

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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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 (~ 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

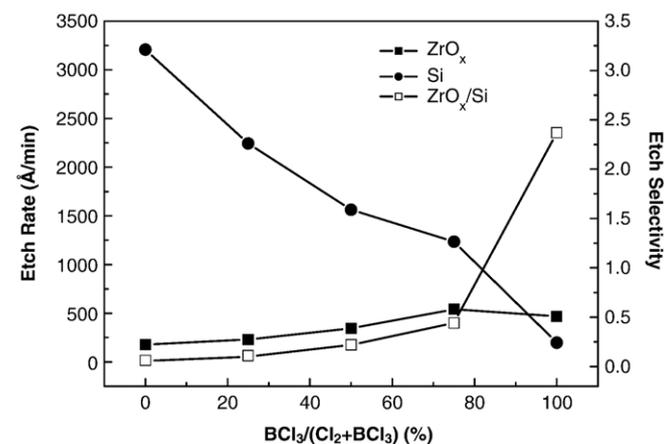


Fig. 1. Etch rates of ZrO_x and Si and etch selectivities of ZrO_x/Si as a function of Cl_2/BCl_3 gas mixture [process condition: inductive power (700 W), dc bias voltage (–70 V), and operating pressure (12 mTorr)].

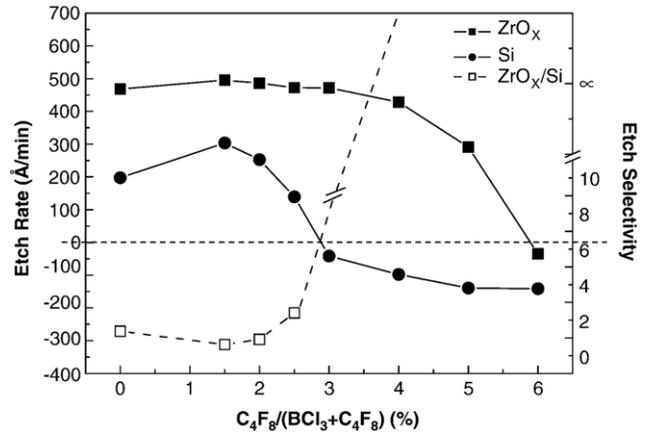


Fig. 2. Etch rates of ZrO_x and Si and etch selectivities of ZrO_x/Si as a function of BCl_3/C_4F_8 gas mixture. [process condition: inductive power (700 W), dc bias voltage (–70 V), and operating pressure (12 mTorr)].

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,

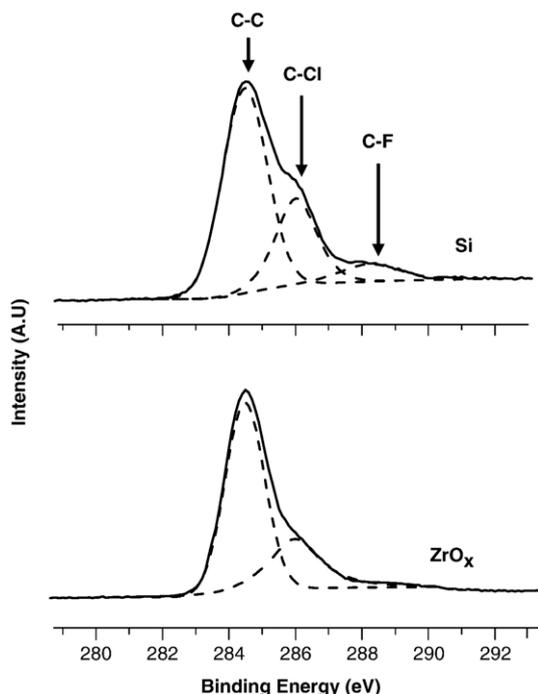


Fig. 3. XPS C1s narrow scan spectra of ZrO_x and Si surfaces exposed to BCl_3/C_4F_8 (4%) plasma [process condition: inductive power (700 W), dc bias voltage (-70 V), and operating pressure (12 mTorr)].

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.

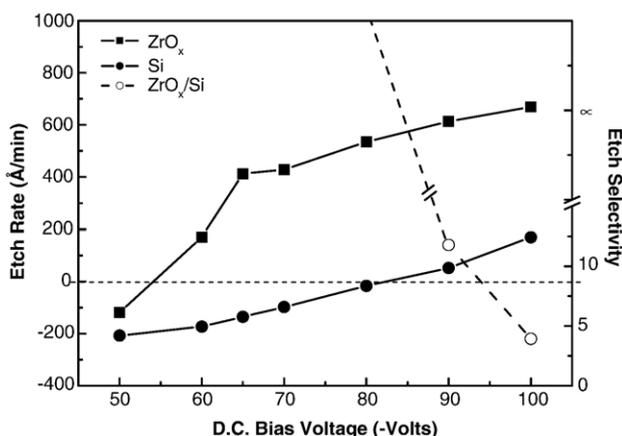


Fig. 4. Etch rates of ZrO_x and Si and etch selectivities of ZrO_x/Si as a function of dc bias voltage [process condition: inductive power (700 W) and operating pressure (12 mTorr)].

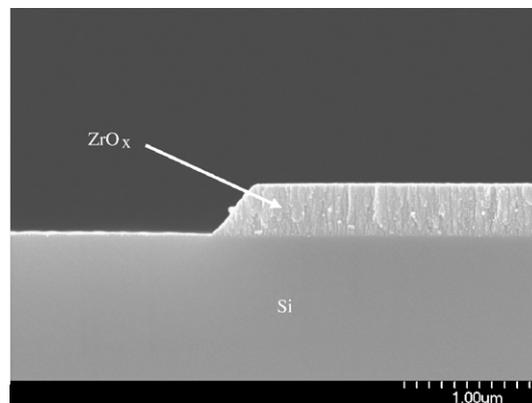


Fig. 5. SEM micrograph of etched ZrO_x layer on silicon after the etching using BCl_3/C_4F_8 (4%) plasma [process condition: inductive power (700 W), dc bias voltage (-70 V), and operating pressure (12 mTorr), etch time: 10 min (20% overetching)].

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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