

# Effect of additive gases on the selective etching of $ZrO_x$ film using inductively coupled $BCl_3$ -based plasmas

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## Abstract

In this study, the effect of  $BCl_3/C_4F_8$  gas mixture on the  $ZrO_x$  etch rates and the etch selectivities of  $ZrO_x/Si$  were investigated and its etch mechanism was studied. The increase of  $C_4F_8$  in  $BCl_3/C_4F_8$  decreased the silicon etch rate significantly and finally deposition instead of etching occurred by mixing  $C_4F_8$  more than 3%. In the case of  $ZrO_x$ , the etch rate remained similar until 4% of  $C_4F_8$  was mixed, however, the further increase of  $C_4F_8$  percentage finally decreased the  $ZrO_x$  etch rate and deposition instead of etching occurred by mixing more than 6%. Therefore, by mixing 3–4% of  $C_4F_8$  to  $BCl_3$ , infinite etch selectivity of  $ZrO_x/Si$  could be obtained while maintaining the similar  $ZrO_x$  etch rate. The differences in the etch behaviors of  $ZrO_x$  and Si were related to the different thickness of C–F polymer formed on the surfaces. The thickness of the C–F polymer on the  $ZrO_x$  surface was smaller due to the removal of carbon incident on the surface by forming  $CO_x$  with oxygen in  $ZrO_x$ . Using 12 mTorr  $BCl_3/C_4F_8$  (4%), 700 W of rf power, and  $-80$  V of dc bias voltage, the  $ZrO_x$  etch rate of about 535 Å/min could be obtained with infinite etch selectivity to Si.

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**Keywords:**  $ZrO_x$  selective etching;  $BCl_3$ ;  $C_4F_8$

## 1. Introduction

Zirconium oxide ( $ZrO_x$ ) has been investigated as a gate dielectric material in metal-oxide-semiconductor field effect transistor (MOSFET) and as a storage capacitor in dynamic random access memory (DRAM) devices.  $ZrO_x$  has the high-dielectric constant ( $\sim 25$ ), wide band gap (4.6–7.8 eV), low-leakage-current level, and superior thermal stability [1–3]. To use  $ZrO_x$  in MOSFET and DRAM devices, the  $ZrO_x$  should be patterned by dry etching because wet etching is difficult to completely remove the compounds such as zirconium silicate ( $ZrSi_xO_y$ ) formed at the  $ZrO_x$  and silicon interface. In addition, wet etching is incapable of etching high-resolution features [4,5].

For some of MOSFET and DRAM devices, silicon is located below the  $ZrO_x$  layer, therefore, to etch  $ZrO_x$  successfully, not only high  $ZrO_x$  etch rates but also high etch selectivities of  $ZrO_x$  over the underlying material such as Si are required in addition

to the high etch selectivities over mask materials. A few researchers have investigated dry etching of  $ZrO_x$  using chlorine-based gases such as  $Cl_2$  [6] and  $Cl_2/BCl_3$  [4,5] for the application of MOSFET devices. However, the etch selectivities of  $ZrO_x$  over underlying materials were not high enough (lower than three) because of the higher vapor pressures of the etch products such as silicon chlorine compounds compare to those of  $ZrO_x$  in  $Cl_2/BCl_3$  gas chemistry and, in these etching conditions, the etch rates of  $ZrO_x$  were lower than 250 Å/min.

In general, fluorocarbon gases such as  $CF_4$ ,  $CHF_3$ , and  $C_4F_8$  have widely been used to improve the etch selectivity of oxide materials including silicon dioxide to silicon due to the formation of passivation layer on silicon during etch process, resulting in lowering the etch rate of silicon. Especially, higher ratios of C/F of fluorocarbon gases lead to the increase in the selectivity to silicon [7]. Therefore, in this study, to obtain higher etch selectivities of  $ZrO_x$  over underlying silicon together with high  $ZrO_x$  etch rates,  $ZrO_x$  film etching was carried out using inductively coupled  $BCl_3/C_4F_8$  plasmas in addition to  $BCl_3/Cl_2$  plasmas. Also, the mechanism obtaining the high etch selectivity was also investigated.

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## 2. Experimental

The  $ZrO_x$  etch behavior was characterized with a home-made inductively coupled plasma (ICP) equipment. The ICP source was composed of a gold-coated three-turn square-shaped spiral coil located on the top of the process chamber and was separated from the plasma by a 1-cm thick quartz window. To generate the inductive plasmas, 13.56 MHz rf power was applied to the coil, while separate 13.56 MHz rf power was supplied to the substrate to provide dc bias voltages to the wafer. The distance between the quartz window and the substrate was 10 cm. Substrate cooling was provided by chilled water, keeping the substrate temperature at near room temperature. Details of the ICP equipment used in the experiment are described elsewhere [8].

The samples consisted of 3500 Å thick  $ZrO_x$  films deposited on p-type Si (100) wafers by reactive rf sputtering. The  $ZrO_x$  films were patterned with 1.2 μm thick photoresist (PR).  $BCl_3$  (100 sccm) gas was used to etch  $ZrO_x$  as a main etch gas, while  $C_4F_8$  (0–6 sccm) and  $Cl_2$  were used as additive gases. The operating pressure was kept at 12 mTorr and was controlled by an automatic throttle valve installed at the pump line. The etch rates were determined using stylus profilometry (Tencor Instrument, Alpha Step 500) of the feature depth after stripping the PR. The etch profiles were observed using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700). X-ray photoelectron spectroscopy (XPS; Thermo VG, SIGMA PROBE) was used to analyze the etch products on the etched  $ZrO_x$  and silicon surfaces.

## 3. Results and discussion

Fig. 1 shows the etch rates of  $ZrO_x$  and Si, and the etch selectivity of  $ZrO_x$  over Si measured as a function of  $BCl_3$  in the  $BCl_3/Cl_2$  mixture using the ICP system. The rf power to the ICP source was 700 W, the dc bias voltage to the substrate was –70 V, and the operating pressure was 12 mTorr. As shown in the figure, when pure  $Cl_2$  was used, the etch rates of  $ZrO_x$  and Si were 177 Å/min and 3207 Å/min, respectively, and the etch

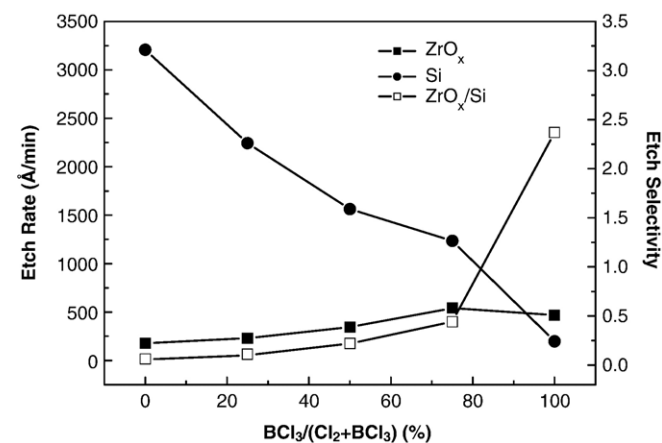


Fig. 1. Etch rates of  $ZrO_x$  and Si and etch selectivities of  $ZrO_x/Si$  as a function of  $Cl_2/BCl_3$  gas mixture [process condition: inductive power (700 W), dc bias voltage (–70 V), and operating pressure (12 mTorr)].

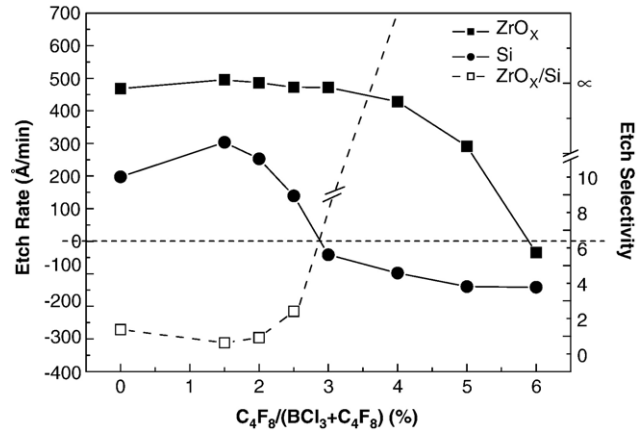


Fig. 2. Etch rates of  $ZrO_x$  and Si and etch selectivities of  $ZrO_x/Si$  as a function of  $BCl_3/C_4F_8$  gas mixture. [process condition: inductive power (700 W), dc bias voltage (–70 V), and operating pressure (12 mTorr)].

selectivity of  $ZrO_x/Si$  was less than 0.06. However, as the  $BCl_3$  was mixed to  $Cl_2$ , while the  $ZrO_x$  etch rate increased linearly with increasing  $BCl_3$ , the silicon etch rate decreased linearly, therefore, the etch selectivity of  $ZrO_x/Si$  was increased with increasing  $BCl_3$ . When pure  $BCl_3$  was used, the etch rates of  $ZrO_x$  and Si were 469 Å/min and 198 Å/min, respectively, and the etch selectivity was 2.37. Therefore, even though the etch rate of  $ZrO_x$  and the etch selectivity of  $ZrO_x/Si$  obtained by using pure  $BCl_3$  were the highest among the  $BCl_3/Cl_2$  gas mixtures, the etch selectivity was still low for the practical purpose.

The low etch rate of  $ZrO_x$  and the low  $ZrO_x/Si$  etch selectivity obtained using pure  $Cl_2$  are related to the difficulty in forming Zr etch products such as Zr chlorides due to the higher bond strength of Zr–O (8.058 eV) compared to that of Zr–Cl (5.114 eV) [9] in addition to low vapor pressures of  $ZrCl_x$  ( $ZrCl_2$ : m.p. 727 °C,  $ZrCl_4$ : m.p. 437 °C), while silicon etch products such as silicon chlorides ( $SiCl_x$ ) are easily formed and volatile ( $SiCl_4$ : mp –69 °C). The increase of  $BCl_3$  in  $BCl_3/Cl_2$  increases the Zr etch rates possibly due to the easier formation of Zr chlorides by removing oxygen on the surface of  $ZrO_x$ . Here, oxygen in  $ZrO_x$  is easily removed by  $BCl_x$  in  $BCl_3$  by forming volatile etch products such as boron dioxide ( $BO_2$ ) and boron oxy-chloride ( $BOCl$ ) due to the higher bond strength of B–O (8.397 eV) compared to the bond strength of Zr–O. The decrease of silicon etch rate with increasing  $BCl_3$  in  $BCl_3/Cl_2$  is believed to be related to the formation of B–Si compounds which act as a passivation layer for the formation of silicon chlorides [4–6].

Therefore, to remove oxygen in  $ZrO_x$  and to form a passivation layer on silicon more effectively, a novel gas mixture consisted of  $BCl_3/C_4F_8$  was used and its effects on the  $ZrO_x$  etch rates and the  $ZrO_x/Si$  etch selectivities were investigated. Fig. 2 shows the etch rates of  $ZrO_x$  and Si and the etch selectivities of  $ZrO_x/Si$  measured as a function of  $C_4F_8$  percentage in the  $BCl_3/C_4F_8$  mixture. Other process conditions are the same as those in Fig. 1. As shown in Fig. 2, the addition of small percentage of  $C_4F_8$  (1.5%) slightly increased both  $ZrO_x$  etch rate and Si etch rate to 495 Å/min and 303 Å/min,

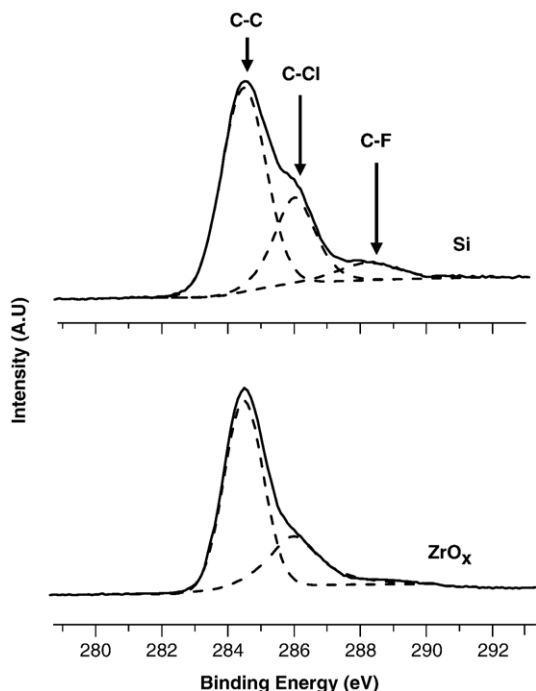


Fig. 3. XPS C1s narrow scan spectra of  $ZrO_x$  and Si surfaces exposed to  $BCl_3/C_4F_8$  (4%) plasma [process condition: inductive power (700 W), dc bias voltage (-70 V), and operating pressure (12 mTorr)].

respectively, however, the further increase of  $C_4F_8$  percentage decreased the etch rates of  $ZrO_x$  and silicon. The decrease of silicon etch rate with increasing  $C_4F_8$  was much faster than that of  $ZrO_x$  etch rate (in fact, no significant decrease of  $ZrO_x$  etch rate was observed until 4% of  $C_4F_8$  was mixed as shown in the figure), therefore, deposition instead of etching occurred for Si when more than 3%  $C_4F_8$  was mixed in  $BCl_3/C_4F_8$  while that occurred for  $ZrO_x$  when more than 6%  $C_4F_8$  was mixed. In the case of the etch selectivity of  $ZrO_x/Si$ , the etch selectivity was decreased to 1.63 until 1.5%  $C_4F_8$  was mixed and the further increase of  $C_4F_8$  increased the etch selectivity significantly.

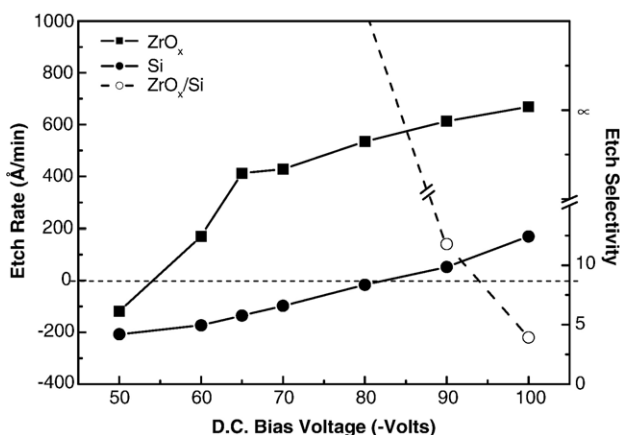


Fig. 4. Etch rates of  $ZrO_x$  and Si and etch selectivities of  $ZrO_x/Si$  as a function of dc bias voltage [process condition: inductive power (700 W) and operating pressure (12 mTorr)].

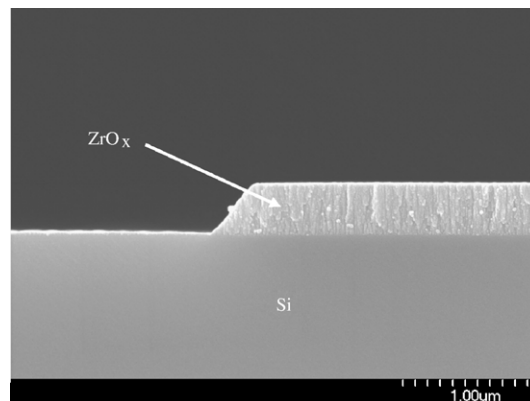


Fig. 5. SEM micrograph of etched  $ZrO_x$  layer on silicon after the etching using  $BCl_3/C_4F_8$  (4%) plasma [process condition: inductive power (700 W), dc bias voltage (-70 V), and operating pressure (12 mTorr), etch time: 10 min (20% overetching)].

When  $C_4F_8$  was mixed from 3 to 4%, infinite etch selectivity of  $ZrO_x/Si$  could be obtained without significantly changing the  $ZrO_x$  etch rate.

The initial increase of silicon etch rate and  $ZrO_x$  etch rate with the small addition of 1.5%  $C_4F_8$  appears to be related to the etching of silicon by fluorine in  $C_4F_8$  by the formation of volatile silicon fluoride ( $SiF_x$ ) and the removal of oxygen by carbon in  $C_4F_8$ , respectively. However, the rapid decrease of silicon etch rate with the further increase of  $C_4F_8$  in the  $BCl_3/C_4F_8$  mixture is believed to be related to the formation of a C–F polymer layer on the silicon surface which prevents the diffusion of fluorine and chlorine to silicon surface in addition to blocking ion bombardment to the surface [10,11]. In the case of  $ZrO_x$ , due to the difficulty in the formation of a C–F polymer on the  $ZrO_x$  surface due to the removal of carbon from  $C_4F_8$  incident on the surface by the formation of  $CO_x$ , the etch rate of  $ZrO_x$  was maintained until 4% of  $C_4F_8$  was mixed to  $BCl_3/C_4F_8$ . However, with the further increase of  $C_4F_8$ , the  $ZrO_x$  etch rate decreased and deposition finally occurred instead of etching by the addition of  $C_4F_8$  more than 6% by the formation of a C–F polymer layer on the  $ZrO_x$  surface.

Fig. 3 shows the XPS narrow scan data of C1s peaks on the  $ZrO_x$  and Si after the etching by  $BCl_3/C_4F_8$  (4%). Other process conditions were the same as those in Fig. 1. The etch time was 5 min. As shown in the figure, the C1s peak of the etched  $ZrO_x$  surface consisted of two sub peaks originated from the C–C bond (284.5 eV) and the C–Cl bond (286 eV). On the other hand, the C1s peak of the etched silicon surface consisted of the peaks from the C–F bond (288.3 eV) in addition to the above peaks. The C–F bond peak observed on the etched silicon surface appears to be related to the C–F polymer formed on the silicon surface while no such C–F bond was observed on the etched  $ZrO_x$  surface possibly due to the removal of carbon from  $C_4F_8$  by the formation of  $CO_x$  with the oxygen in  $ZrO_x$ . However, the mixture of  $C_4F_8$  in the  $BCl_3/C_4F_8$  more than 4% increases the carbon on the  $ZrO_x$  surface more than carbon amount that can be consumed by the formation of  $CO_x$  with the oxygen in  $ZrO_x$ , therefore, a C–F polymer layer is expected to

be formed on the  $ZrO_x$  surface and the decrease of  $ZrO_x$  etch rate is expected with the further increase of  $C_4F_8$  percentage.

Fig. 4 shows the etch rates of  $ZrO_x$  and Si measured as a function of dc bias voltage from  $-50$  to  $-100$  V for  $BCl_3/C_4F_8$  (4%). Other process conditions are the same as those in Fig. 1. As shown in the figure, in general, the etch rates of  $ZrO_x$  and Si increased with the increase of dc bias voltage. However, when the dc bias voltage was  $-50$  V, deposition instead of etching occurred on the surface of both  $ZrO_x$  and Si and, in the case of Si, no etching was observed until the dc bias voltage was higher than  $-80$  V. Therefore, infinite etch selectivity of  $ZrO_x/Si$  was observed for the dc bias from  $-60$  to  $-80$  V. The differences in the etch behaviors of  $ZrO_x$  and Si are related to the difference thickness of the C–F polymer on those surfaces and the removal of the polymer by the ion bombardment. At  $-80$  V of dc bias voltage, the highest  $ZrO_x$  etch rate of  $535 \text{ \AA}/\text{min}$  with infinite etch selectivity of  $ZrO_x/Si$  could be obtained.

Fig. 5 shows an SEM etch profile of  $ZrO_x$  on silicon after the removal of the PR mask.  $BCl_3/C_4F_8$  (4%) was used and the etch time was 10 min, which corresponds to 20% overetching. Other etch process conditions were the same as those in Fig. 1. As shown in the SEM micrograph, even with 20% overetching, no removal of underlying silicon was observed after the etching possibly due to the infinite etch selectivity of  $ZrO_x/Si$  obtained with the process condition.

#### 4. Conclusions

In this study, the effect of gas mixtures such as  $BCl_3/Cl_2$  and  $BCl_3/C_4F_8$  on the  $ZrO_x$  etch rates and the etch selectivities of  $ZrO_x/Si$  was investigated. The addition of  $BCl_3$  to  $Cl_2$  increased  $ZrO_x$  etch rate and the etch selectivity possibly due to the removal of oxygen in  $ZrO_x$  by B in  $BCl_3$  while it decreased silicon etch rate by the formation of a passivation layer composed of B–Si. The further increase of  $ZrO_x$  etch rate and etch selectivity could be obtained by mixing  $C_4F_8$  to  $BCl_3$ . The mixture of  $C_4F_8$  more than 1.5% decreased the silicon etch rate significantly and finally deposition instead of etching was occurred by the mixture of  $C_4F_8$  more than 3% due to the

formation of a C–F polymer on the silicon surface. In the case of  $ZrO_x$ , due to the removal of carbon incident on the  $ZrO_x$  surface by the formation of  $CO_x$  with oxygen in  $ZrO_x$ , the  $ZrO_x$  etch rate was remained similar until 4% of  $C_4F_8$  was mixed, however, the further increase of  $C_4F_8$  percentage finally decreased the  $ZrO_x$  etch rate and deposition instead of etching was occurred by the mixture of  $C_4F_8$  more than 6% possibly due to the formation of a C–F polymer similar to the case of silicon. The mixture of 3 to 4%  $C_4F_8$  to  $BCl_3$  showed the infinite etch selectivity of  $ZrO_x/Si$  while the  $ZrO_x$  etch rate remained similar. Using 12 mTorr  $BCl_3/C_4F_8$  (4%), 700 W of rf power, and  $-80$  V of dc bias voltage, the  $ZrO_x$  etch rate of about  $535 \text{ \AA}/\text{min}$  could be obtained with infinite etch selectivity to Si.

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