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Highly selective etching of LaAlSiO$_x$ to Si using C$_4$F$_8$/Ar/H$_2$ plasma

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1. Introduction

With the down scaling of device dimensions, high-$k$ materials have been developed as gate dielectrics of complementary metal–oxide–silicon (CMOS) devices owing to its low gate-leakage current compared with those of conventional ultra-thin SiO$_2$ gate dielectrics. High-$k$ gate dielectrics, however, require the suppression of interfacial layer formation between the high-$k$ gate dielectric and Si substrate to achieve the exceedingly thin equivalent oxide thickness (EOT). La$_2$O$_3$ has been assumed two possible reasons for the low etch rate of highly selective etching of the high-$k$ materials to SiO$_2$ and Si. However, for lanthanum compounds, only a few studies have been carried out, although it has been reported that LaAlSiO$_x$ etching by forming a high-C/F-ratio polymer on the Si surface, while it enhanced LaAlSiO$_x$ etching by breaking the stable metal–oxygen bonds of LaAlSiO$_x$.© 2015 The Japan Society of Applied Physics

Table I. Boiling points (°C) of halogen compounds.

| Halogen compound | Boiling point |
|------------------|--------------|
| SiF$_4$          | −86          |
| SiCl$_4$         | 58           |
| HF$_4$           | 970          |
| HCl$_4$          | 432          |
| ZrF$_4$          | 912          |
| ZrCl$_4$         | 331          |
| AlF$_3$          | 1275         |
| AlCl$_3$         | 180          |
| LaF$_3$          | 2327         |
| LaCl$_3$         | 1000         |

Table II. Standard molar enthalpy of formation at 298.15 K ($\Delta_H^0$) and standard molar Gibbs energy of formation at 298.15 K ($\Delta_G^0$) of oxide compounds (units: kJ/mol).

| Compound | $\Delta_H^0$ | $\Delta_G^0$ |
|----------|--------------|--------------|
| SiO$_2$  | −910.7       | −856.3       |
| ZrO$_2$  | −1100.6      | −1042.8      |
| HfO$_2$  | −1144.7      | −1088.2      |
| Al$_2$O$_3$ | −1675.7       | −1582.3      |
| La$_2$O$_3$ | −1793.7       | −1705.8      |

Concerning Hf- or Zr-based conventional high-$k$ materials, many studies have been reported, as mentioned above. However, for lanthanum compounds, only a few studies have so far been carried out, although it has been reported that lanthanum compounds are difficult-to-etch materials. We assumed two possible reasons for the low etch rate of lanthanum compounds. One is the higher boiling point of lanthanum reaction products than those of hafnium and zirconium. The other is the higher thermodynamic stability of lanthanum oxide than those of hafnium oxide and zirconium oxide. The values of the standard molar enthalpy of formation are $-1793.7$ (La$_2$O$_3$), $-1144.7$ (HfO$_2$), and $-1100.6$ kJ/mol (ZrO$_2$), and the values of the standard molar Gibbs energy of formation are $-1705.8$ (La$_2$O$_3$), $-1088.2$ (HfO$_2$), and $-1042.8$ kJ/mol (ZrO$_2$) respectively, as shown in Table II. This implies that the dissociative reaction of lanthanum oxide into lanthanum and oxygen is difficult to occur compared with that of hafnium oxide or zirconium oxide.

Therefore, three different approaches to achieving a high etch selectivity of LaAlSiO$_x$ to Si were studied in this paper. First, we investigated an inductively coupled BCl$_3$ plasma with a hot cathode (210°C), focused on the enhancement of LaAlSiO$_x$ etching, by increasing the vapor pressure of lanthanum reaction products. Second, we investigated a pressure of lanthanum reaction products are lower than those of hafnium or zirconium. The other is the higher thermodynamic stability of lanthanum oxide than those of hafnium oxide and zirconium oxide. The values of the standard molar enthalpy of formation are $-1793.7$ (La$_2$O$_3$), $-1144.7$ (HfO$_2$), and $-1100.6$ kJ/mol (ZrO$_2$), and the values of the standard molar Gibbs energy of formation are $-1705.8$ (La$_2$O$_3$), $-1088.2$ (HfO$_2$), and $-1042.8$ kJ/mol (ZrO$_2$) respectively, as shown in Table II. This implies that the dissociative reaction of lanthanum oxide into lanthanum and oxygen is difficult to occur compared with that of hafnium oxide or zirconium oxide.

Therefore, three different approaches to achieving a high etch selectivity of LaAlSiO$_x$ to Si were studied in this paper. First, we investigated an inductively coupled BCl$_3$ plasma with a hot cathode (210°C), focused on the enhancement of LaAlSiO$_x$ etching, by increasing the vapor pressure of lanthanum reaction products. Second, we investigated a
The thicknesses of pristine LaAlSiO$_{3.1}$ LaAlSiO$_x$

Figures 2(a) and 2(b) show the etch rates of LaAlSiO$_x$ etching by breaking the stable lanthanum–oxygen bond, and moreover, the suppression of Si etching by forming the fluorocarbon polymer on its surface in a similar way to selective etching of SiO$_2$ to Si. Finally, hydrogen addition to C$_4$F$_8$/Ar plasma was investigated. Hydrogen addition to fluorocarbon plasma has the effect of promoting polymer formation on the Si surface, and many studies have been reported of its application to selective etching of SiO$_2$ over Si, as well as some studies on selective etching of high-k material over Si (HfO$_2$/Si).

2. Experimental methods

Etching experiments were carried out on 300-mm-diameter wafers using two different reactive ion etching (RIE) apparatuses. Figure 1(a) shows the schematic of inductive coupled plasma used in this study, supplied at 13.56 MHz rf power and a bottom electrode powered at 13.56 MHz rf bias power. The wafer is chucked on the hot cathode whose temperature was set at 210 °C in this experiment. Also, a chamber that has the same RF system with a normal cathode temperature (60 °C) was used as the reference. Etching gases used in this experiment were BCl$_3$ and Ar, introduced into the chamber with constant flow rates.

Figure 1(b) shows the dual-frequency superimposed capacitively coupled plasma (DFS-CCP) employing 100/13.56 MHz RF. Etching gas mixtures used in this experiment were C$_4$F$_8$/Ar, C$_4$F$_8$/Ar/H$_2$, BCl$_3$, and Ar plasma. The cathode temperature was kept at 40 °C. We used LaAlSiO$_x$, HfO$_2$, Al$_2$O$_3$, and polysilicon blanket films in these studies. The thicknesses of pristine LaAlSiO$_x$, and polysilicon films were 15 and 200 nm, and that of HfO$_2$ and Al$_2$O$_3$ blanket films was 10 nm, respectively. Film thickness was measured by ellipsometry before and after plasma exposure. To observe the chemical composition of the etched film surface, X-ray photoelectron spectroscopy (XPS) was employed. The XPS measurements are performed with an Al Kα X-ray source and the photoelectrons were collected at 45°.

3. Results and discussion

3.1 LaAlSiO$_x$ etching in inductively coupled BCl$_3$ plasma at high substrate temperature

Figures 2(a) and 2(b) show the etch rates of LaAlSiO$_x$, HfO$_2$, Al$_2$O$_3$, and Si in inductively coupled BCl$_3$ plasma at a high substrate temperature (201 °C) as a function of bias power. Compared with the etch rates at 60 °C, the etch rates of HfO$_2$ and Al$_2$O$_3$ increase from 26 to 41 nm/min, and from 13 to 24 nm/min, respectively, at 50 W bias power, which indicates that HfO$_2$ and Al$_2$O$_3$ etching is enhanced by increasing the substrate temperature. The LaAlSiO$_x$ etch rate also increases, however, it is 1 nm/min only at 50 W bias power. By increasing the bias power from 50 to 300 W, the etch rate of LaAlSiO$_x$ drastically increases from 1 to 16 nm/min. On the other hand, the etch rate of Si is considerably higher than that of LaAlSiO$_x$, over 100 nm/min at 300 W bias power. This indicates that the protection layer formed by irradiating BCl$_3$ plasma onto the Si surface is insufficient to inhibit Si etching with high ion energy. As a consequence, the etch selectivity of LaAlSiO$_x$ to Si is 0.05 at 50 W bias power and 0.15 at 300 W bias power. These results reveal that the 210 °C substrate temperature in BCl$_3$ plasma was insufficient for the promotion of LaAlSiO$_x$ etching with a high etch selectivity of LaAlSiO$_x$ to Si, and it was considered that the enhancement of LaAlSiO$_x$ etching was required by increasing the ion energy, as was the suppression of Si.
etching at high ion energy by changing the gas chemistries, in order to increase the etch selectivity of LaAlSiO₅ to Si.

3.2 LaAlSiO₅ etching in capacitively coupled C₄F₈/Ar plasma at high ion energy

In the case of selective etching of SiO₂ to Si, it was considered that the higher selectivity of SiO₂ to Si is obtained by using CCP plasma than by using ICP plasma employing the same fluorocarbon gas chemistry, because of its low degree of molecular dissociation ratio in the CCP plasma. Moreover, high ion energy was likely obtained because of its high coupling efficiency of the cathode to the anode. Thus we chose the CCP source for the enhancement of LaAlSiO₅ etching by increasing the ion energy and adopted the C₄F₈/Ar gas chemistries for the suppression of Si etching by forming fluorocarbon polymer on its surface.

Figure 4 shows the etch rates of LaAlSiO₅ and Si in capacitively coupled C₄F₈/Ar plasma and BCl₃ plasma, and the etch rate of LaAlSiO₅ in capacitively coupled Ar plasma as a function of bias power. By increasing the bias power from 300 to 900 W, the LaAlSiO₅ etch rate in C₄F₈/Ar plasma increases from 4 to 31 nm/min, and that in BCl₃ plasma increases from 6 to 32 nm/min. The enhancement of LaAlSiO₅ etching is clearly observed by increasing the ion energy. In both C₄F₈/Ar and BCl₃ plasmas, etch rates of LaAlSiO₅ at 300 W are about the same as that in Ar plasma. On the other hand, etch rates of LaAlSiO₅ at 900 W are much larger than that in Ar plasma. The enhancement ratios of etch rates of C₄F₈/Ar and BCl₃ plasmas to that of Ar plasma at 900 W bias power are 2.2 and 2.3, respectively. This suggests that the ion-assisted chemical reaction of LaAlSiO₅ etching is more notable in the high-ion-energy region.

Figure 5 shows the etch rates of LaAlSiO₅ and Si, and selectivity of LaAlSiO₅ to Si in capacitively coupled BCl₃ and C₄F₈/Ar plasmas at 900 W bias power. The etch rate of Si in C₄F₈/Ar plasma is much lower than that in BCl₃ plasma. Consequently, the selectivity of LaAlSiO₅ to Si is higher, 0.88 in C₄F₈/Ar plasma compared with 0.44 in BCl₃ plasma. This result suggests that a more resistive polymer had formed on the Si surface when using C₄F₈/Ar plasma than when using BCl₃ plasma, which led to the suppression of the Si etch rate. On the other hand, the etching mechanism of LaAlSiO₅ at high ion energy in C₄F₈/Ar plasma was speculated to be as follows. First, the high-energy ion breaks the strong oxygen–metal bonds, and then oxygen is removed as volatile CO₂ or O₂ and metals are removed as metal fluoride reaction products. These two effects contributed to the enhancement of the etch selectivity of LaAlSiO₅ to Si.

3.3 Effect of H₂ addition to C₄F₈/Ar plasma

In selective etching of SiO₂ to Si, the Si etch rate suppression effect upon hydrogen addition to the fluorocarbon gases is well understood. Hydrogen extracts fluorine from the plasma or fluorocarbon polymer, and a high-C/F-ratio fluorocarbon polymer is formed on the Si surface. It has been reported that high-C/F-ratio fluorocarbon polymer...
has high etch resistivity, which results in high etch selectivity of SiO$_2$ to Si. By analogy, it was expected that in selective etching of LaAlSiO$_x$ to Si, hydrogen may play a similar role of suppressing Si etching.

In addition, hydrogen was expected to play another role on the LaAlSiO$_x$ surface, that is, it promotes LaAlSiO$_x$ etching. The ion energy distribution of hydrogen has the largest probability of high ion energy than any other gas in the same RF bias power discharge, because its light mass causes the ion energy distribution function to spread the widest. In addition, hydrogen ion has the largest projection range at the same ion energy because of its small atomic radius. It follows that hydrogen is likely to penetrate deeply and effectively break the stable metal–oxygen bonds in the LaAlSiO$_x$ film.

Figure 6 shows the H$_2$ flow rate ratio dependence of the etch rates of LaAlSiO$_x$ and Si, and etch selectivity of LaAlSiO$_x$ to Si in C$_4$F$_8$/H$_2$/Ar plasma. The etch rate of LaAlSiO$_x$ increases when the hydrogen flow rate ratio is increased from 0 to 13%. On the other hand, the etch rate of Si decreases, and as a result, the etch selectivity drastically increases and reaches a maximum of 6.7 at an H$_2$ flow rate ratio of 13%.

To understand the mechanism of selective etching in C$_4$F$_8$/H$_2$/Ar plasma, XPS analyses of the LaAlSiO$_x$ and Si surface after C$_4$F$_8$/Ar, C$_4$F$_8$/Ar/H$_2$ plasma etching were performed. Figure 7(a) shows the result of the LaAlSiO$_x$ surface analysis. The element concentration of the substrate is represented by the sum of La, Al, Si, and O concentrations. The concentration of the substrate increases with H$_2$ addition. This indicates that the thickness of fluorocarbon film on LaAlSiO$_x$ decreases with H$_2$ addition. On the contrary, as shown in Fig. 7(b), on the Si surface, the element concentration of the substrate decreases and the carbon concentration in fluorocarbon film on the Si surface increases with H$_2$ addition. It was confirmed that the mechanism of the suppression of Si etching on forming a thick and high-C/F-ratio polymer also applies to this case of selective etching of LaAlSiO$_x$ to Si. Figure 8 shows the correlation of the LaAlSiO$_x$ etch rate with the oxygen content in the LaAlSiO$_x$ surface from the XPS results. It was found that the etch rate of LaAlSiO$_x$ is inversely proportional to oxygen content. It is assumed that the reason for the reduction of fluorocarbon film on LaAlSiO$_x$ surface upon 13% H$_2$ addition shown in Fig. 7(a) is the enhancement of carbon consumption by oxygen desorption from the LaAlSiO$_x$ film, which is promoted by the breaking of the strong metal–oxygen bonds upon hydrogen addition.

Next, the role of hydrogen in breaking the metal–oxygen bonds of LaAlSiO$_x$ was investigated. If hydrogen actually promotes the breaking of the metal–oxygen bonds, exposure to hydrogen plasma before C$_4$F$_8$/Ar plasma etching should enhance the LaAlSiO$_x$ etching reaction, in the same way as it does in C$_4$F$_8$/Ar plasma with H$_2$ addition. Figure 9 shows the comparison of the etching depth of LaAlSiO$_x$ among C$_4$F$_8$/Ar plasma, H$_2$ plasma, C$_4$F$_8$/Ar plasma after exposure to H$_2$ plasma, and C$_4$F$_8$/Ar/H$_2$ plasma. The bias power was 1200 W and the exposure time was 5 s in all cases. The etch depth of LaAlSiO$_x$ etched for 5 s in C$_4$F$_8$/Ar plasma was about 2 nm. On the other hand, the etch depth of LaAlSiO$_x$ exposed to...
hydrogen and then etched by C\textsubscript{4}F\textsubscript{8}/Ar plasma. In the H\textsubscript{2} plasma, hydrogen penetrates deeply and breaks the strong metal–oxygen bonds, although the etch depth is small. Then in C\textsubscript{4}F\textsubscript{8}/Ar plasma, LaAlSiO\textsubscript{x} is easily etched to the extent of this broken-bond depth. Consequently, LaAlSiO\textsubscript{x} etching is enhanced. In the C\textsubscript{4}F\textsubscript{8}/Ar/H\textsubscript{2} plasma, both steps proceed at the same time. From these results, it was confirmed that hydrogen plays a role in breaking the metal–oxygen bond in LaAlSiO\textsubscript{x} etching.

In conclusion, C\textsubscript{4}F\textsubscript{8}/Ar plasma etching with H\textsubscript{2} addition enhanced LaAlSiO\textsubscript{x} etching and suppressed Si etching, and high selectivity of LaAlSiO\textsubscript{x} to Si was successfully realized.

4. Conclusions

The etch rates of LaAlSiO\textsubscript{x} and Si, and the etch selectivity of LaAlSiO\textsubscript{x} to Si using inductively coupled BCl\textsubscript{3} plasma at a high cathode temperature and capacitively coupled C\textsubscript{4}F\textsubscript{8}/Ar and C\textsubscript{4}F\textsubscript{8}/Ar/H\textsubscript{2} plasmas were investigated in this paper. From the results on LaAlSiO\textsubscript{x} etching in BCl\textsubscript{3} plasma at high substrate temperature, it was found that the etch rate of LaAlSiO\textsubscript{x} is exceedingly low compared with that of HfO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}, even at a substrate temperature of 210 °C. From the results on LaAlSiO\textsubscript{x} etching in C\textsubscript{4}F\textsubscript{8}/Ar plasma at high ion energy, it was found that the LaAlSiO\textsubscript{x} etch rate is enhanced by promoting the ion-assisted chemical reaction by increasing the ion energy, and the Si etch rate is reduced to one-half that in the case of BCl\textsubscript{3} plasma by forming fluorocarbon polymer on its surface. As a result, the etch selectivity of LaAlSiO\textsubscript{x} to Si in C\textsubscript{4}F\textsubscript{8}/Ar plasma increased to 0.88 at 900 W bias power. Then, H\textsubscript{2} addition to C\textsubscript{4}F\textsubscript{8}/Ar plasma was investigated. Upon hydrogen addition to C\textsubscript{4}F\textsubscript{8}/Ar plasma, the etch selectivity of LaAlSiO\textsubscript{x} to Si increased and reached a maximum of 6.7 at an H\textsubscript{2} flow rate ratio of 13%. H\textsubscript{2} played different roles on the LaAlSiO\textsubscript{x} surface and the Si surface. On the Si surface, H\textsubscript{2} suppressed Si etching by forming the high-C:F-ratio polymer, and on the LaAlSiO\textsubscript{x} surface, H\textsubscript{2} enhanced LaAlSiO\textsubscript{x} etching by breaking the strong metal–oxygen bonds. From the results of comparisons of the LaAlSiO\textsubscript{x} etching depth among C\textsubscript{4}F\textsubscript{8}/Ar, C\textsubscript{4}F\textsubscript{8}/Ar plasma after exposure to H\textsubscript{2} plasma, and C\textsubscript{4}F\textsubscript{8}/Ar/H\textsubscript{2} plasma, it was confirmed that H\textsubscript{2} plays the role of breaking the metal–oxygen bonds in LaAlSiO\textsubscript{x} etching. Thus, high selectivity of LaAlSiO\textsubscript{x} to Si was successfully realized.