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$_4$F$_8$ 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$_4$F$_8$ in BCl$_3$/C$_4$F$_8$ decreased the silicon etch rate significantly and finally deposition instead of etching occurred by mixing C$_4$F$_8$ more than 3%. In the case of ZrO$_x$, the etch rate remained similar until 4% of C$_4$F$_8$ was mixed, however, the further increase of C$_4$F$_8$ 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$_4$F$_8$ 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 with oxygen in ZrO$_x$. Using 12 mTorr BCl$_3$/C$_4$F$_8$ (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.

Keywords: ZrO$_x$, selective etching; BCl$_3$; C$_4$F$_8$

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 (∼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 (ZrSiO$_4$) 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$_4$F$_8$ 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$_4$F$_8$ plasmas in addition to BCl$_3$/Cl$_2$ plasmas. Also, the mechanism obtaining the high etch selectivity was also investigated.
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$_4$F$_8$ (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 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 the bond strength of Zr–Cl (5.114 eV) [9] in addition to low vapor pressures of ZrCl$_3$ (ZrCl$_3$: m.p. 727 °C, ZrCl$_4$: m.p. 437 °C), while silicon etch products such as silicon chlorides (SiCl$_4$) 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$_3$ 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$_4$F$_8$ 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$_4$F$_8$ percentage in the BCl$_3$/C$_4$F$_8$ mixture. Other process conditions are the same as those in Fig. 1. As shown in Fig. 2, the addition of small percentage of C$_4$F$_8$ (1.5%) slightly increased both ZrO$_x$ etch rate and Si etch rate to 495 Å/min and 303 Å/min,

![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)].](image1)

![Fig. 2. Etch rates of ZrO$_x$, Si and etch selectivities of ZrO$_x$/Si as a function of BCl$_3$/C$_4$F$_8$ gas mixture. [process condition: inductive power (700 W), dc bias voltage (~70 V), and operating pressure (12 mTorr)].](image2)
respectively, however, the further increase of C₄F₈ percentage decreased the etch rates of ZrOₓ and silicon. The decrease of silicon etch rate with increasing C₄F₈ was much faster than that of ZrOₓ etch rate (in fact, no significant decrease of ZrOₓ etch rate was observed until 4% of C₄F₈ was mixed as shown in the figure), therefore, deposition instead of etching occurred for Si when more than 3% C₄F₈ was mixed in BCl₃/C₄F₈ while that occurred for ZrOₓ when more than 6% C₄F₈ was mixed. In the case of the etch selectivity of ZrOₓ/Si, the etch selectivity was decreased to 1.63 until 1.5% C₄F₈ was mixed and the further increase of C₄F₈ increased the etch selectivity significantly.

When C₄F₈ was mixed from 3 to 4%, infinite etch selectivity of ZrOₓ/Si could be obtained without significantly changing the ZrOₓ etch rate.

The initial increase of silicon etch rate and ZrOₓ etch rate with the small addition of 1.5% C₄F₈ appears to be related to the etching of silicon by fluorine in C₄F₈ by the formation of volatile silicon fluoride (SiFₓ) and the removal of oxygen by carbon in C₄F₈, respectively. However, the rapid decrease of silicon etch rate with the further increase of C₄F₈ in the BCl₃/C₄F₈ 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 ZrOₓ due to the difficulty in the formation of a C–F polymer on the ZrOₓ surface due to the removal of carbon from C₄F₈ incident on the surface by the formation of COₓ, the etch rate of ZrOₓ was maintained until 4% of C₄F₈ was mixed to BCl₃/C₄F₈. However, with the further increase of C₄F₈, the ZrOₓ etch rate decreased and deposition finally occurred instead of etching by the addition of C₄F₈ more than 6% by the formation of a C–F polymer layer on the ZrOₓ surface.

Fig. 3 shows the XPS narrow scan data of C₁s peaks on the ZrOₓ and Si surfaces exposed to BCl₃/C₄F₈ (4%) plasma [process condition: inductive power (700 W), dc bias voltage (−70 V), and operating pressure (12 mTorr)].

Fig. 4. Etch rates of ZrOₓ and Si and etch selectivities of ZrOₓ/Si as a function of dc bias voltage [process condition: inductive power (700 W) and operating pressure (12 mTorr)].
be formed on the ZrO$_x$ surface and the decrease of ZrO$_x$ etch rate is expected with the further increase of C$_4$F$_8$ 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$_4$F$_8$ (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 Å/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$_4$F$_8$ (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$_4$F$_8$ 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$_4$F$_8$ to BCl$_3$. The mixture of C$_4$F$_8$ more than 1.5% decreased the silicon etch rate significantly and finally deposition instead of etching was occurred by the mixture of C$_4$F$_8$ 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 with oxygen in ZrO$_x$, the ZrO$_x$ etch rate was remained similar until 4% of C$_4$F$_8$ was mixed, however, the further increase of C$_4$F$_8$ percentage finally decreased the ZrO$_x$ etch rate and deposition instead of etching was occurred by the mixture of C$_4$F$_8$ more than 6% possibly due the formation of a C–F polymer similar to the case of silicon. The mixture of 3 to 4% C$_4$F$_8$ 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$_4$F$_8$ (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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References