Etch Properties of HfO_2 Thin Films using CH_4/Ar Inductively Coupled Plasma

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In this study, we carried out an investigation of the etching characteristics (etch rate, selectivity) of HfO_2 thin films in the CH_4/Ar inductively coupled plasma. It was found that variations of input power and negative dc-bias voltage are investigated by the monotonic changes of the HfO_2 etch rate as it generally expected from the corresponding variations of plasma parameters. At the same time, a change in either gas pressure or in gas mixing ratio result in non-monotonic etch rate that reaches a maximum at 2 Pa and for CH_4 (20 %)/Ar (80 %) gas mixture, respectively. The X-ray photoelectron spectroscopy analysis showed an efficient destruction of the oxide bonds by the ion bombardment as well as showed an accumulation of low volatile reaction products on the etched surface. Based on these data, the ion-assisted chemical reaction was proposed as the main etch mechanism for the CH_4-containing plasmas.

Keywords : Etching, HfO_2, Inductively coupled plasma

1. INTRODUCTION

The New high-k dielectrics are being developed to replace SiO_2 in future generations of complementary metal-oxide semiconductor applications in the 65 nm technology node and beyond[1]. Among several candidates, HfO_2 is being extensively studied because of its modest dielectric constant and thermal stability at the interface with Si[2,3]. The thickness reduction of SiO_2 brings many serious problems such as increased gate leakage current and reduced oxide reliability[4,5]. To overcome this drawback, many metal oxides with high dielectric constant materials have been reported, such as TiO_2[6], Ta_2O_5[7], Al_2O_3[8], Y_2O_3[9], HfO_2[10], ZrO_2 [11], and $ZrSiO_4$, Hf_xSiO_y[12,13]. Although these materials have high dielectric constant, some of these fail one or more of the criteria. Al_2O_3 and Y_2O_3 did not provide sufficient advantages over SiO_2 or Si_3N_4[14]. TiO_2 and Ta_2O_5 were observed to react with Si substrate [15]. $SrTiO_3$ thin films or $(Ba_{0.6}Sr_{0.4})TiO_3$ thin films may cause fringing field induced barrier lowering effect[16].

In this study, HfO_2 thin films were etched with CH_4/Ar gas chemistries in inductively coupled plasma (ICP). Etching characteristics on the HfO_2 thin films have been investigated in terms of etch rate and selectivity[12]. The chemical binding states in the surface of the etched HfO_2 thin films were investigate with X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL

The HfO_2 thin film used in this work were deposited by atomic layer chemical vapor deposition[16]. It was obtained to the final thickness of HfO_2 films of about 70 nm. Etching experiments were performed in a planar ICP system which is schematically shown in Fig. 1. The reactor chamber is made from aluminum with anodizing of the inner walls. A 3.5 turn spiral induction coil is located above the 24 mm-thick horizontal quartz window that separates the coil from the process chamber. The height of working zone, i.e. the distance between quartz window and bottom electrode, was 14 cm. The bottom electrode used as substrate holder is connected to another asymmetric RF 13.56 MHz generator.

The HfO_2 thin films were etched as a function CH_4/Ar plasma. The gas mixing ratio was varied to find the characteristics of etching. For these experiments, process pressure, RF power, DC-bias voltage, and substrate temperature was 2 Pa, 600 W, -150 V and 30 °C, respectively.

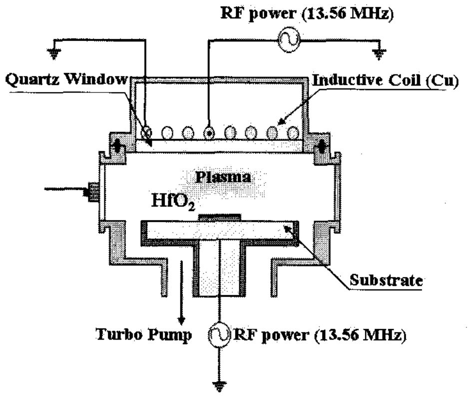

Fig. 1. Schematic of inductively coupled plasma system.

Table 1. Process conditions.

Process parameter	Parameter range
Gas mixture	CH_4 / Ar
Top RF power	400 ~ 700 W
DC-bias voltage	- 50 ~ - 200 V
Process pressure	1 ~ 2.5 Pa

In addition, plasma etching of HfO_2 films was investigated by changing the etching parameter including in Table 1.

The etch rate was measured by the surface profiler (KLA Tencor, α-step 500). The compositional changes on the etched HfO_2 surface were investigated using X-ray photoelectron spectroscopy(ESCALAB 250).

3. RESULTS AND DISCUSSION

For the characterization of HfO_2 thin film in an ICP system, the plasma etching of HfO_2 thin film and Si was systematically investigated as a function of the CH_4/Ar gas mixing ratio. Figure 2 shows that the etch rate of HfO_2 thin film and Si as a function of CH_4/Ar plasma gas mixing ratio when total flow rate was maintained at 20 sccm. Other process conditions such as RF power, DC-bias voltage and process pressure were also maintained at 600 W, -150 V, and 2 Pa, respectively. As the CH_4/Ar gas mixing ratio increases, the etch rates of HfO_2 thin film decreases, whereas the selectivity of HfO_2 to Si decreases. The maximum etch rate of HfO_2 is 28.8 nm/min at a $CH_4/(CH_4+Ar)$ of 20 % and decreased with further addition of CH_4 gas.

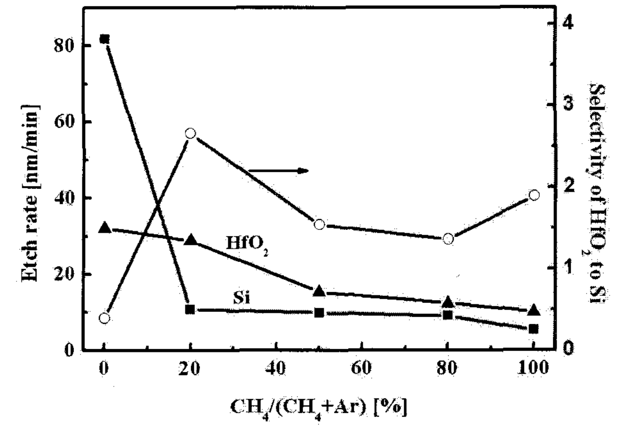

Fig. 2. Etch rate of HfO_2 thin film and selectivity of HfO_2 thin films to Si as a function of CH_4/Ar gas mixing ratio.

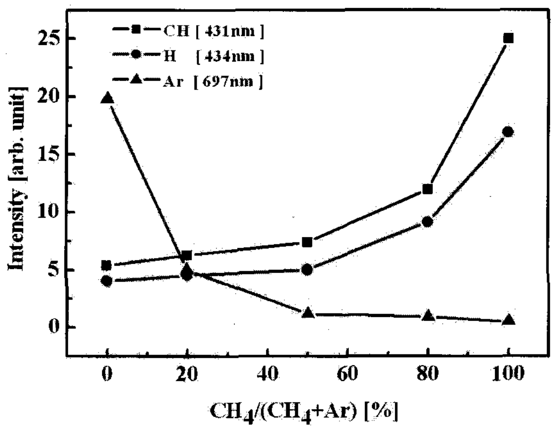

Fig. 3. The optical emission intensity as a function of CH_4/Ar gas mixing ratio.

This fact allows one to assume that, for a given range of experimental condition, physical etch pathway is more effective than chemical one. In our opinion, a domination of physical etch pathway may be explained by two reasons. The first of the melting point for HfC is about 3000 °C, so that it cannot be related to hardly volatile compounds. The second of the strength of Hf-C chemical bond (540 kJ/mol) is higher than one for Hf-O (802 kJ/mol). Therefore, C atoms formed in plasma can react with HfO_2 spontaneously and no ion bombardment is needed to support physical reaction by breaking oxide bonds. As for the non-monotonic behavior of the HfO_2 etch rate, one can propose at least three mechanisms to explain this effect: 1) non-monotonic changes of both volume densities and fluxes of active species resulted from the influence of plasma parameters on volume kinetics; 2) a concurrence of two etching mechanisms with monotonic, but opposite tendencies to change with

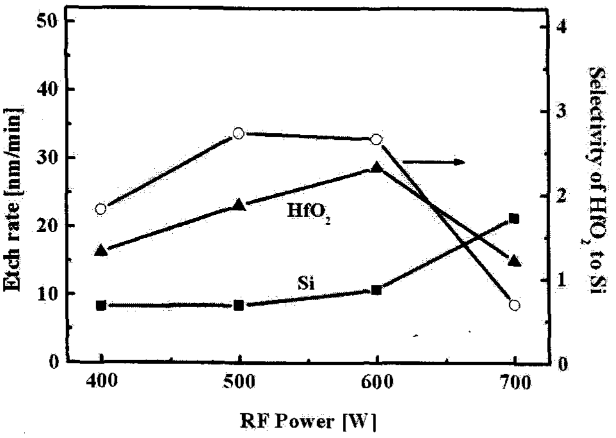

Fig. 4. Etch rate of HfO_2 thin film and selectivity of HfO_2 thin films to Si as a function of RF power.

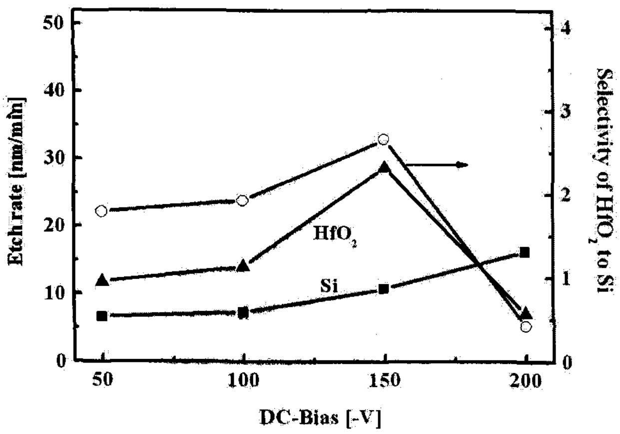

Fig. 5. Etch rate of HfO_2 thin film and selectivity of HfO_2 thin films to Si as a function of DC-Bias voltage.

decreasing CH_4 mixing ratio (for example, decreasing flux of chemically active species and increasing efficiency of ion stimulated desorption of reaction products due to increasing flux of Ar^+ ions); and 3) lowering the rate of physical reaction in CH_4-rich plasma due to a deposition of solid inorganic compounds resulted from a complete dissociation of CH_4 molecules. In earlier works devoted to both experimental investigation[16] and modeling[17] of CH_4/Ar plasma in ICP systems, it was shown that variation of gas mixing ratio causes monotonic changes of electron density, electron temperature, total ion density and C atom density. Accordingly, we can assume the same monotonic behaviors for fluxes of these species and, in fact, the first mechanism among ones proposed above can be neglected. As for second and third mechanism, in our opinion they do work simultaneously; this conclusion is in good agreement with the data of Fig. 4 and Fig. 6.

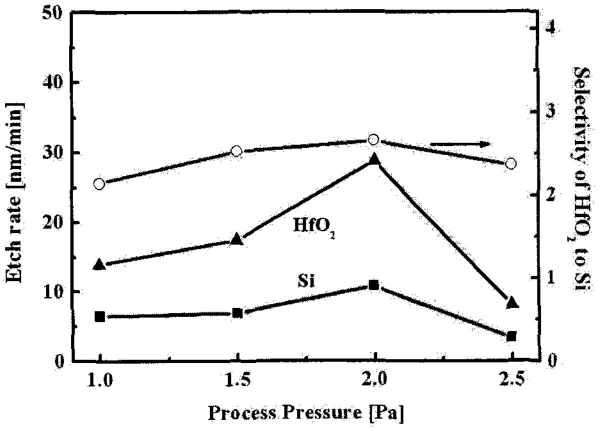

Fig. 6. Etch rate of HfO_2 thin film and selectivity of HfO_2 thin films to Si as a function of process pressure.

To get more information on the HfO_2 etch mechanism, we used OES analysis to determine the ionic composition of CH_4/Ar plasma. As shown in Fig. 3, it can be seen that a dominant type of positive ion in CH_4-rich plasma is CH; this fact is in good agreement with published data[18]. Although the intensity of CH peak has a weak maximum at pure CH_4 that corresponds to a maximum of HfO_2 etch rate, the difference between maximum intensity and the intensity in pure CH_4 plasma is small and quite close to an experimental error. That is why we prefer to speak only about a saturation of CH density in CH_4-rich plasma.

However, even it such maximum do exist, the non-monotonic behavior of CH density cannot be accepted as an explanation for a non-monotonic HfO_2 etch rate. In CH_4-rich plasma, chemical etch pathway dominates over physical one, so the contribution of physical sputtering by CH ions seems to be insufficient. Therefore, it is hardly believable that a weak maximum on the CH density can produce a strong maximum on the HfO_2 etch rate.

Figure 4 shows the etch rate of HfO_2 as a function of RF power for CH_4 (20 %)/Ar (80 %) plasma. As RF power increases, the HfO_2 etch rate also increases starting from 16.3 nm/min at 400 W, but then reaches a maximum of 28.8 nm/min at 600 W and decreases rapidly down to 15.1 nm/min at 700 W. From Refs, it can be seen that an increase in RF power causes a monotonic increase in both dissociation and ionization rates and thus, in densities and fluxes of C atoms and positive ions. In our case, such layer can result from the deposition of solid C that then is bonded with surface oxygen to form Hf-H as well as from H radicals incorporated in the polymer-like structure.

The etch rates of HfO_2 and Si, and the selectivity of HfO_2 to Si are shown in Fig. 5 as functions of dc-bias voltage. As the dc-bias voltage increases from 50 to 200 V, the etch rate of HfO_2 increases from 11.8 to 28.8 nm/min. The etch rates of Si increases from 6.6 to 10.8 nm/min,

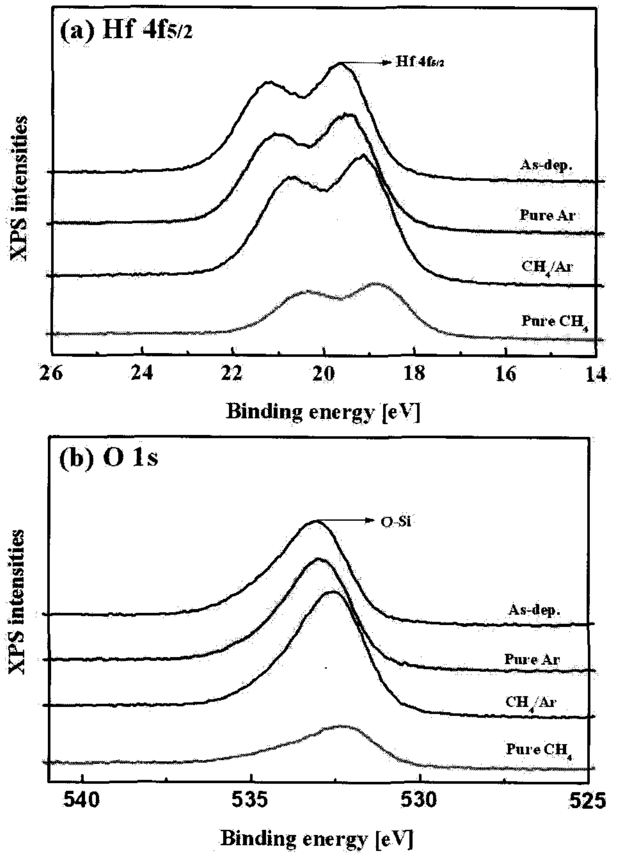

Fig. 7. (a) Hf 4f and (b) O 1s XPS narrow scan spectra of HfO_2 thin film surface etched.

respectively. The selectivity of HfO_2 to Si was slightly increased. An increase in etch rate can be related to the increase of mean ion energy resulting in increasing sputtering yields for both HfO_2 and reaction products[19].

Figure 6 shows the etch rate of HfO_2 as a function of process pressure for CH_4 (20 %)/Ar (80 %) plasma. As for the effect of process pressure, in our opinion the situation looks as follows. An increase in process pressure increases the density of neutral chemically active species, but lowers ion mean free path and ion energy. As a result, with increasing process pressure, we have a tendency to acceleration in physical etch pathway, but a worse condition for ion stimulated desorption of reaction products resulting, probably, in decreasing fraction of free surface acceptable for chemical reaction. Similarly to the effect of gas mixing ratio, these two factors working in opposite direction produce a non-monotonic behavior of the etch rate.

To investigate chemical states of the etched surfaces of the HfO_2 thin films, the XPS analysis was used. Figure 7 shows that the $Hf_{5/2}$ 4f (a) and O 1s (b) spectra were at a binding energy of 19.65 eV and 533.1 eV respectively[18], suggesting that Hf remained fully oxidized after etching. These spectra intensity on the as-deposition, pure Ar plasma, CH_4/Ar plasma were closely similar because of volatile etching by-product. The etching in pure Ar plasma causes a noticeable decrease in $Hf_{5/2}$ 4f peak that can be attributed to a destruction of oxide bonds by ion bombardment. However, as the CH_4 content in the CH_4/Ar plasma increases, the intensity of this peak also increases[20,21]. This effect can connected with an accumulation of etch products because the difference between binding energies for Hf(4f) – O and Hf(4f) – C is very small. Figure 7(b) show that the intensities of 533.1 eV peak was reversed for the data obtained from the as-deposited and etched samples. That is, the shoulder peak indicated as O-Si from the as-deposited sample is related to the formation of Hf-O bonds decreased significantly as a result of the preferential removal of the Hf atoms. With the addition of CH_4 gas, the Hf-O peak intensity became negligible, which demonstrates a dramatic increased chlorination of the etched surface. The intensities of the O-Si peaks decreased presumably due to the increased formation of $(CH_3)Hf_x$ in the air. There is also the possibility of O-H bond formation even though that was not demonstrated here.

4. CONCLUSION

We investigated etching characteristics of HfO_2 thin film and Si using inductive coupled plasma (ICP) system. Etching characteristics were investigated in the terms of HfO_2 thin film and selectivity of HfO_2 thin film over Si as a function of CH_4/Ar gas mixing ratio. The maximum etch rate of HfO_2 is 28.8 nm/min at a $CH_4/(CH_4+Ar)$ of 20 % and decreased with further addition of CH_4 gas. Due to the relatively high volatility of by-products formed during the etching by CH_4/Ar plasma, ion bombardment in addition to physical sputtering was required to obtain high HfO_2 selectivity. It was found that the reason for etch rate maximum is the concurrence of physical and chemical pathways in ion-assisted physical reaction. It was suggested that volatile oxygen compound such as the XPS result showed that the composition of the etched sampled in the CH_4 plasma is identical to that of the as-deposited sample. These tendency was very similar to the etch characteristics. This result agreed with the general energy dependency of ion enhanced chemical etching yields.

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