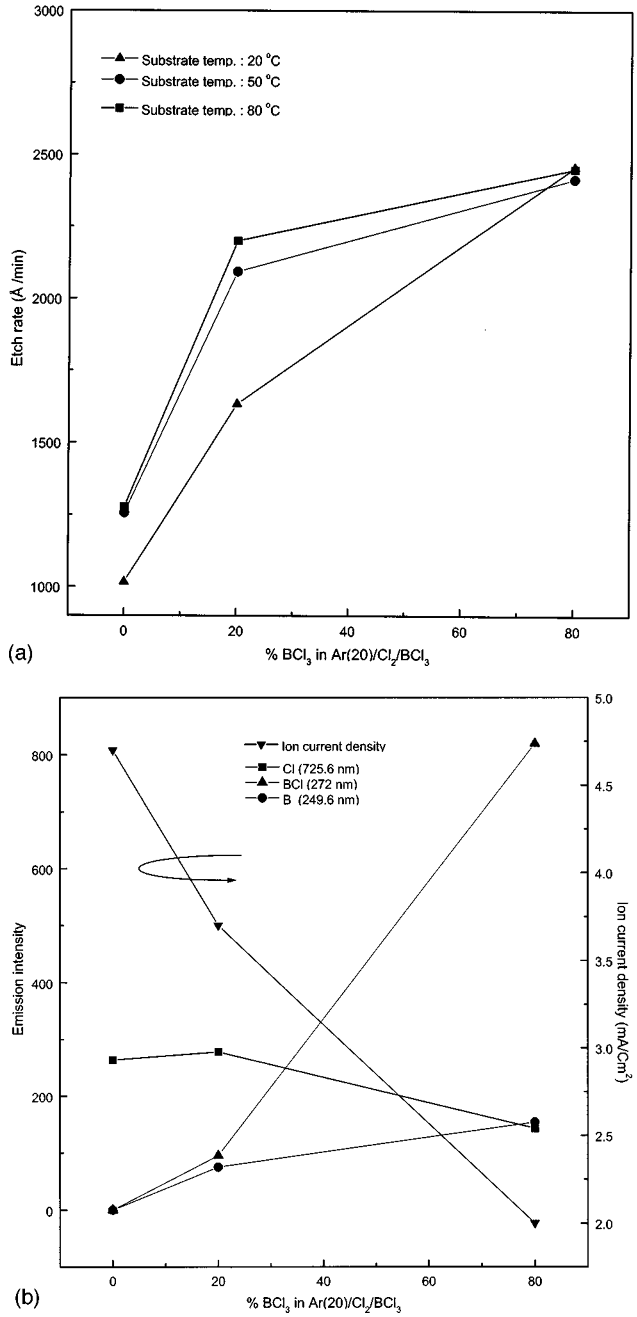

FIG. 1. (a) PZT etch rate, (b) ion current density and relative OES signal intensities as a function of gas combination of $Ar(20)/Cl_2/BCl_3$ plasma for the substrate temperature from 20 to 80 °C at inductive power of 500 W, dc-bias voltage of −300 V, and chamber pressure of 20 mTorr.

by 1 cm-thick quartz window located on the top of the process chamber. A separated 13.56 MHz rf power was also applied to the bottom electrode. A single Langmuir probe inserted in the center of the chamber and biased at −40 V to collect ion currents was used to measure ion current densities of the chlorine-based ICP as a measure of total positive ion densities. OES (SC Tech. PCM 402) was used to monitor plasma species such as Cl, B, and BCl. The PZT films were etched by ICP equipment using various combinations of $Ar(20)/Cl_2/BCl_3$ at substrate temperatures of 20–80 °C while inductive power, bias voltage, and pressure were fixed at 500 W, −300 V, and 20 mTorr, respectively. The chlorine containing gases are very effective in forming volatile compounds with PZT films, depending on the etching conditions. Etching of Pt films was also carried out under the same conditions as PZT etching to examine the selectivity of PZT to Pt films. The composition of the chlorine based gases (Cl_2/BCl_3) was varied to find optimum gas concentration of giving a high etch rate of the PZT film with a high selectivity of PZT to Pt. The ratio of Ar to (Cl_2+BCl_3) was fixed at 20%. The etch rate was measured by using an α-step. The etch profile was observed by using scanning electron microscopy (SEM) (Hitachi S-800 system).

TABLE I. Selectivities of PZT to Pt and PR as a function of BCl_3 content in $Ar(20)/Cl_2/BCl_3$ gas mixing ratio and substrate temperature.

Materials	Substrate temperature (°C)	Ar/Cl_2 (20/80)	$Ar/Cl_2/BCl_3$ (20/60/20)	Ar/BCl_3 (20/80)
PZT/Pt	20	1.03	1.28	3.13
	50	1.17	1.77	3.09
	80	1.42	2.69	3.68
PZT/PR	20	0.18	0.36	0.9
	50	0.23	0.49	0.71
	80	0.26	0.53	0.94

III. RESULTS AND DISCUSSION

PZT films were etched with various $Ar(20)/Cl_2/BCl_3$ combinations at substrate temperatures from 20 to 80 °C at the inductive power of 500 W, dc-bias voltage of −300 V, and total pressure of 20 mTorr. The etch rates of PZT thin film are shown in Fig. 1. The etch rate of PZT increased with increasing content of BCl_3 in the $Ar(20)/Cl_2/BCl_3$ gas mixture. As the content of BCl_3 gas increases up to 20%, the etch rate of PZT increases rapidly. However, as the content of BCl_3 gas exceeds over 20%, the etch rate of PZT increases slowly. At $Ar(20)/BCl_3(80)$ and substrate temperature of 80 °C, the etch rate of PZT film was 2450 Å/min. To understand the effects of the gas combination and the substrate temperature on the PZT etch rates, plasma characterization tools such as a Langmuir probe and an OES were used, and the results are shown in Fig. 1(b) for $Ar(20)/Cl_2/BCl_3$ at the total gas pressure of 20 mTorr. Ion current densities were measured as an estimation of total positive ion densities in the plasmas using Langmuir probe. Estimation of Cl, B, and BCl radical peak intensity was obtained using OES. As shown in Fig. 1(b), the ion current density decreased with addition of BCl_3 to $Ar(20)/Cl_2(80)$ (e.g., total positive ion density). As an increase of 20% BCl_3, the chlorine radical slightly increased. However, with a further increase of the BCl_3 content, the chlorine radical reduced monotonically, whereas, B and BCl radicals increased linearly. The selectivity of PZT to both PR and Pt film are shown in Table I as a function of substrate temperature and gas combination of $Ar(20)/Cl_2/BCl_3$. As the content of BCl_3, increases the selectivities of PZT to Pt and PR increase linearly, and are directly proportional to the substrate temperature in less than an amount of 50% BCl_3. However, at the condition over

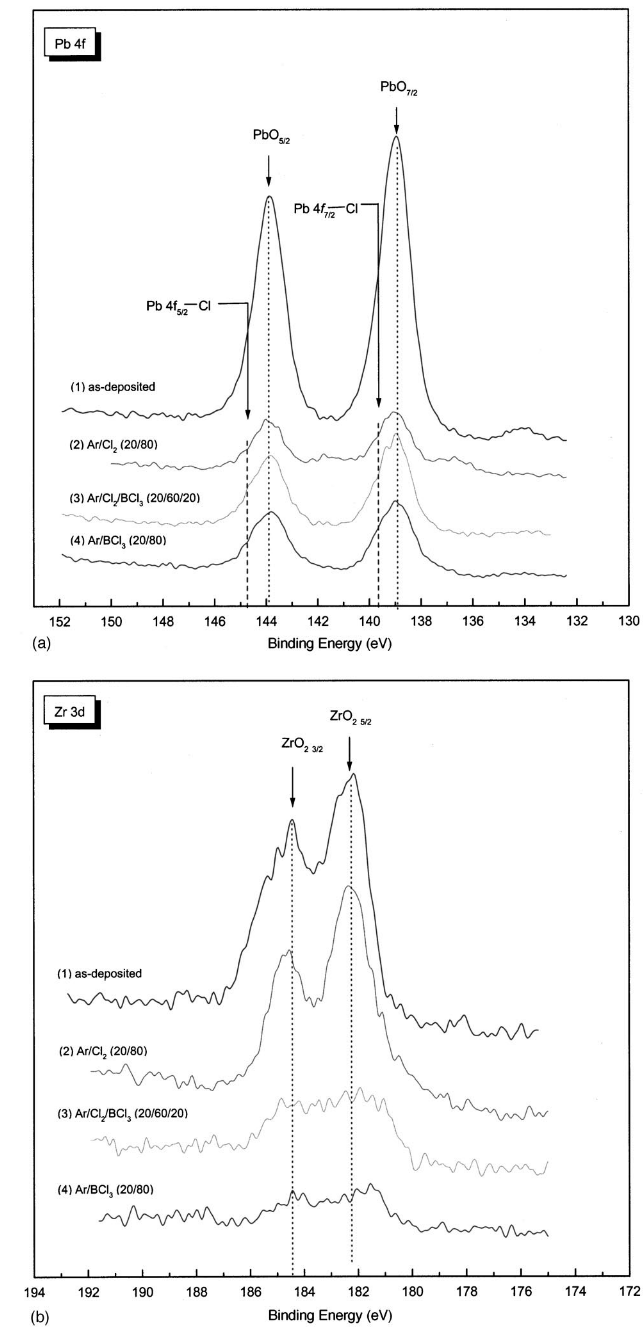

FIG. 2. XPS (a) Pb $4f$, (b) Zr $3d$, and (c) Ti $2p$ narrow scan spectra of PZT films etched at various BCl_3 gases mixing ratio at coil rf power of 500 W, operational pressure of 20 mTorr, dc-bias voltage of −300 V, and substrate temperature of 80 °C.

50% BCl_3, the etch rate of PZT has no dependence on the substrate temperature. The selectivities of PZT to Pt and PR were 2.7 and 0.9, respectively, at the Ar(20)/BCl_3(80) gas mixing ratio and the substrate temperature of 80 °C.

The PZT film consists of three components (e.g., PbO, ZrO_2, and TiO_2) in the PZT solid solution. Table II shows the composition changes of the etched PZT film surface as a function of Ar(20)/Cl_2/BCl_3 gas ratio. The relative atomic percentages of Pb, Zr, Cl, B, O, and Ti elements were estimated from XPS analysis. The relative atomic percentage of Pb decreases rapidly at Ar/Cl_2 gas mixture and seems to slightly increase as an increased content of BCl_3 in Table II. It means that PbO in PZT is easily attacked by ion bombardment in plasma and transformed to Pb, relative to ZrO_2 and TiO_2 in PZT. Figure 2(a) shows that the Pb $4f$ spectra can be resolved into PbO, $PbCl_2$, and Pb. The peak at 138.9, 139.6, and 136.8 eV binding energies correspond to PbO, $PbCl_x$, and Pb, respectively. The variation of Pb $4f$ peaks on the etched PZT surfaces is shown in Fig. 2(a) for various contents of BCl_3. It is evident from Fig. 2(a) that the chemical bond of PbO is broken to react with Cl gas and the peak of metal Pb in the Pb $4f$ peak begins to appear upon etching, decreasing the Pb content faster than Zr and Ti. As shown in Fig. 1(b), ion current density was decreased with increasing BCl_3 content. Therefore, PbO peaks relatively disappeared in Ar/Cl_2 plasma condition. The Zr $3d$ spectra resolved into ZrO_2 in Fig. 2(b). The peaks at 181.1 and 178.8 eV binding energies correspond to Zr $3d_{3/2}$ and Zr $3d_{5/2}$ of element Zr, and the peaks of ZrO_2 were observed at 182.2 eV binding energy. The intensity of the ZrO_2 peak is the highest in the condition of Ar/Cl_2 gas ratio. Therefore, the etch rate is the lowest in that gas mixture. On the other hand, the intensity of the ZrO_2 peak was lower than that of the as-deposited film. The ZrO_2 in PZT film is easily broken comparatively with adding BCl_3 gas to Ar/Cl_2 gas. The Ti $2p$ narrow scan spectra are appeared in Fig. 2(c). The peaks at 454.1 and 460.1 eV binding energy correspond to Ti $2p_{3/2}$ and Ti $2p_{1/2}$. Also, the peak of TiO_2 is observed at 459.2 binding energy. While the relative atomic percentage of oxygen decreases rapidly in Table II. So, we thought that volatile oxycompound such as B_xO_y and/or BCl–O is formed by interacting oxygen with B and/or BCl radicals. From these results, the increase of BCl_3 in Ar(20)/Cl_2/BCl_3 increased the etch rate of PZT film.

TABLE II. Relative atomic percentage of the etched PZT film as a function of BCl_3 gas mixing ratio at coil rf power of 500 W, operational pressure of 20 mTorr, dc-bias voltage of −300 V, and substrate temperature of 80 °C.

Gas mixing ratio	Elements					
	Pb	Zr	Ti	O	Cl	B
As-deposited	15	33	4.4	67.6	0	0
Ar/Cl_2 (20/80)	5.1	13.7	5.9	69.8	5.5	0
$Ar/Cl_2/BCl_3$ (20/60/20)	4.2	3.2	3.3	43.3	2.3	43.7
Ar/BCl_3 (20/80)	5.7	3.6	3.8	32.4	1	53.5

Figure 3 shows the SEM micrograph of the etched pattern with a line of 5μm. The patterned samples were etched at the coil rf power of 500 W, dc-bias voltage of −300 V, chamber pressure of 20 mTorr, substrate temperature of 80 °C, and gas combination of Ar/BCl_3:20/80. The etched profile of PZT films with the 5μm line was obtained above 80°.

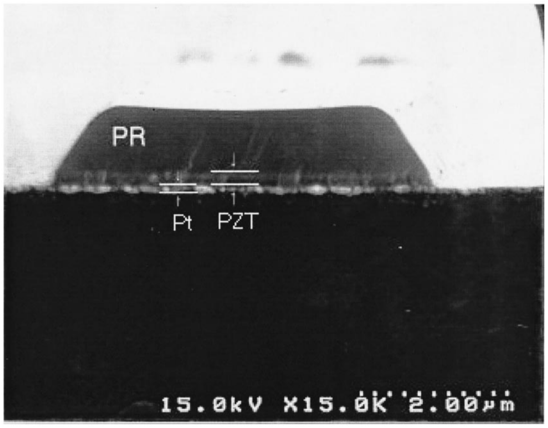

FIG. 3. SEM micrograph of PR/PZT/Pt/Ti/SiO_2/Si etched using 80% BCl_3 in Ar/BCl_3 gas mixing ratio at substrate temperature of 80 °C, inductive power of 500 W, bias voltage of −300 V, and chamber pressure of 20 mTorr.

IV. CONCLUSION

Reactive ion etching of PZT thin film was studies by using an Ar(20)/Cl_2/BCl_3 gas mixture in an ICP. The PZT etch rate of 2450 Å/min was obtained at an inductive power of 500 W, dc-bias voltage of −300 V, total pressure of 20 mTorr, and substrate temperature of 80 °C. The selectivities of PZT to Pt and PR were 3.68 and 0.94, respectively. Also, the etch slope of 80° achieved at above the same condition. As increasing content of BCl_3 in Ar(20)/Cl_2/BCl_3 gas mixing ratio, the etch rate of the PZT film increased, because the oxygen content of the etched PZT surface decreased after etching. Consequently, we thought that volatile oxycompound such as B_xO_y and/or BCl–O is made by abundant B and BCl radicals. From XPS analysis, it was found that PbO in PZT film was readily broken and transformed to Pb relative to ZrO_2 and TiO_2. It resulted in faster consumption of PbO than that of ZrO_2 and TiO_2.

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