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Etching characteristics of high-\textit{k} dielectric HfO$_2$ thin films in inductively coupled fluorocarbon plasmas

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Inductively coupled fluorocarbon (CF$_4$/Ar and C$_4$F$_8$/Ar) plasmas were used to etch HfO$_2$, which is a promising high-dielectric-constant material for the gate of complementary metal-oxide-semiconductor devices. The etch rates of HfO$_2$ in CF$_4$/Ar plasmas exceeded those in C$_4$F$_8$/Ar plasmas. The tendency for etch rates to become higher in fluorine-rich (high F/C ratio) conditions indicates that HfO$_2$ can be chemically etched by fluorine-containing species. In C$_4$F$_8$/Ar plasmas with a high Ar dilution ratio, the etch rate of HfO$_2$ increased with increasing bias power. The etch rate of Si, however, decreased with bias power, suggesting that the deposition of carbon-containing species increased with increasing power and inhibited the etching of Si. The HfO$_2$/Si selectivity monotonically increased with increasing power, then became more than 5 at the highest tested bias power. The carbon-containing species to inhibit etching of Si play an important role in enhancing the HfO$_2$/Si selectivity in C$_4$F$_8$/Ar plasmas. © 2005 American Vacuum Society. [DOI: 10.1116/1.2073468]

I. INTRODUCTION

As integrated-circuit device dimensions continue to be scaled down, increasingly strict requirements are being imposed on plasma etching technology. The requirements include the etch anisotropy, profile control, feature size, or critical dimension control relative to the mask layer, selectivity to the underlying layers and, also, microscopic uniformity of these etch parameters. For the gate etch process of a complementary metal-oxide-semiconductor (CMOS) device application, historically the two most important issues to be addressed have been a precise control of the profile and critical dimension of gate electrodes, and a high selectivity to gate oxides. In practice, the gate width of advanced devices is projected to be scaled down to much less than 100 nm, and the thickness of gate oxides is also reduced to 2 nm or less for the present material, SiO$_2$. The thickness reduction brings a number of serious problems such as increased gate leakage current and reduced oxide reliability.

Regarding gate dielectrics, the technological challenge continues for growing ultrathin SiO$_2$ films of high quality; however, the ultimate solution relies on high-dielectric-constant (\textit{k}) materials. Recent efforts have been made to replace SiO$_2$ with silicon oxynitrides of slightly higher dielectric constant, and, nowadays, new high-\textit{k} (>20) dielectrics, or metal oxides such as Al$_2$O$_3$, HfO$_2$, and ZrO$_2$, are being developed to replace SiO$_2$. They provide the required specific capacitance at a considerably larger thickness than SiO$_2$, thus allowing the reduction of gate leakage current. In integrating these materials into device fabrication, an understanding of the etching characteristics of high-\textit{k} materials is required for their removal and for contact etching.

Plasma etching of metal oxides with a high \textit{k} has been studied for the application of ferroelectric materials, buffer layers, and capacitor dielectrics. However, only a few studies have been concerned with the plasma etching of high-\textit{k} materials for gate-dielectrics application. Pelhos \textit{et al.} reported on the etching of high-\textit{k} gate dielectric Zr$_{1-x}$Al$_x$O$_2$ thin films with helical resonator plasmas in BCl$_3$/Cl$_2$. Sha \textit{et al.} reported on the etching of ZrO$_2$ with electron cyclotron resonance plasmas in Cl$_2$ (Ref. 7) and BCl$_3$/Cl$_2$. They also etched HfO$_2$ thin films in chlorine chemistries. In their studies of HfO$_2$ etching, chlorine-based chemistries not fluorine were chosen, because in previous works, HfO$_2$ etching stopped in CHF$_3$ plasmas, whereas the fluorinated Hf compound can be formed as sidewall masks. Moreover, Norasetthekul \textit{et al.} reported on the etching of HfO$_2$ with inductively coupled plasmas in Cl$_2$/Ar, SF$_6$/Ar, and CH$_4$/H$_2$/Ar. They concluded that the etch rates in Cl$_2$ were higher than those in SF$_6$/Ar.

An emphasis in these studies has been placed on etch chemistries giving the selectivity of more than one over the underlying Si substrate, as well as a better understanding of the corresponding physics and chemistry under processing. The thickness of the gate dielectrics for next-generation CMOS devices (in the 65 nm technology node and beyond) will be several nm. Therefore, selectivity to underlying layers or mask materials will be more important than the etch rate in the gate process. From the point of view of HfO$_2$/Si selectivity, highly selective etching may be achieved in fluorocarbon plasmas, because a surface inhibitor of polymer probably sticks on Si that does not include oxygen. In this paper we present results of the etching of HfO$_2$ thin films on Si substrates in inductively coupled fluorocarbon (CF$_4$/Ar and C$_4$F$_8$/Ar) plasmas. Then we discuss the performance of...
fluorocarbon plasmas in etching HfO₂ and try to understand the etch mechanism by comparing it with that of SiO₂, which is well known in previous works.¹⁶

II. EXPERIMENT

Samples for etching were 60 nm thick HfO₂ films on Si substrates prepared by chemical vapor deposition, SiO₂ films formed by thermal oxidation and bare Si substrates. The samples were cleaved into 2 cm² pieces and attached on a 4 in. diameter Si wafer, which was then clamped onto a wafer stage.

Etching experiments were performed in a low-pressure inductively coupled plasma reactor supplied with 13.56 MHz rf power. The reactor consisted of a grounded stainless-steel chamber 25 cm in diameter and 25 cm high. The rf power supply was coupled to the plasma via a three-turn planar rf induction coil 15 cm in outer diameter, positioned on a quartz window 20 cm in diameter and 1.2 cm thick, located at the top side of the chamber. The wafer stage was 13 cm in diameter, being located at the bottom side of the chamber, where a close-fitting ground shield surrounded the stage. The distance from the bottom edge of the rf coupling window to the wafer stage was 5 cm. Gas mixtures of CF₄/Ar and C₄F₈/Ar and pure Ar were introduced into the reactor evacuated to a base pressure <1 × 10⁻⁶ Torr, and the gas pressure was typically 20 mTorr at a flow rate of 50 or 250 sccm.

The discharge was established at a nominal rf power of 100–300 W, corresponding to net powers to the π-type matching circuit driving the induction coil. The wafer stage was capacitively coupled to a separate 13.56 MHz rf power supply for additional biasing; the rf bias power was varied between 10 and 150 W (net power), resulting in a dc self-bias voltage on the stage down to between −40 and −160 V.

Sample pieces covered with a Si wafer were etched for several minutes. Steps appeared on the sample pieces after removing the Si wafer. To determine etch rates, step height on the sample pieces was measured by stylus profilometry. For evaluating a real gate etch process of industrial applications, photoresist masks should be used. In the present study, the Si wafer was used as a mask to make experimental procedures more convenient. The basic aspect of etch characteristics, however, can be understood by using the Si masks.

The chemical composition of the surface was analyzed by x-ray photoelectron spectroscopy (XPS) using Mg Kα x-ray radiation and a pass energy of 50 eV at a takeoff angle of 90°. A cylindrical Langmuir probe was placed 2 cm above the wafer stage to measure plasma parameters (ion density, electron temperature, and plasma potential).

III. RESULTS AND DISCUSSION

A. CF₄/Ar and C₄F₈/Ar plasmas

Figure 2(a) shows the etch rate of HfO₂ in CF₄/Ar plasmas as a function of the gas–mixture ratio [Ar]/([CF₄] + [Ar]) at constant rf powers of 280 W (to the coil) and 50 W (for bias), together with that of Si and the etch selectivity of HfO₂/Si. In generating the plasmas, the gas flow rate and the pressure were maintained at 50 sccm and
20 mTorr, respectively. Here the etched depth was measured as a function of the etch time up to several minutes, exhibiting an approximately linear increase with time; thus, the etch rate was calculated as the ratio of the depth to time.

The etch rate of Si decreased with an increasing gas–mixture ratio, indicating that the amount of fluorine radicals or etchants for Si decreases with decreasing $\text{H}_2\text{O}/\text{CF}_4$. The etch rate of HfO$_2$ was not changed so much. The result was that the selectivity was enhanced with increasing $\text{H}_2\text{O}/\text{Ar}$. The dc self-bias voltage on the wafer stage was reduced from $-160$ to $-110$ V with increasing $\text{H}_2\text{O}/\text{Ar}$, implying that the bombarding ion energy was decreased with increasing $\text{H}_2\text{O}/\text{Ar}$. The ion density, however, increased slightly with increasing $\text{H}_2\text{O}/\text{Ar}$. The ion flux should have been kept almost constant in the tested regime of the gas–mixture ratio. If the ion flux maintained the etch rate of HfO$_2$, one can guess that Ar ion sputtering contributes to HfO$_2$ etching.

Assuming the etch mechanism of HfO$_2$ to mainly be sputtering by ion bombardment, the samples were then exposed to pure Ar plasmas at a constant power of 120 W to the coil and bias power varied between 10 and 50 W. The gas flow rate and pressure were 50 sccm and 20 mTorr, respectively. The dc self-bias voltage increased with increasing bias power [Fig. 3(a)]. Then the etch rates of HfO$_2$ and Si increased with increasing the self-bias voltage [Fig. 3(b)]. At a bias power of 50 W, the rate of HfO$_2$ was higher than that of Si (HfO$_2$/Si selectivity $>1$). Furthermore, the etch rate was no more than 10 nm/min even at a constant power increased to 280 W (to the coil). The rate was half as high as that in CF$_4$/Ar plasmas. Therefore, the etching of HfO$_2$ may be caused not only by ion sputtering, but also, by chemical reactions in CF$_4$/Ar plasmas.

The etching characteristics of SiO$_2$ were also examined in the CF$_4$/Ar plasmas [Fig. 2(b)]. The etch rate increased with increasing [Ar] in the range of the gas–mixture ratio from 0.5 to 0.8, and then decreased. The dependence of the SiO$_2$ etch rate on the gas–mixture ratio was similar to that of the HfO$_2$ etch rate, rather than that of Si. Therefore, the etch mechanism of HfO$_2$ may be partly understood on the analogy of that of SiO$_2$. The etching of SiO$_2$ can proceed with dissociation of the Si–O bond in the reaction of fluorocarbon radicals on the surface activated by ion bombardment,

$$\text{SiO}_2 + \text{CF}_x \rightarrow \text{SiF}_4 \uparrow + \text{COF}_2 \uparrow.$$ \hspace{1cm} (1)

Similarly, fluorocarbon species and ion impact on the surface may also play an important role in HfO$_2$ etching. Moreover, the reaction involving fluorocarbon species can be effective, not for Si etching, but for protecting Si surfaces.

Assuming the same chemistry as selective etching of SiO$_2$ over Si in fluorocarbon plasmas, the carbon-rich compound of C$_4$F$_8$ was employed for HfO$_2$ etching. Generally, C$_4$F$_8$ plasmas can produce more fluorocarbon species contributing to SiO$_2$ etching and protect the Si surface than CF$_4$ plasmas. Consequently, the fluorine radical as a etchant...
in Si etching becomes a relatively minor product in C4F8 plasmas, and HfO2/Si selectivity is expected to be higher in comparison with CF4 plasmas. Figure 4 shows the etch rates of HfO2, SiO2, and Si, and the selectivities of HfO2/Si and SiO2/Si in C4F8/Ar plasmas. The total gas flow rate, pressure, power to the coil, and rf bias power were set at 250 sccm, 20 mTorr, 280 W, and 50 W, respectively.

On the other hand, there was no conspicuous advantage in the SiO2/Si selectivity obtained in the C4F8 plasmas. Because the etch rates of SiO2 in the C4F8 plasmas were lower than those in the CF4 plasmas, the fluorine radical, not fluorocarbon species, seemed to work mainly in SiO2 etching, as well as in Si etching. Therefore, the reduction of the etch rate of Si in the C4F8/Ar plasmas resulted from the reduction of fluorine content; as a result, the HfO2/Si selectivity improved in the plasma.

To obtain a higher selectivity of HfO2/Si, one must suppress Si etching with depositing a surface inhibitor and enhance HfO2 etching caused by fluorocarbon radicals. Assuming that the Hf–O bond can be dissociated in the same chemistry as SiO2 etching, requiring much bombarding by Ar ions,

\[ \text{HfO}_2 + \text{CF}_x \rightarrow \text{HfF}_4 \uparrow + \text{COF}_2 \uparrow, \]

it would be necessary to increase the CF3 radical densities and ion flux activating the reactions on the surface. Therefore, the conditions with a high Ar dilution ratio, which are preferable for SiO2/Si selective etching, were employed in the present study.

Figure 5 shows the etch rates of HfO2, SiO2, and Si, and the selectivities of HfO2/Si and SiO2/Si in C4F8/Ar plasmas with a high Ar dilution ratio. Figure 6 shows those values for the case of C4F8/Ar plasmas. In these experiments, the total flow rate was increased to 250 sccm, and other conditions, powers, pressure, and so on were the same as the former experiments. The etch rates of HfO2 and Si decreased with increasing Ar dilution ratio in both the C4F8/Ar and C4F8/Si plasmas [Figs. 5(a) and 6(a)]. The tendency seems to indicate that the etch mechanism gradually changed from

\[ \text{HfO}_2 + \text{CF}_x \rightarrow \text{HfF}_4 \uparrow + \text{COF}_2 \uparrow, \]
chemical etching to physical sputtering with increasing [Ar]. In the C₄F₈/Ar plasmas, the HfO₂/Si selectivity became more than unity at the gas-mixture ratios of 0.2, and 0.4% close to the pure Ar plasma condition. In contrast, in CF₄/Ar plasmas, the HfO₂/Si selectivity could not be more than unity. In SiO₂ etching [Figs. 5(b) and 6(b)], the etch rate of SiO₂ decreased with increasing [Ar] in the same way as the cases of HfO₂ and Si. The SiO₂/Si selectivity in the C₄F₈ plasmas rises to the peak at the gas–mixture ratio of 2%, and that in the CF₄ plasmas keeps under 2.5 over all the tested gas–mixture ratios. In the C₄F₈ plasmas, SiO₂ must have been chemically etched by an etchant of the fluorocarbon species not fluorine radical in the conditions around the peak. Nevertheless there was no peculiarity in the tendency of the HfO₂ etch rate, indicating that the reactions caused by bombarding ions were dominant in the mechanism of the HfO₂ etching. Besides, it can be safely said that HfO₂ can be etched, in part, by chemically reactive species such as the fluorine radical, as mentioned above. The chemical etching of HfO₂ will be an important means of controlling the etch profile, because the profile formed in the chemical will be better for device manufacturing than that in the Ar ion sputtering process only.

B. Increasing rf bias power

The results mentioned above show that HfO₂ can be etched by chemical reactions appearing in the fluorine-rich conditions such as CF₄/Ar plasmas and by physical sputtering. From the point of view of etch profile control, one of the best solutions for the HfO₂ etching in fluorocarbon plasmas must be practical use of energetic ion bombardment with chemically reactive species. Therefore, HfO₂ samples were treated with increasing rf bias power to enhance bombarding Ar ion energy in CF₄/Ar and C₄F₈/Ar plasmas, where the flow rates of the fluorocarbon gases were maintained at a constant of 1%. The etching was performed in the same condition as in Fig. 7.

![Fig. 7. Etch rates of (a) HfO₂ and (b) SiO₂ in CF₄(1 %)/Ar plasmas with high Ar dilution ratio plotted with that of Si, and etch selectivities of (a) HfO₂/Si and (b) SiO₂/Si as a function of self-bias voltage.](image1)

![Fig. 8. Etch rates of (a) HfO₂ and (b) SiO₂ in C₄F₈(1 %)/Ar plasmas with high Ar dilution ratio plotted with that of Si, and etch selectivities of (a) HfO₂/Si and (b) SiO₂/Si as a function of self-bias voltage.](image2)
shown in Table I. The Langmuir probe and changed with power to the coil, as indicated by the notation of “Ref.”. The experimental parameters were the same as in Fig. 8. The rf bias power conditions are shown in the graphs. The values of 50, 70, and 150 W correspond to the self-bias voltages of −45, −72, and −154 V, respectively.

The etch rates can be higher with a higher energy of ion into the surface,25 On HfO2 and SiO2 surfaces, the etching reaction increased with increasing rf bias power, and that of the C1s peak increased. Thus, increasing rf bias power enhanced the deposition reaction of carbon, implied because the surface reaction probability for deposition can be higher with a higher energy of ion into the surface.25 On HfO2 and SiO2 surfaces, the etching reaction may be proceeded with the formation of volatile etch products containing C and O atoms. On the Si surface without O atoms, however, the deposition of C atoms prevented the etching of the surface. Therefore, the selectivities of HfO2/Si and SiO2/Si increased with increasing rf bias power in C4F8/Ar plasmas (Fig. 8).

To understand the etch mechanism, the etch rates of HfO2, Si, and SiO2 were measured, depending on ion energy. Figure 10 shows the etch rates in C4F8/Ar plasmas at coil powers of 200 and 300 W. Here, the ion energy was defined by \( \frac{V_p - V_d}{N_e} \), where \( V_p \) and \( V_d \) correspond to plasma potential measured by Langmuir probe and self-bias voltage, respectively. The gas flow rate and the pressure were set at 250 sccm and 20 mTorr, respectively. The gas–mixture ratio of \([\text{C}_4\text{F}_8]\) to the total was maintained at 1%.

**IV. CONCLUSION**

The etch characteristics of HfO2 were examined in CF4/Ar and C4F8/Ar plasmas. The etch rate of HfO2 tends to be high in fluorine-rich (e.g., CF4/Ar) plasmas and where there is abundant Ar ion bombardment of the surface (e.g., CF4/Ar and C4F8/Ar plasmas with high Ar dilution ratio, and with high self-bias voltage). These results indicated that HfO2 could be etched both chemically by fluorine radical and physically by Ar ion bombardment. This was confirmed by the dependence of the HfO2 etch rate on ion energy and ion density.

Here, we consider the application of fluorocarbon plasmas to actual gate etch processes. In physical sputtering without chemical reactions, redeposition of sputtered atoms makes the etch profile worse. Hence, an etch process involving chemical reactions with volatile etch products is required. The gate materials should be etched by fluorine-containing reactive species with ion bombardment. For HfO2/Si selectivity greater than unity, it was necessary to increase the power was increased from 200 to 300 W. The \( T_e \), however, was maintained at a constant. The etch rate of Si did not change much, even with changes of ion energy and \( N_e \), and implied that the deposition of C atoms prevented the etching of the Si surface. The etch rate of SiO2 increased with increasing ion energy, and became 1.2 times higher with increasing \( N_e \). Furthermore, the etch rate of HfO2 increased with increasing ion density, and HfO2 etching could be two times faster with increasing \( N_e \). This result indicates that HfO2 can be etched by an ion-assisted reaction and ion sputtering.

**Table I. Ion density \( (N_e) \) and electron temperature \( (T_e) \) depending on power to the coil.**

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>( N_e ) (cm(^{-3}))</th>
<th>( T_e ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>( 1.1 \times 10^{11} )</td>
<td>2.9</td>
</tr>
<tr>
<td>300</td>
<td>( 1.9 \times 10^{11} )</td>
<td>2.8</td>
</tr>
</tbody>
</table>
HfO$_2$ etch rate and decrease the Si etch rate. This situation was produced in C$_4$F$_8$/Ar plasmas with high Ar dilution ratio and high self-bias power, and the HfO$_2$/Si selectivity of more than 5 was obtained.

In the present study, the same concept in the SiO$_2$/Si selective etching was applied to the HfO$_2$/Si selective etching, based on understanding previous works. We do not understand all the chemistries for HfO$_2$ etching. For further qualified etching with high selectivity, it will be significant to use a fluorocarbon polymer efficiently, increasing surface inhibitors for Si etching.

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