

Dry Etching of High-k Dielectric Thin Films in HBr/Ar Plasma

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High-k thin films (HfO_2 and Al_2O_3) were etched in HBr/Ar high-density plasma. HfO_2 and Al_2O_3 with high dielectric constants are promising candidates for the gates of metal-oxide-semiconductor devices. The maximum etch rates for HfO_2 and Al_2O_3 were 49.1 nm/min and 42.5 nm/min, respectively. The etch rates of both HfO_2 and Al_2O_3 thin films were faster for higher contents of HBr. The chemical states of high-k thin films were investigated using X-ray photoelectron spectroscopy. The comparisons of the as-deposited and the etched thin films for Hf 4f, Al 2p and O 1s showed few changes in the peak shapes and their binding energies were moved to higher energy after exposure to a HBr plasma. No new peaks due to etching byproducts appeared. Clean side wall and the steep etch profiles for high-k thin films could be obtained using a 100 % HBr plasma. These results indicate that HfO_2 and Al_2O_3 thin films can be effectively removed by using a chemical etching process.

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I. INTRODUCTION

As dimensions of metal-oxide-semiconductor field-effect transistor (MOSFET) devices are scaled down, the gate width will decrease to much less than 50 nm. The thickness of gate dielectrics, SiO_2 , should be reduced down to 2 nm or less. The thickness reduction of SiO_2 brings many serious problems, such as increased gate leakage current and reduced oxide reliability [1–6]. In order to overcome these challenges, high dielectric constant materials, such as HfO_2 , Al_2O_3 and ZrO_2 , have been widely studied and can be obtained as stable thin films. In the manufacturing process for ultra large scale integration (ULSI) device, the feature size of the etching mask was defined by using photolithography and was then precisely transferred by using a dry etch process. Therefore, plasma etching has largely been used because the characteristics of vertical direction etching make it possible to obtain an anisotropic etching profile.

The etching process of HfO_2 and Al_2O_3 thin films has been investigated using $\text{BCl}_3/\text{C}_4\text{F}_8/\text{Ar}$, $\text{Cl}_2/\text{SF}_6/\text{Ar}$ and $\text{BCl}_3/\text{Ar}/\text{O}_2$ plasmas [7–9]. Obtaining patterns for high-

k thin films is well known to be difficult when using current lithography with a photoresist mask and a dry etching process. The most important factor is the selectivity against both the etching mask and the underlayer. The advantage of using a HBr plasma is that the 193-nm photoresist deformation caused by UV radiation from the plasma was effectively reduced by the HBr pretreatment [10–12]. The boiling points of the etch byproducts are relatively low: HfBr_2 (319 °C), AlBr_3 (255 °C) and ZrBr_4 (360 °C). In addition, in our previous study on etching in a 100 % HBr plasma, we obtained a higher etch rate of over 40 nm/min than we did with 100 % Ar, 100 % CF_4 and 100 % SF_6 plasmas. There was no degradation of the photomask, such as bull's horn in a 100 % SF_6 plasma and no slop on the top corner photoresist mask in a 100 % Cl_2 plasma. In order to understand what plasma parameters are important in etching high-k materials in HBr/Ar plasma, we investigated the behavior of etch rate and the etch selectivity as well as the etch profile.

In this research, we investigated the etch characteristics of high-k thin films by using a high-density plasma (HDP) etching system with a HBr/Ar plasma. The etch rates of HfO_2 and Al_2O_3 were monitored for various gas

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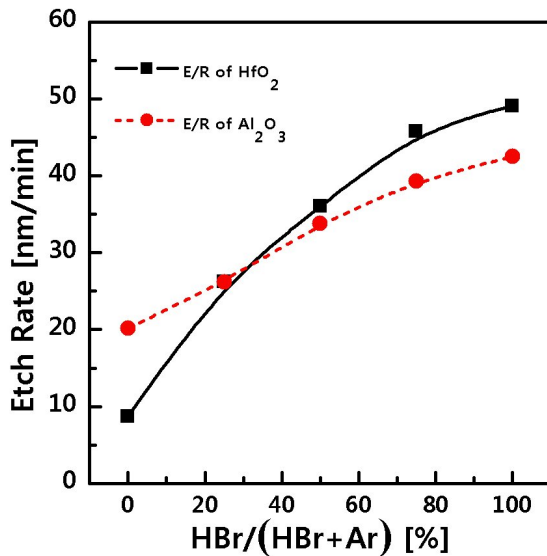


Fig. 1. Etch rate of HfO₂ and Al₂O₃ thin films as a function of HBr mixing ratio in a HBr/Ar plasma.

mixing ratios. The adaptation and the optimization of the etching processes for high-k thin films require a full-scale understanding of the relationships between the gas mixing ratio and the chemical reactions on the surface. The chemical states of high-k thin films were investigated using X-ray photoelectron spectroscopy (XPS) on the etched surfaces and the results were compared with those for the as-deposited films. The patterns of Al₂O₃ and HfO₂ were investigated with using field emission scanning electron microscopy (FE-SEM)

II. EXPERIMENT

The high-k thin films (HfO₂ and Al₂O₃) was deposited on p-type Si (100) 5-inch wafers (5 ~ 30 Ω·cm) by using a Nano ALD 2000™ system [13]. In order to remove the native oxide, we cleaned the wafers in a HF solution and rinsed them in de-ionized water before deposition process. The precursor of hafnium was tetrakis (ethyl-methylamino) hafnium (TEMAHf) and the precursor of aluminum was tri-methyl-aluminum (TMA). Ozone was used as an oxidant. TEMAHf and TMA were sustained at 90 °C and 40 °C, respectively and were delivered to the reactor through a bubbler. The carrier gas was Ar and its flow rate was 400 sccm. The ALD deposited high-k thin films (HfO₂ and Al₂O₃) were etched in a HDP etcher [14].

The etching conditions were as follows: a total pressure of 10 mTorr, a source power of 400 W, a bias power of 100 W, a total gas flow rate of 100 sccm and a temperature of 45 °C. The etch rate of the high-k thin films was measured, by using a surface profiler (KLA Tecor, a-step 500), as a function of the HBr gas mixing ra-

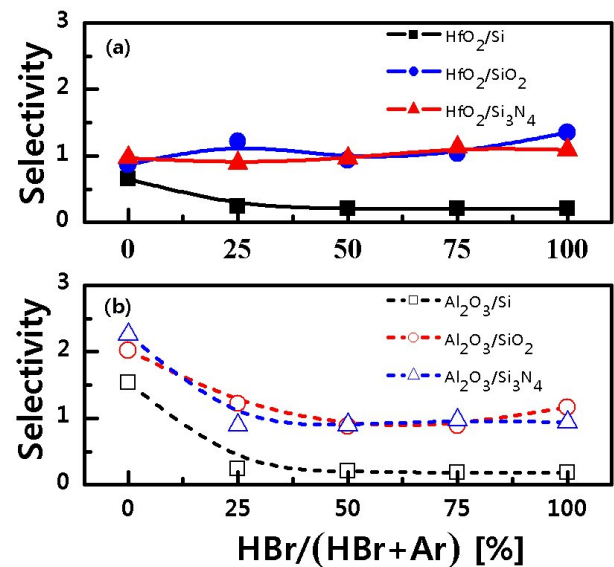


Fig. 2. Selectivity of high-k thin films (HfO₂ and Al₂O₃) to Si, SiO₂ and Si₃N₄ as a function of the HBr mixing ratio in a HBr/Ar plasma.

tio in a HBr/Ar plasma. The analysis of the chemical states of the etched surfaces was carried out using XPS (SIGMA PROBE, Thermo VG Scientific). The 100 W XPS Al Kα source provided non-monochromatic X-rays at 1486.6 eV. Narrow scan spectra of all interested regions were recorded at a pass energy of 20 or 40 eV to identify the chemical binding state. The etch profiles of the HfO₂ and the Al₂O₃ thin films were investigated using FE-SEM (Sirion 400, FEI).

III. RESULTS AND DISCUSSION

The etch rates, etch selectivities and the surface states of the high-k thin films were investigated as a function of the HBr mixing ratio in a HBr/Ar plasma. Figure 1 describes the etch rates of the HfO₂ and the Al₂O₃ thin films as functions of HBr mixing ratio in a high-density HBr/Ar plasma. As shown in Figure 1, in an Ar-only plasma, the etch rates of HfO₂ and Al₂O₃ were 8.7 nm/min and 20.2 nm/min, respectively. As the HBr mixing ratio increase from 25 % to 100 %, the etch rates of both HfO₂ and Al₂O₃ tended to increase and reached a maximum etch rate. The maximum etch rates for HfO₂ and Al₂O₃ for a 100 % HBr plasma were 49.1 nm/min and 42.5 nm/min, respectively. This result can be explained as follows: The melting points of the etch byproducts (HfBr₄: 424 °C and AlBr₃: 97.5 °C) are low and the byproducts can be easily removed from the surface of high-k thin films surface [15]. In addition, the higher etch rates for both HfO₂ and Al₂O₃ in HBr compared with an Ar-only plasma can be explained by the fact that the bias voltage in HBr is higher than that in

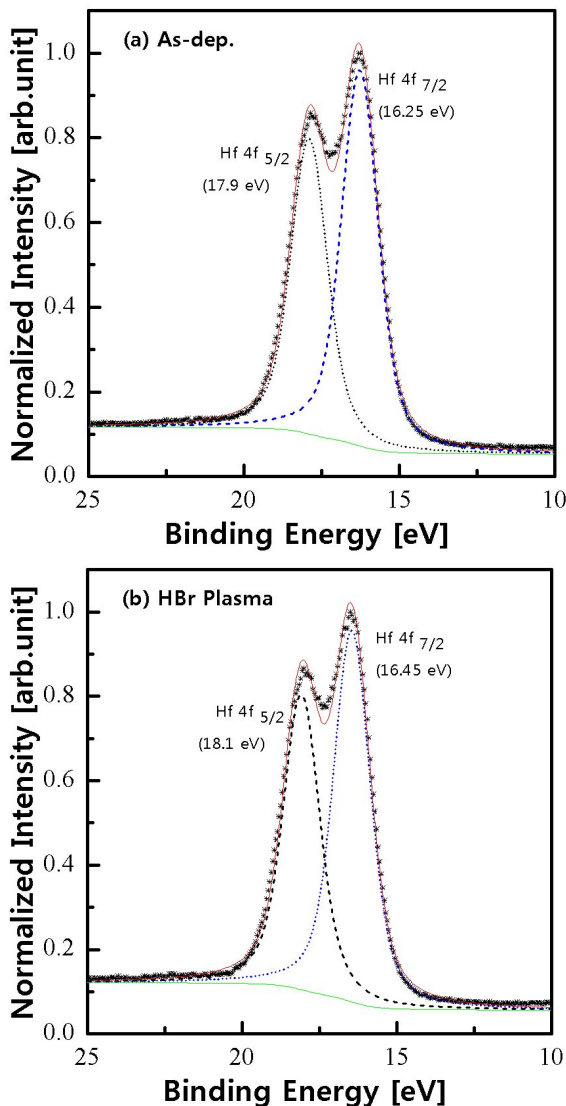


Fig. 3. XPS narrow scan spectra of Hf4f of HfO₂ thin films: (a) as-deposited and (b) etched by using a HBr plasma.

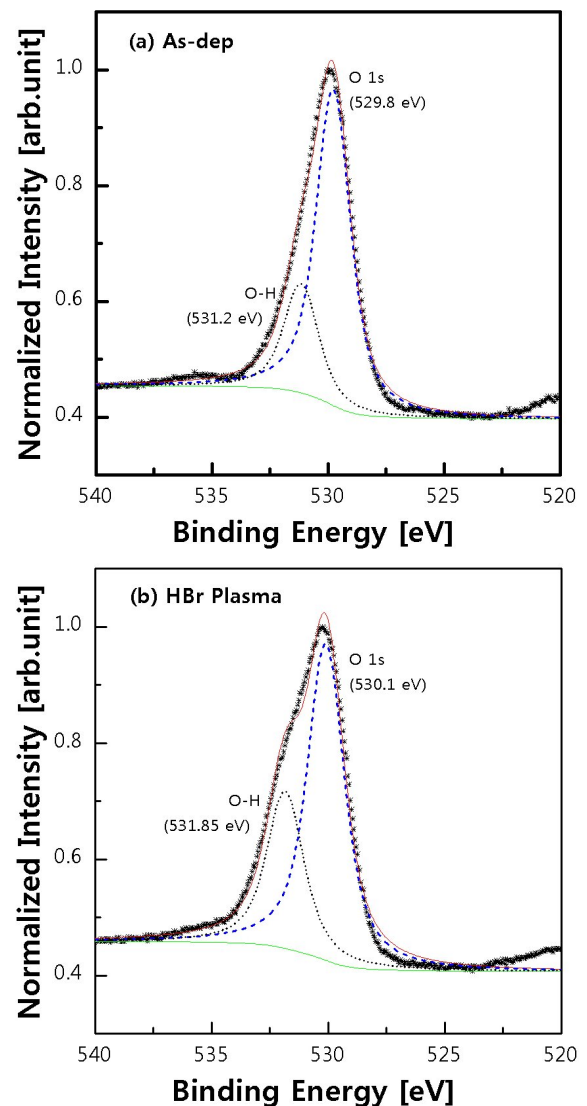


Fig. 4. XPS narrow scan spectra of O 1s of HfO₂ thin films: (a) as-deposited and (b) etched by using a HBr plasma.

an Ar-only plasma at a fixed bias power [16].

Figure 2 shows the selectivities of high-k thin films (HfO₂ and Al₂O₃) to Si, SiO₂ and Si₃N₄, which can be used as underlayers or mask materials. The selectivities of HfO₂ to SiO₂ and Si₃N₄ showed little variation. On the other hand, the selectivities of HfO₂ to Si and Al₂O₃ decreased with increasing HBr from 0 % to 100 % in a HBr/Ar plasma. This can be explained by the Si being effectively removed in HBr and the selectivities becoming worse. The different tendencies of the selectivities of high-k materials to SiO₂ and Si₃N₄ are still under discussion.

The etch rate highly depends on the etching conditions, such as the gas mixing ratio, the RF power, pressure, the temperature and the etch system. As a result, the adaptation and the optimization of etching processes

for high-k dielectrics require a full-scale understanding of the relationships between the gas mixing ratio and the chemical reactions on the surface. The chemical states of high-k dielectrics were investigated using XPS from the etched surfaces and the results were compared with those for as-deposited dielectrics. The narrow scan spectra of the Hf 4f, Al 2p and O 1s peaks were fitted using XPS Fitt 1.2 (GTK) program.

Figures 3 and 4 show narrow scans of Hf 4f and O 1s peaks from as-deposited and etched HfO₂ thin films. For the as-deposited HfO₂ film in Figure 3(a), the Hf 4f peak can be decomposed into two peaks, one at 16.25 eV (Hf4f_{7/2}-O) and the other 17.9 eV (Hf4f_{5/2}-O) [17]. After the HfO₂ thin film was exposed in a HBr plasma, the peak shapes of the Hf 4f spectra did not change drastically. Only the binding energies of Hf 4f shifted

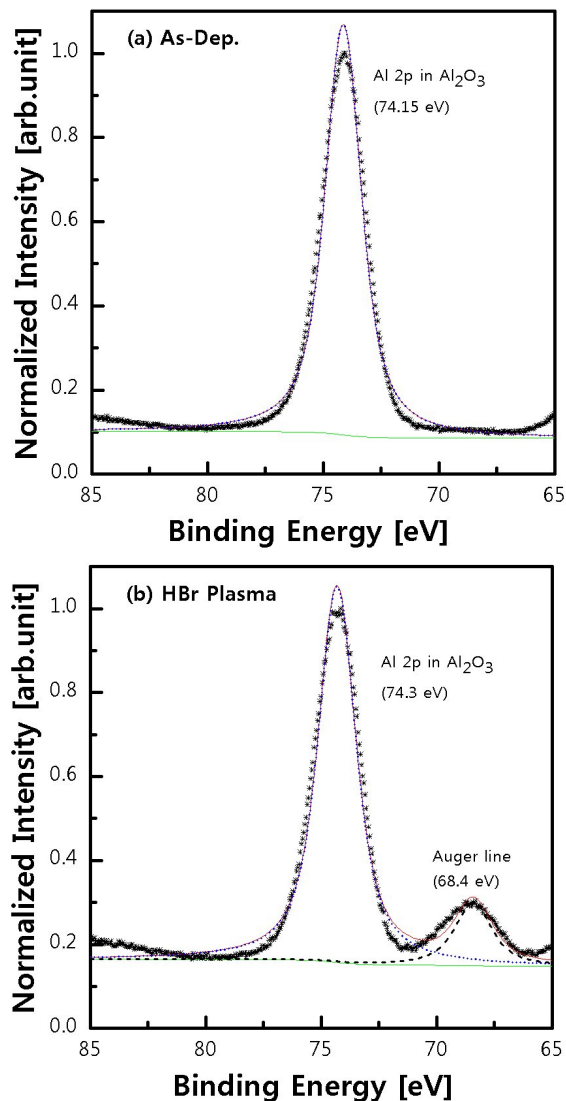


Fig. 5. XPS narrow scan spectra Al 2p of Al₂O₃ thin films: (a) as-deposited, and (b) etched by using a HBr plasma.

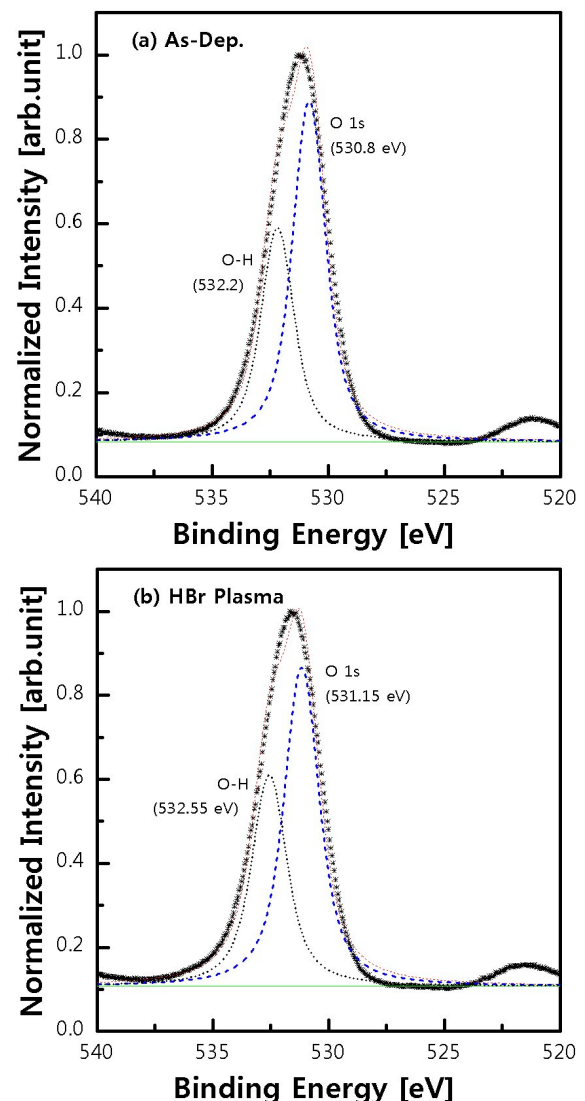


Fig. 6. XPS narrow scan spectra O 1s of Al₂O₃ thin films: (a) as-deposited and (b) etched by using a HBr plasma. (a) HfO₂ (b) Al₂O₃.

to about 0.2-eV-higher binding energies. This result can be explained by the fact that the surface was chemically modified deep into the layer up to a couple of nanometers [17]. In Figure 4(a), the O 1s peak can be decomposed into two peaks, one at 529.8 eV (Hf-O) and the other at 531.2 eV (O-H) from absorbed water [18,19]. After etching HfO₂ in a HBr plasma, these peaks shifted to about 0.3- and 0.65-eV-higher binding energies of 530.1 eV and 531.85 eV. This can be also explained by the modification of the surface layer.

The narrow scan of the Al 2p and the O 1s peaks from as-deposited and etched Al₂O₃ thin films are shown in Figure 5 and Figure 6. Similar results were obtained in the Al₂O₃ narrow scan spectra. As shown in Figure 5(a), the Al 2p peak consisted of a peak at 74.15 eV, which is metallic Al in Al₂O₃. After etching in a HBr

plasma, a new peak appeared at 68.4 eV and this peak corresponded to Auger electron lines [18,19]. There is no chemical residue, such as an Al-Br bond, on the etched surface owing to the low melting point of AlBr₃ (97.5 °C). In Figure 6(a), two peaks, one at 530.8 eV and the other at 532.2 eV, corresponded to the Al-O bond and the O-H bond from absorbed water, respectively [20]. When the Al₂O₃ thin film was etched in a HBr plasma, no new peaks appeared. The binding energies for Al-O and O-H were shifted to by only about 0.3 eV to higher binding energies of 531.15 eV and 532.55 eV, respectively.

Figure 7 shows SEM images of the HfO₂ and the Al₂O₃ thin films. After etching the high-k thin films in a HBr (25 %)/Ar (75 %) plasma, we could obtain a clean side wall and a steep etch profile for HfO₂ and Al₂O₃. The interface between Al₂O₃ and SiO₂ was unclear. The clean

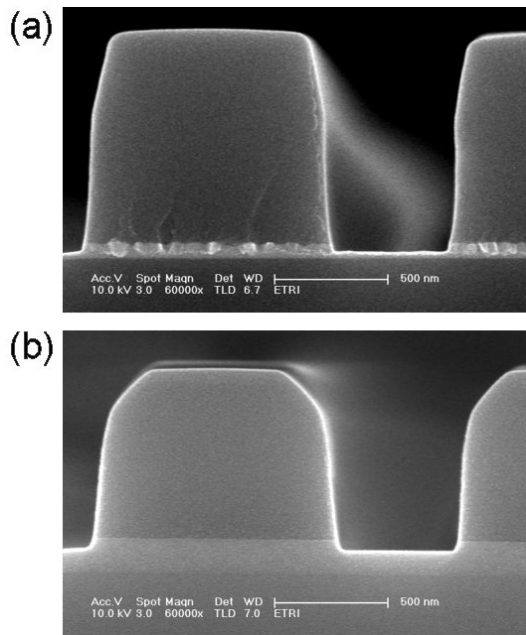


Fig. 7. SEM images of HfO_2 and Al_2O_3 etched in a HBr (25 %)/Ar (75 %) plasma.

surface confirmed the estimate of no etch residue in a HBr plasma, which was discussed above in the XPS analysis.

IV. CONCLUSION

High-k thin films (HfO_2 and Al_2O_3) were etched in a HBr/Ar plasma. The maximum etch rates of both the HfO_2 and the Al_2O_3 thin films were obtained in a 100 % HBr plasma. The etch rates for both HfO_2 and Al_2O_3 thin films became faster for high contents of HBr. The XPS narrow scan spectra showed that the peak shapes of Hf 4f, Al 2p and O 1s from the as-deposited thin films were similar to those from the thin films etched in a HBr plasma. In the narrow scan XPS analysis, HfBr_4 and AlBr_3 did not appear. Steep etch profiles and clean side walls were obtained for HfO_2 and Al_2O_3 when using a 100 % HBr plasma. From the results of our experiments, we can conclude that HfO_2 and Al_2O_3 thin films can be effectively removed by using a chemical etching process without producing etching byproducts.

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