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Etching Characteristics of HfAlO₃ Thin Films Using an Cl₂/BCl₃/Ar Inductively Coupled Plasma

Tae-Kyung Ha, Jong-Chang Woo, and Chang-Il Kim[†]
School of Electrical and Electronics Engineering, Chung-Ang University, Seoul 156-756, Korea

In this study, we changed the etch parameters (gas mixing ratio, radio frequency [RF] power, direct current [DC]-bias voltage, and process pressure) and then monitored the effect on the HfAlO₃ thin film etch rate and the selectivity with SiO₂. A maximum etch rate of 108.7 nm/min was obtained in Cl₂ (3 sccm)/BCl₃ (4 sccm)/Ar (16 sccm) plasma. The etch selectivity of HfAlO₃ to SiO₂ reached 1.11. As the RF power and the DC-bias voltage increased, the etch rate of the HfAlO₃ thin film increased. As the process pressure increased, the etch rate of the HfAlO₃ thin films increased. The chemical state of the etched surfaces was investigated with X-ray photoelectron spectroscopy. According to the results, the etching of HfAlO₃ thin film follows the ion-assisted chemical etching.

Keywords: Etch, HfAlO₃, Inductively coupled plasma, X-ray photoelectron spectroscopy

1. INTRODUCTION

Recently, High-k materials have been widely studied as potential candidates for alternative gate dielectrics in the 30 nm technology node and below. Continuous downscaling of devices brings new challenges to gate insulator materials. To increase density and speed as well as decrease operating power, the thickness of gate material has been decreased to below 1.2 nm. SiO₂ at thicknesses below 1.2 nm suffers from increased gate leakage, reduced reliability, and increased dopant diffusion [1]. One solution to the problem is the replacement of SiO₂ by High-k material. Hf-based High-k dielectric materials are investigated such as HfO₂, HfON, HfSiO, and HfSiON have been investigated. However, the HfAlO₃ has better material properties than does HfO₂. Zhu et al. [2] reported that the inclusion of Al in HfO₂ increases the crystallization temperature from 375°C to 1,000°C and the band gap from 5.8 eV to 6.5 eV. The HfAlO₃ thin film is the most advanced candidate to substitute present gate oxides because of its stable oxide formation.

Until now, there has been a little research devoted to the investigation of the etching characteristics of HfAlO₃ thin films using chlorine-based plasma chemistries but the etch mechanisms

have not been considered and the relationships between the process parameters or the chemistry involved have not been discussed [3, 4]. Therefore, further work on the study of HfAlO₃ thin films is needed.

In this study, the HfAlO₃ thin films were etched in a Cl₂/BCl₃/Ar plasma. The etching characteristics of the HfAlO₃ thin films were investigated in terms of the etch rates and selectivity as a function of the gas mixing ratio, radio frequency (RF) power, direct current (DC)-bias voltage, and process pressure. The chemical reaction on the surface of the etched HfAlO₃ thin films was investigated using X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTS

The HfAlO₃ and SiO₂ thin films were deposited on Si(100) wafers by atomic layer deposition (ALD) and thermal oxidation, respectively. The thickness of the HfAlO₃ thin films was 50 nm and that of SiO₂ was 10 nm. Before the deposition of the HfAlO₃ thin films, a pre cleaning and oxidation step of the Si wafer is required in order to obtain good thermal interface compatibility between HfAlO₃ thin film and the silicon substrate. The dry etching of the HfAlO₃ thin films was performed using an inductively coupled plasma (ICP) system (Fig. 1) [5]. The gases used in the etching experiments include Cl₂, BCl₃, and Ar. The gas mixing ratio was

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[†] Author to whom all correspondence should be addressed:
E-mail: cikim@cau.ac.kr

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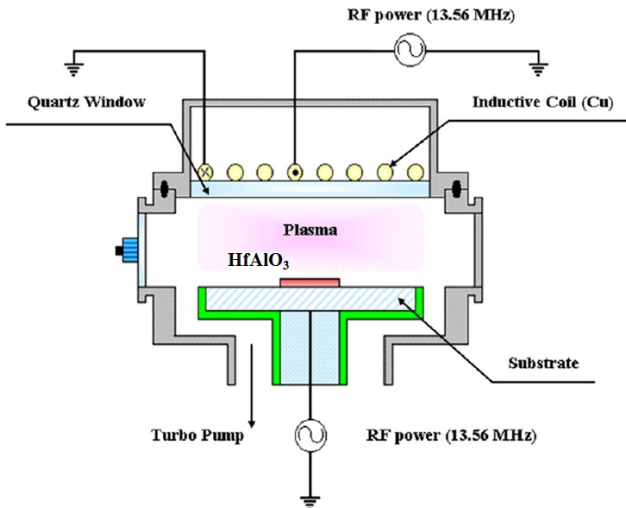Trans. Electr. Electron. Mater. 11(4) 166 (2010): T.-K. Ha *et al.*

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Fig. 1. The inductively coupled plasma system.

Table 1. Melting point and boiling point of the etch products at atmospheric pressure.

Materials	Melting point (°C)	Boiling point (°C)
HfO_2	2,774	-
$HfCl_4$	319	432
Al_2O_3	2,053	3,000
$AlCl_3$	192.6	180

Table 2. Gibb's free energy of volatile etch products in Hf-based material.

	Reaction	$\triangle G°f$ (kJ/mol)
	$HfCl_2$ (g)	-326.546
HfN	$HfCl_3$ (g)	-636.76
	$HfCl_4$ (g)	-850.774

fixed at BCl_3 (4 sccm)/Ar (16 sccm). The etching conditions were as follows: an RF power of 500 W, a DC-bias voltage of -100 V, and a process pressure of 2 Pa. The etch rates were measured using a depth profiler (alpha step 500, KLA Tencor). The chemical state of the etched $HfAlO_3$ surface was analyzed by XPS. The XPS spectra were collected using a VG Scientific ESCALAB 250 instrument equipped with an analytical chamber pumped to a base pressure of ~10^{-10} torr, a twin-anode X-ray source, and a spherical sector analyzer with multichannel detectors. For the analysis, the samples were mounted on stainless steel stubs using doublesided adhesive tape. The spectra were excited using Al *K*α radiation (*hν* = 1,486.6 eV). All XPS data were corrected for sample charging during X-ray irradiation using adventitious hydrocarbon referencing (C 1s at 284.6 eV).

3. RESULTS AND DISCUSSION

For the characterization of the $HfAlO_3$ thin films used in an ICP etching system, the plasma etching of the $HfAlO_3$ thin films and the selectivity of $HfAlO_3$ to SiO_2 was investigated as a function of the Cl_2/BCl_3/Ar gas mixing ratio, an RF power, a DC-bias voltage and a process pressure.

Figure 2 shows the etch rate of the $HfAlO_3$ thin films and selectivity of the $HfAlO_3$ to SiO_2 as a function of the gas mixing ratio. The maximum etch rate of the $HfAlO_3$ thin films were 66 nm/min on addition of Cl_2 (3 sccm) to BCl_3 (4 sccm)/Ar (16 sccm). The
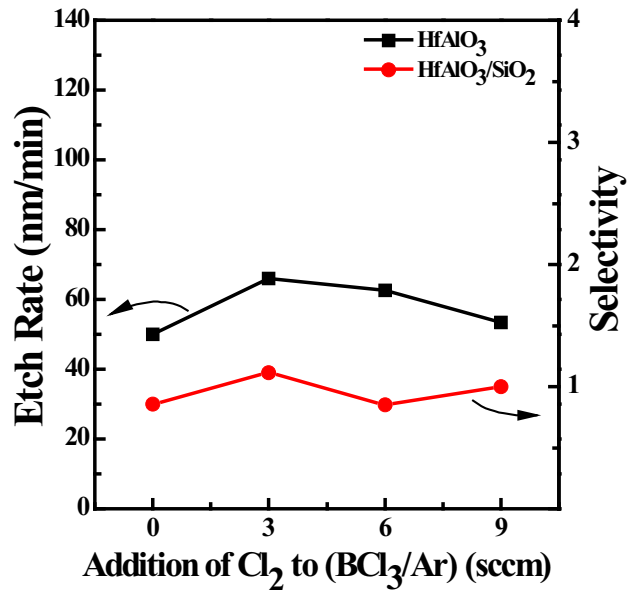

Fig. 2. Etch rate of $HfAlO_3$ thin films and selectivity of $HfAlO_3$ to SiO_2 as a function of the Cl_2/BCl_3/Ar gas mixing ratio.
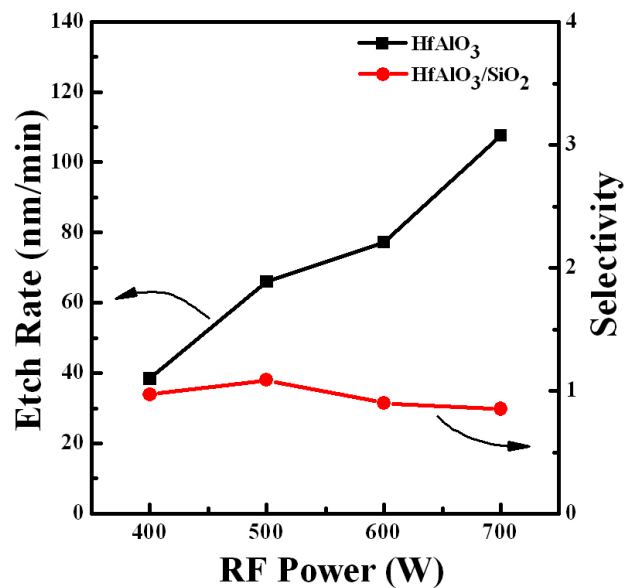

Fig. 3. Etch rate of $HfAlO_3$ thin films and selectivity of $HfAlO_3$ to SiO_2 as a function of the RF power.

selectivity was maintained between 0.85 and 1.11. Tables 1 and 2 show the melting point, boiling point, and Gibb's free energy, respectively. These data be explained by the fact by-products such as $HfCl_4$ and $AlCl_3$ were formed on the $HfAlO_3$ thin films in the etching process [6]. When the Cl_2 in BCl_3 was increased from 0 sccm to 3 sccm (4 sccm)/Ar (16 sccm) plasma, the density of the Cl radical increased, which resulted in an increasing etch rate. However, the etch rate showed decreasing tendencies when the Cl_2 content was increased from 3 sccm to 9 sccm in the BCl_3 (4 sccm)/Ar (16 sccm) plasma. This result can be explained by the fact that the kinetic energy was decreased, which leads to fewer bonds breaking inside the $HfAlO_3$ thin films under the influence of the Ar ion sputtering. Thus, the etch rate was decreased because of fewer reactions taking place on the surface, because of the low energy of the radical [7]. From these facts it is evident
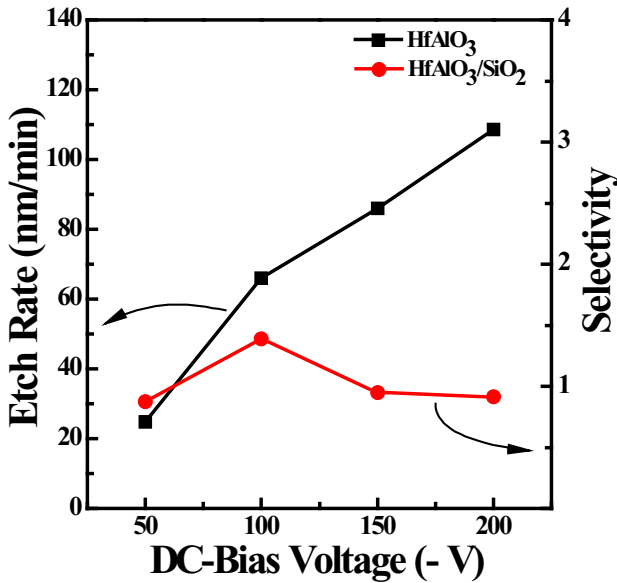
Fig. 4. Etch rate of HfAlO$_3$ thin films and selectivity of HfAlO$_3$ to SiO$_2$ as a function of the DC-bias voltage.
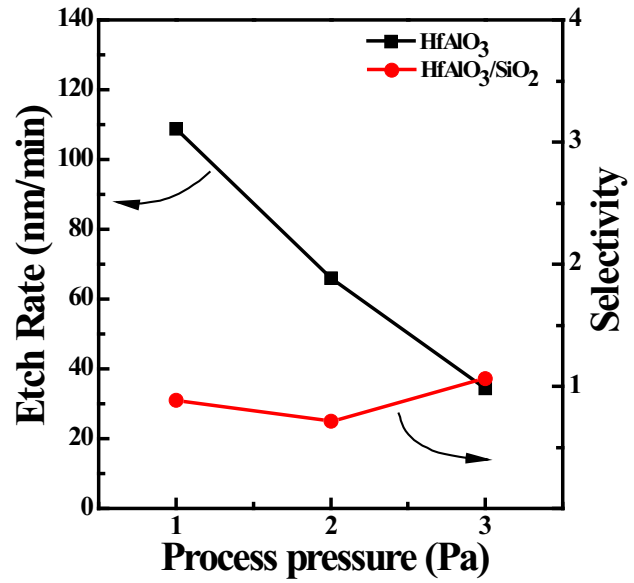
Fig. 5. Etch rate of HfAlO$_3$ thin films and selectivity of HfAlO$_3$ to SiO$_2$ as a function of the process pressure.
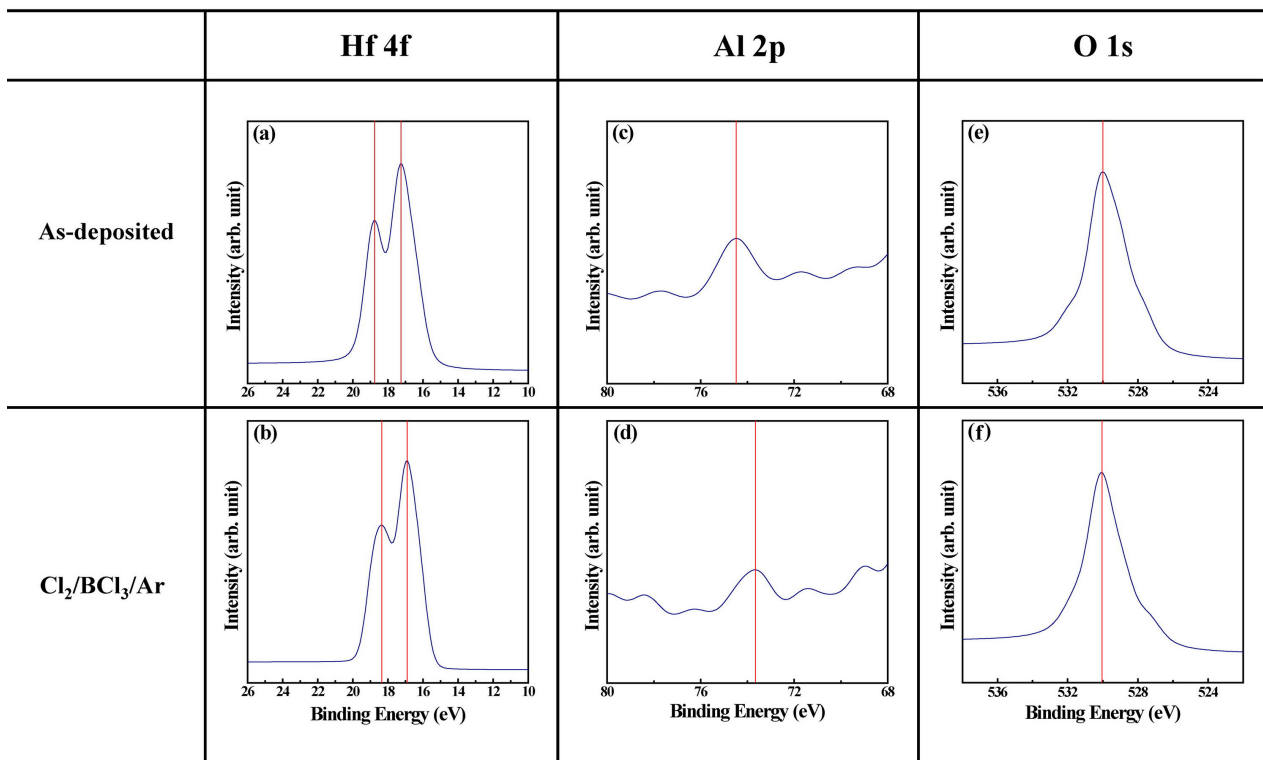

Fig. 6. The Hf 4f, Al 2p, and O 1s X-ray photoelectron spectroscopy narrow scan spectra of the HfAlO$_3$ with as-deposited and etched in Cl$_2$/BCl$_3$/Ar plasma.

that the etching mechanism acting on theHfAlO$_3$ thin film can be described as a physically-assisted chemical reaction in the Cl$_2$/BCl$_3$/Ar plasma.

Figure 3 shows the etch rate of the HfAlO$_3$ thin films and the selectivity of the HfAlO$_3$ to SiO$_2$ as a function of RF power. As the RF power applied to the ICP coil was raised from 400 to 700 W, the etch rates of the HfAlO$_3$ thin films increased from 38.4 to 107.7 nm/min. As the RF power was increased, the etch rate of HfAlO$_3$ also increased. Such behavior in response to increasing

input power at all etch rates may be explained by the acceleration of both the physical and chemical etching pathways through the growth of volume densities and fluxes of ions and chlorine atoms [8].

Figure 4 shows the etch rate of the HfAlO$_3$ thin films and selectivity of HfAlO$_3$ to SiO$_2$ as a function of DC-bias voltage. As the DC-bias voltage is increased from 50 to 200 V, the etch rate of the HfAlO$_3$ thin films increases from 24.8 to 108.6 nm/min. As the DC-bias voltage increases, the etch rate of the HfAlO$_3$ increased.

We can explain this result in terms of the increased electric field intensity caused by the increase in DC-bias voltage. An increased electric field intensity produces a higher ion bombardment energy [9]. Also, an increase in the etch rate can be related to the increase in the mean ion energy which generates increased sputtering yields for both the $HfAlO_3$ thin films and the reaction products.

Figure 5 shows the etch rate of the $HfAlO_3$ thin films and the selectivity of $HfAlO_3$ to SiO_2 as a function of process pressure. As the process pressure is increased from 1 to 3 Pa, a furthermore decrease in gas pressure up to 3 Pa results in a decrease in the $HfAlO_3$ thin film etch rate in the range of 108.75-34.5 nm/min. With a decrease in process pressure, the average ion energy increases because of the longer mean-free-path. When the mean-free-path increases, the probability of collisions and charge transfer decrease in the substrate sheath region [10]. This can be explained by the fact that the increase in the etch rate at low-pressure is due to an increase in both the flux and energy of the bombarding ions, caused by the increased mean-free-path.

In order to analyze the chemical states for the $HfAlO_3$ thin films, the $HfAlO_3$ surface exposed to the Cl_2 (3 sccm)/BCl_3 (4 sccm)/Ar (16 sccm) plasma was investigated by XPS. The input plasma parameters were set to an RF power of 500 W, a DC-bias voltage of -100 V, a process pressure of 2 Pa and a substrate temperature of 40°C. Figures 6(a)-(f) show the XPS narrow scan spectra of the $HfAlO_3$. No boron or chlorine peaks were detected. This result implies that the boron and chlorine compounds are highly volatile ones such as boron-oxy-chloride (BOCl) or trichloro-boroxin $(BOCl)_3$ [11].

Figures 6(a) and (b) show the peaks of the Hf 4f XPS narrow scan spectra of the as-deposited and etched $HfAlO_3$ thin films in Cl_2/BCl_3/Ar. There are two strong peaks at 18.8 eV and 17.1 eV from the as-deposited sample, which correspond to Hf $4f_{5/2}$ and Hf $4f_{7/2}$, respectively. These peaks moved toward a lower binding energy and their maximum deviation was about Δ 0.3 eV when the $HfAlO_3$ thin films were exposed to the Cl_2/BCl_3/Ar plasma. This chemical shift indicates that there are chemical reactions between the Hf and Cl radicals and the resulting etch byproducts remain on the surface. Figures 6(c) and (d) show the peaks of the Al 2p XPS narrow scan spectra of the as-deposited and etched $HfAlO_3$ thin films in Cl_2/BCl_3/Ar. There are peaks at 74.5 eV and 73.7 eV from the as-deposited sample and the sample etched in Cl_2/BCl_3/Ar, respectively. These peaks moved toward a lower binding energy and the maximum deviation was about Δ 0.8 eV. Compared with the as-deposited film, the Al peak intensity decreased when the $HfAlO_3$ thin films were exposed to the Cl_2/BCl_3/Ar plasma. This result means that Al atoms were removed from the $HfAlO_3$ thin films. The surface of the $HfAlO_3$ thin film reacts with the Cl radicals dissociated in the plasma, producing chloride compounds such as $AlCl_3$. Figures 6(e) and (f) show the peaks of the O 1s XPS narrow scan spectra of the as-deposited and etched $HfAlO_3$ thin films in Cl_2/BCl_3/Ar. There are strong peaks at 530 eV from the as-deposited sample and sample etched in Cl_2/BCl_3/Ar, respectively. There are no changes of intensity and binding energy for the O 1s peaks. This result means that the O atoms did not react.

Therefore, the XPS data give clear confirmation that the surface of the etched $HfAlO_3$ film is covered by low volatility etch products such as $Hf-Cl_4$ and $Al-Cl_3$. In this situation, the ion-stimulated desorption of the reaction products can be assumed to be the limiting stage for the etching process in the Cl_2 and BCl_3 rich plasmas whilst the etch rate is expected to be rather sensitive to the factors which are influenced by the ion bombardment.

4. CONCLUSIONS

In this study, the etching trend of the $HfAlO_3$ thin films was investigated as functions of the Cl_2/BCl_3/Ar gas mixing ratio, the RF power, the DC-bias voltage and the process pressure, using ICP. The maximum etch rate of the $HfAlO_3$ thin films was 108.7 nm/min and the selectivity of $HfAlO_3$ to SiO_2 was 1.11 at Cl_2 (3 ccm)/BCl_3 (4 sccm)/Ar (16 sccm). When the Cl_2 concentration was increased beyond 3 sccm, the etch rate of the $HfAlO_3$ thin film decreased, because higher concentrations of Cl_2 in the plasma decreased the physical effect. The $HfAlO_3$ etch rate increased linearly with increasing RF power and DC-bias voltage. However, we found that the maximum etch rate trend did not follow this trend. This result can be explained by the characteristics of the inner plasma, which is easily affected by the input parameters. The narrow scan of the XPS measurement showed that the binding energies of the Hf $4f_{7/2}$, Hf $4f_{5/2}$, and Al 2p peaks were shifted toward lower binding energies after the exposure of the films to the Cl_2/BCl_3/Ar plasma caused by the chemical reaction or intensity changes. From the results of the etch rate and analyses of XPS for $HfAlO_3$, the most probable determinant of the maximum etch rate can be defined as an ion-assisted chemical etching in Cl_2/BCl_3/Ar plasma.

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