



Dry Etching of Al_2O_3 Thin Films in $\text{O}_2/\text{BCl}_3/\text{Ar}$ Inductively Coupled Plasma

Xeng Yang, Jong-Chang Woo, Doo-Seung Um, and Chang-Il Kim[†]

School of Electrical and Electronics Engineering, Chung-Ang University, Seoul 156-756, Korea

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In this study, the etch properties of Al_2O_3 thin films deposited by atomic layer deposition were investigated as a function of the O_2 content in BCl_3/Ar inductively coupled plasma. The experiments were performed by comparing the etch rates and selectivity of Al_2O_3 over the hard mask materials as functions of the input plasma parameters, such as the gas mixing ratio, DC-bias voltage, radio-frequency (RF) power and process pressure. The highest obtained etch rate was 477 nm/min at an RF power of 700 W, O_2 to BCl_3/Ar gas ratio of 15%, DC-bias voltage of -100 V and process pressure of 15 mTorr. The deposition occurred on the surfaces when the amount of O_2 added to the BCl_3/Ar gas was too high at a low DC-bias voltage or high process pressure. X-ray photoelectron spectroscopy was used to investigate the chemical reactions on the etched surface.

Keywords: Al_2O_3 , $\text{O}_2/\text{BCl}_3/\text{Ar}$, Inductively coupled plasma, Etch

1. INTRODUCTION

The integrated circuit industry is always under pressure to shrink down the device size while maintaining good performance and many studies have been performed to address associated problems. In CMOS technology, the development of high- k materials, i.e. with a high dielectric constant (k), to address the current leakage problem has attracted a great deal of attention [1]. Concurrently, in mass storage memory devices, high- k dielectrics are also of great interest for applications driven by scaling [2]. According to the 2007 Edition of the International Technology Roadmap for Semiconductors (ITRSs), high- k materials will be introduced as a replacement for interpoly dielectrics in sub-28 nm NAND Flash technological nodes [3]. Among the various high- k materials, aluminum oxide (Al_2O_3) has the potential to be used for future generation devices due to its special physical and chemical properties [2]. With a k -value of ~ 10 , large bandgap (~ 6.5 eV) and elevated crystallization temperature [4], Al_2O_3 has been studied as a main candidate to replace oxide nitride oxide (ONO) as the poly-Si dielectric (IPD) in floating gate devices or as the blocking oxide (BO) for charge trap memories [5,6].

Several etching techniques have been studied to obtain a high etch rate and etch selectivity. Among them, the inductively coupled plasma (ICP) system was employed in our experiments due to the good properties of the high-density plasma, easy control of the ion energy and flux, and simple structure. Various gases, such as BCl_3 , CCl_4 , SiCl_4 , HF , and CHF_3 have been used to remove the native oxide (Al_2O_3) on the aluminum surface. The choice of BCl_3 as the chemically active gas in the present study results from the fact that it is widely used for the etching of materials covered by native oxides due to its effective extraction of oxygen in the form of BCl_xO_y compounds [7].

In this study, we used a BCl_3/Ar inductively coupled plasma with additional O_2 to etch the Al_2O_3 thin film. The etch rate and selectivity of Al_2O_3 over SiO_2 were investigated as functions of the gas ratio, RF power, DC-bias voltage and process pressure. X-ray photoelectron spectroscopy (XPS) was performed to investigate the chemical reactions between the surface of the Al_2O_3 films and $\text{O}_2/\text{BCl}_3/\text{Ar}$ plasma.

2. EXPERIMENTS

The Al_2O_3 thin films were etched by an ICP system. The substrates used were Al_2O_3 thin films deposited on a Si wafer using ALD. The thickness of the Al_2O_3 films was approximately 50 nm.

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

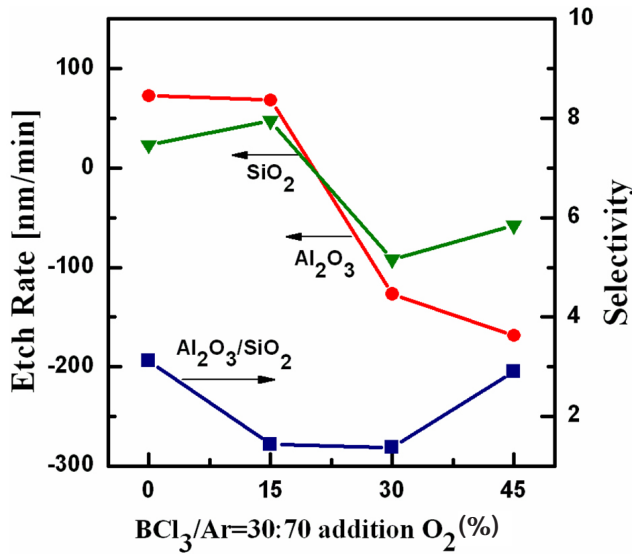


Fig. 1. The etch rates of the Al₂O₃ thin films and SiO₂ and selectivity of Al₂O₃ with respect to SiO₂ as a function of the amount of O₂ in the (BCl₃/Ar) plasma.

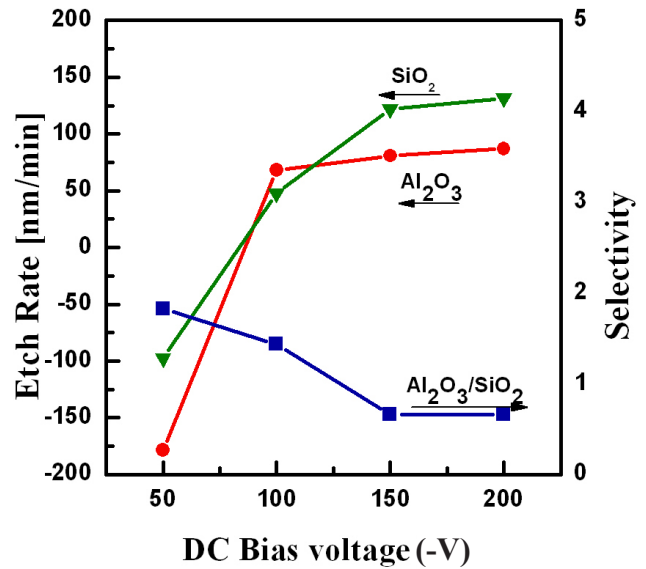


Fig. 3. The etch rates of the Al₂O₃ thin films and SiO₂ and selectivity of Al₂O₃ with respect to SiO₂ as a function of the DC bias voltage.

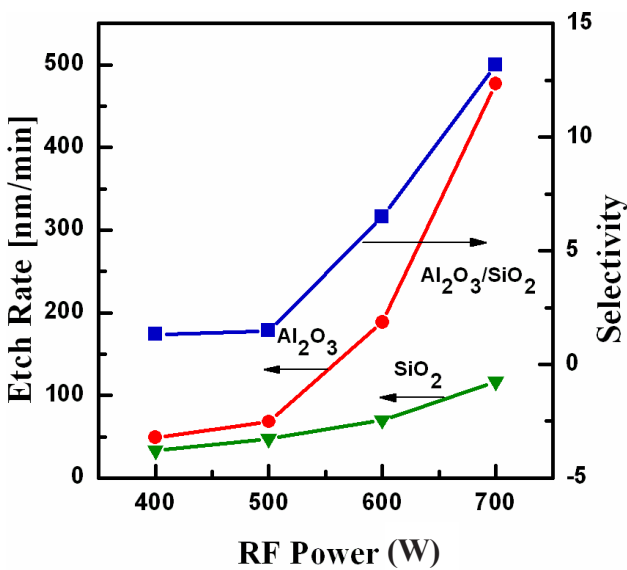


Fig. 2. The etch rates of the Al₂O₃ thin films and SiO₂ and selectivity of Al₂O₃ with respect to SiO₂ as a function of the RF power.

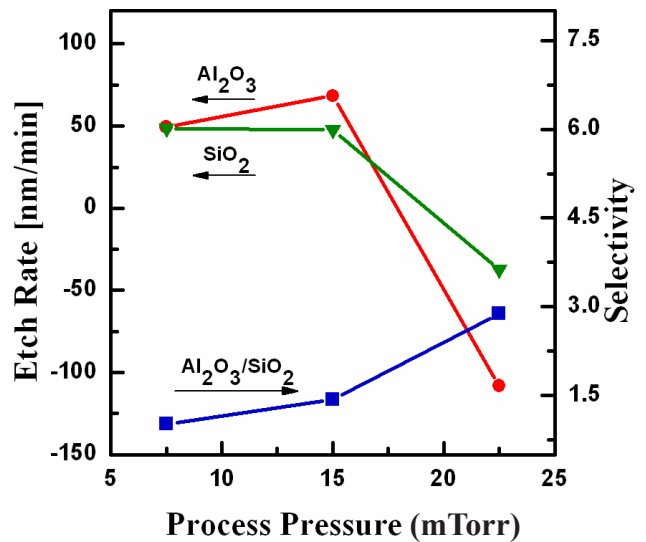


Fig. 4. The etch rates of the Al₂O₃ thin films and SiO₂ and selectivity of Al₂O₃ with respect to SiO₂ as a function of the process pressure.

The chamber was evacuated to a base pressure less than 1.3×10^{-4} Pa and then the etching gases were introduced. There was a gold-coated 3.5-turn copper coil on the top of the chamber separated by a 24 mm-thick quartz window. A 13.56 MHz RF power generator was connected through a matching network to the coil, in order to generate the plasma at the top of the process chamber. The wafers were placed on a chuck, which was used as the bottom electrode. The bottom electrode, which was used as the substrate holder, was connected to another 13.56 MHz asymmetric RF generator to apply a DC-bias voltage to the wafer.

In this experiment, the etching characteristics of Al₂O₃ as functions of the RF power in the range of 400-700 W, DC-bias voltage in the range of -50 to -200 V, process pressure in the range of 7.5-22.5 mTorr and gas ratio were investigated. The total flow of BCl₃/Ar was fixed at 20 sccm. A surface profiler (KLA Tencor, a-

step 500) was used to measure the etch thickness. XPS was used to analyze the elements on the film surface. The samples were prepared to 1 cm × 1 cm without any pattern.

3. RESULTS AND DISCUSSION

Figure 1 shows the etch rates of Al₂O₃ and SiO₂, the selectivity of the Al₂O₃ film over SiO₂ as a function of the gas ratio of O₂ to (BCl₃ + Ar). The total flow rate of BCl₃/Ar was fixed at 20 sccm and the flow rate of O₂ was varied from 0 to 9 sccm. The RF power, DC-bias voltage, process pressure and substrate temperature were 500 W, -100 V, 15 mTorr, and 40 °C, respectively. The BCl₃ gas facilitated the extraction of oxygen in the form of BCl_xO_y in the Al₂O₃ etching process. A high etch rate of 72 nm/min was obtained at O₂/BCl₃/Ar = 0/6/14. When 15% O₂ was added to the BCl₃/Ar gas, the etch rate was approximately 68.4 nm/min.

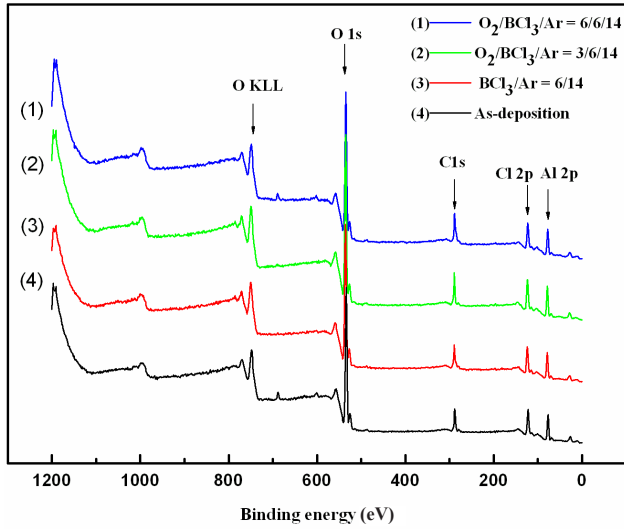


Fig. 5. The XPS wide-scan spectra of the Al_2O_3 surface for the as-deposited film and the film etched in the $\text{O}_2/\text{BCl}_3/\text{Ar}$ plasma.

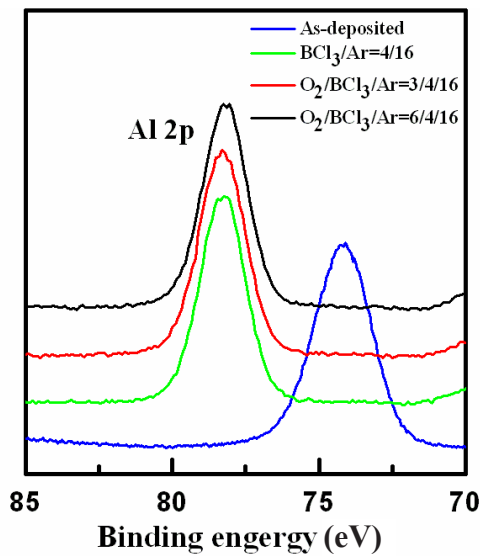


Fig. 6. The XPS narrow-scan spectra of Al 2p on the Al_2O_3 surface for the as-deposited film and the film etched in the $\text{O}_2/\text{BCl}_3/\text{Ar}$ plasma.

Continually increasing the gas ratio of O_2 caused heavy deposition, inhibiting the etching process on the surfaces of Al_2O_3 and SiO_2 . BCl_3 is highly reactive and a good at acquiring oxygen can form nonvolatile residues upon contact with oxygen or water [8]. One of the reactions between BCl_3 and O is $2\text{BCl}_3 + \text{O} \rightarrow \text{B}_2\text{O}_3 + 6\text{Cl}$. The melting point of the byproduct B_2O_3 is as high as 450°C . When a small amount of O_2 was added to the gas mixture, passivation layers of B_xCl_y formed on the surfaces would be suppressed due to the concentration reduction of the inhibitor species BCl_3 in the plasma through the formation of gaseous products via various reactions [e.g., $2\text{BCl}_2 + \text{O} \rightarrow \text{BOCl} + \text{BCl} + 2\text{Cl}$]. When an excessive amount of O_2 was added to the gas mixture, thick layers of B_xO_y would be deposited on the surface due to the formation of solid products in the plasma [e.g., $2\text{BCl}_3 + 3\text{O} \rightarrow \text{B}_2\text{O}_3 + 6\text{Cl}$] [9]. The highest selectivity of Al_2O_3 with respect to SiO_2 of 3.1 was obtained at $\text{O}_2/\text{BCl}_3/\text{Ar} = 0/6/14$.

Figure 2 shows the etch rates of Al_2O_3 and SiO_2 and the selectivity of the Al_2O_3 thin film with respect to SiO_2 as a function of

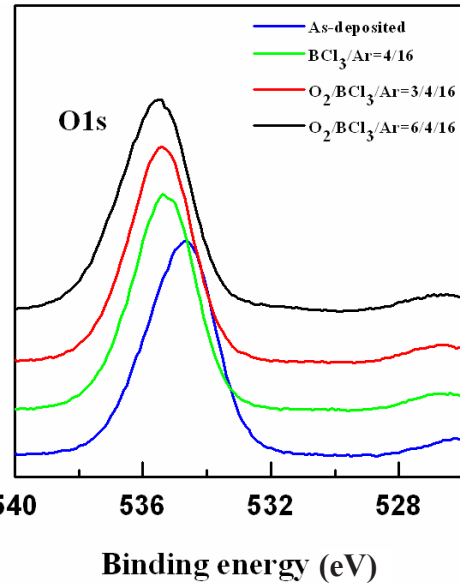


Fig. 7. The XPS narrow-scan spectra of O 1s on the Al_2O_3 surface for the as-deposited film and the film etched in the $\text{O}_2/\text{BCl}_3/\text{Ar}$ plasma.

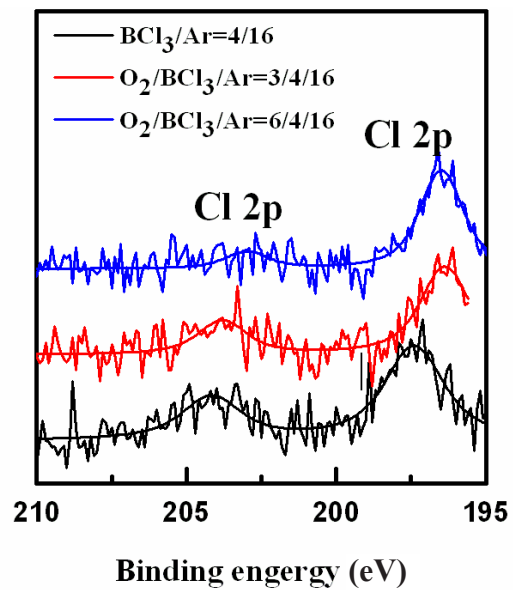


Fig. 8. The XPS narrow-scan spectra of Cl 2p on the Al_2O_3 surface for the as-deposited film and the film etched in the $\text{O}_2/\text{BCl}_3/\text{Ar}$ plasma.

the RF power in the range from 400 to 700 W, while the other parameters were $\text{O}_2/\text{BCl}_3/\text{Ar} = 3/6/14$, a DC-bias voltage of -100 V , and a process pressure of 15 mTorr. Figure 2 illustrates the monotonic increase of the etch rate with increasing RF Power. A high etch rate of 477 nm/min was obtained at an RF power of 700 W and SiO_2 also showed the same trend with a high etch rate of 36 nm/min obtained at an RF power of 700 W. The increase in etch rate could be explained by the fact that with increasing RF power, the plasma density increased due to the increase in the number of reactive free radicals and ions. Thus, enhancing the etch rates of Al_2O_3 and SiO_2 [10]. The acceleration of the chemical reactions as well as that of the physical ion bombardment occurred simultaneously. The selectivity of Al_2O_3 with respect to SiO_2 showed a monotonic increase in Fig. 2. A high selectivity of 13 was obtained at an RF power of 700 W.

Figure 3 shows the etch rates of Al₂O₃ and SiO₂ and selectivity of the Al₂O₃ film with respect to SiO₂ as a function of the DC-bias voltage in the range from -50 to -200 V, while the other parameters were O₂/BCl₃/Ar = 3/6/14, an RF power of 500 W, and a process pressure of 15 mTorr. As shown in Fig. 3, when the DC-bias voltage increased from -50 V to -200 V, the etch rates on Al₂O₃ and SiO₂ increased. According to this trend, high Al₂O₃ and SiO₂ etch rates of 87 nm/min and 131 nm/min, respectively, were obtained at a DC-bias voltage of -200 V. With increasing DC-bias voltage, the self-bias applied to the samples and the kinetic energy of the impinging ions increased [11,12]. At a DC-bias voltage of -50 V, deposition occurred on the Al₂O₃ and SiO₂ surfaces. A low DC-bias voltage led to ions with a low energy being drawn onto the film surface, which could not remove the less volatile byproducts through physical sputtering by ion bombardment. As shown in Fig. 3, the DC-bias voltage had a greater influence on SiO₂ than on Al₂O₃, which caused the selectivity of Al₂O₃ with respect to SiO₂ to decrease. A high selectivity of 1.8 was obtained at a DC-bias voltage of -50 V.

Figure 4 shows the etch rates of Al₂O₃ and SiO₂ and the selectivity of the Al₂O₃ film with respect to SiO₂ as a function of the process pressure in the range from 7.5 mTorr to 22.5 mTorr, while the other parameters were O₂/BCl₃/Ar = 3/6/14, an RF power of 500 W and a DC-bias voltage of -100 V. As shown in Fig. 4, the etch rate increased when the process pressure was increased from 7.5 mTorr to 15 mTorr, but deposition occurred on both Al₂O₃ and SiO₂ when the process pressure was further increased to 22.5 mTorr. When the process pressure was too low, the gas would flow directly away, without participating in the etching process, thus causing the etch rate to be lower. When the process pressure was increased, the etch rate increased due to the increase in the density of the radicals. However, when the process pressure was increased beyond a certain threshold, deposition occurred on the surfaces. This could be explained by the fact that frequent scattering occurred, due to the shortening of the mean free path at the high process pressure, which accelerated the reactions between (boron - chloride) and oxygen, resulting in deposition. The selectivity of Al₂O₃ with respect to SiO₂ increased and a high etch rate of 2.8 was obtained at a process pressure of 22.5 mTorr.

Figure 5 shows the wide-scan spectra obtained from the as-deposited and etched Al₂O₃ thin films surfaces. Figure 6 shows the narrow scan spectra of the Al 2p photoelectron peak, which were obtained from the as-deposited and etched Al₂O₃ thin films surfaces. The photoelectron peak at a binding energy of 74.3 eV corresponds to Al 2p of Al₂O₃. Compared with the spectrum of the as-deposited film, the Al 2p peak was shifted to 78 eV after etching, potentially due to Al-chlorine byproducts remaining on the surface after the reactions between Al and Cl. The O 1s photoelectron peaks are shown in Fig. 7. The O 1s photoelectron peak at a binding energy of 534.4 eV originated from the Al-O bonds in the as-deposited sample. The O 1s photoelectron peaks were shifted to 535-536 eV, possibly due to the B-O species from the boron-oxygen compounds B_xO_y deposited on the surfaces, which prevented the formation and sputtering of volatile byproducts [13]. Figure 8 shows the Cl 2p photoelectron peaks after etching in the BCl₃-based gas mixture. The Cl that appeared on the etched surface may have originated from Al_xCl_y compounds. The peaks of Cl 2p decreased as the amount of O₂ increased. As the amount of O₂ increased, more BCl reacted with the O radicals to produce nonvolatile byproducts, which led to less Al_xCl_y be-

ing produced.

4. CONCLUSIONS

In this study, we investigated the etch characteristics of ALD-deposited Al₂O₃ thin films as functions of the amount of O₂ in the BCl₃/Ar plasma, RF power, DC-bias voltage and process pressure using an inductively coupled plasma system. As the RF power and DC-bias voltage increased, the etch rates of Al₂O₃ and SiO₂ increased due to the increasing density of the radicals and kinetic energy of the ions. The highest etch rate of 477 nm/min was obtained at an RF power of 700 W with the addition of 15% O₂ to the BCl₃/Ar gas, a DC-bias voltage of -100 V and a process pressure of 15 mTorr. As the process pressure was increased, deposition occurred at a high process pressure, due to the frequent scattering which accelerated the reactions in the plasma. Since BCl₃ is highly reactive and good at acquiring oxygen, it can form nonvolatile residues upon contact with oxygen or water. When a small amount of O₂ was added, the concentration of the inhibitor species of boron chlorides in the plasma was reduced, suppressing the formation of a passivation layer on the surface. However, as the amount of O₂ was increased, solid products consisting of boron oxides were formed in the plasma, resulting in heavy deposition on both Al₂O₃ and SiO₂ surfaces.

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