The Dry Etching Characteristics of TiO_2 Thin Films in $\text{N}_2/\text{CF}_4/\text{Ar}$ Plasma

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In this study, the etching characteristics of titanium dioxide (TiO_2) thin films were investigated with the addition of N_2 to CF_4/Ar plasma. The crystal structure of the TiO_2 was amorphous. A maximum etch rate of 111.7 nm/min and selectivity of 0.37 were obtained in an $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm) gas mixture. The RF power was maintained at 700 W, the DC-bias voltage was -150 V, and the process pressure was 2 Pa. In addition, the etch rate was measured as functions of the etching parameters, such as the gas mixture, RF power, DC-bias voltage, and process pressure. We used X-ray photoelectron spectroscopy to investigate the chemical state on the surface of the etched TiO_2 thin films. To determine the re-deposition and reorganization of residues on the surface, atomic force microscopy was used to examine the surface morphology and roughness of TiO_2 thin films.

Keywords: TiO_2 , XPS, CF_4/Ar , Etching, AFM

1. INTRODUCTION

Titanium dioxide (TiO_2) thin films have received remarkable interest because of their interesting electrical properties. The high dielectric constant of TiO_2 allows its various applications in logic CMOS devices and memory technology like SRAM, DRAM, etc. High dielectric constant materials are being considered as a replacement for conventional silicon dioxide (SiO_2) [1,2]. ITRS 2004 calls for gate dielectrics of less than 1 nm in equivalent oxide thickness (EOT) with a low leakage current. The operation of devices requires that the thickness of the gate oxide be scaled along with the length of the gate. Since the dimensions of the device are reduced to the nanoscale, there is a strong need to reduce the gate oxide thickness. However, due to the tunneling effect, the current gate oxides used as the gate dielectric have leakage current problems. The tunneling effect dramatically increases the leakage current, leading to degradation of the device

performance. The purpose of using high dielectric constant materials with a larger physical thickness to achieve the same EOT is to reduce the tunneling leakage current. Therefore, to solve this problem, high dielectric constant (high- k) materials have been studied to replace the conventional gate oxide [3]. Among many high- k materials, TiO_2 has been studied as a strong candidate due to its very high dielectric constant [2].

To date, there have been a few studies related to the dry etching of TiO_2 thin films using fluorine-based chemistries [4,5]. However, the influences of N_2 additive on the etching characteristics of TiO_2 thin films in fluorine-based plasma were not fully explored in detail. It is important to understand the relationships between plasma parameters and the effect of N_2 gas in fluorine-based chemistries. The most significant advantage of added N_2 gas is that it provides good film surface morphologies and higher etch rate [6]. So, the dry etching characteristics of TiO_2 thin films with the addition of N_2 should be investigated.

In this work, TiO_2 thin films were etched using an inductively coupled plasma (ICP) system with the addition of N_2 to CF_4/Ar plasma. The etching characteristics of TiO_2 thin films were investigated in $\text{N}_2/\text{CF}_4/\text{Ar}$ plasma. The etch rates of the TiO_2 thin films were measured using a surface profiler. The chemical state on the etched surface of TiO_2 thin films was investigated by X-

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ray photoelectron spectroscopy (XPS). The surface morphology and roughness of TiO_2 thin films were examined by atomic force microscopy (AFM).

2. EXPERIMENT

TiO_2 thin films were deposited by an E-beam evaporator system. The source material for deposition was TiO_2 pellets. The overall thickness of the deposited thin films was measured by a quartz crystal microbalance, and the final thickness was about 200 nm. The dry etching of the TiO_2 thin films was performed in a planar inductively coupled plasma (ICP) system. Figure 1 shows the schematic of the ICP system. The planar ICP etching equipment has a 3.5-turn copper coil located above the 24 mm thick horizontal quartz window, and 13.56 MHz RF power is applied to the coil to induce an inductively coupled plasma. Another 13.56 MHz RF power is applied to the substrate to induce DC-bias voltage to the wafer [7]. The chemical reaction of TiO_2 thin films was investigated with the addition of N_2 to a CF_4/Ar gas mixture as functions of the etching parameters listed in Table 1. The etch rate of the TiO_2 thin films was measured using a surface profiler (KLA Tencor, -step 500). The chemical state on the surface of the etched TiO_2 thin films was investigated using XPS (PHI 5000 Versa Probe, Ulvac-PHI). Al $K\alpha$ radiation ($h\nu = 1,486.6$ eV) was used as an X-ray source, and the minimum energy resolution was about 0.48 eV during the testing. The carbon C 1s peak at 284.6 eV was used as a reference for charging correction. The detailed information of the films was provided by the spectra angle of 45° . The surface morphology and roughness of TiO_2 thin films were examined using AFM (Park Scientific Instrument, Auto probe cpap-0100). All of the samples for the XPS and AFM analysis were bare TiO_2 thin films without any photo-resist patterns, and the size of the samples was $1 \times 1 \text{ cm}^2$.

3. RESULTS AND DISCUSSION

Figure 2 shows the etch rate of TiO_2 thin films with the addition of N_2 to CF_4/Ar plasma. The RF power was maintained at 700 W, the DC-bias voltage was -150 V, and the process pressure was 2 Pa. The maximum etch rate of TiO_2 thin films was 111.7 nm/min in $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm) plasma. It can be seen that, as the N_2 gas increases from 0 to 6 sccm, the etch rate of TiO_2 thin films increases from 87 nm/min to 111.7 nm/min and decreases with further increases in N_2 (up to 9 sccm) gas. The selectivity of TiO_2 to SiO_2 gradually decreased from 0.51 to 0.33. These results confirm that the TiO_2 thin film etching in $\text{N}_2/\text{CF}_4/\text{Ar}$ plasma is not a simple sputter etching but a chemically assisted sputter etching. The domination of the chemically assisted sputter etch pathway can be explained in two aspects. First, the effect of ion bombardment assisted the chemical reaction by breaking oxide bonds. Second, the addition of N_2 to CF_4/Ar plasma enhances the F radicals, leading to the release of more F radicals [8]. The F radical can react with TiO_2 thin films through the effect of ion bombardment, leading to the formation of Ti-F bonds. The melting point of TiF_4 is about 284°C , and it can be considered as a volatile compound. As a result, as the N_2 gas increases from 0 to 6 sccm, the etch rate of TiO_2 thin films increases. However, with a further increase in N_2 (= 9 sccm) gas, the addition of N_2 to CF_4/Ar plasma enhances the F radicals as well as N in the plasma, leading to the formation of Ti-N bonds. Since the melting point of TiN is about $2,950^\circ\text{C}$, it can be related to nonvolatile compounds. As a result, as the N_2 gas increases from 6 to 9 sccm, the etch rate of TiO_2 thin films decreases [9].

Figure 3 shows the etch rate of TiO_2 thin films as a function of

Fig. 1. Schematic diagram of inductively coupled plasma system.

Table 1. Process conditions.

Gas mixture	$\text{N}_2/\text{CF}_4/\text{Ar}$
RF power (W)	700
DC-bias voltage (-V)	150
Process pressure (Pa)	2

Fig. 2. Etch rate of TiO_2 thin films as a function of the $\text{N}_2/\text{CF}_4/\text{Ar}$ gas mixture. The RF power was maintained at 700 W, the DC-bias voltage was -150 V, and the process pressure was 2 Pa.

the RF power in $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm) plasma. The DC-bias voltage was maintained at -150 V, and the process pressure was 2 Pa. As the RF power increases from 400 to 800 W, the etch rate of TiO_2 thin films increases from 74.7 nm/min to 119.1 nm/min, whereas the selectivity of TiO_2 to SiO_2 decreases from 0.65 to 0.36. These results with increasing RF power can be explained by the acceleration of both ionization and dissociation. With an increase in RF power, the density and flux of ions increase through the acceleration of both dissociation and the ionization rates. Therefore, the increase of density of reactive species and Ar ion flow rate enhanced the acceleration of chemical reactions as well as the physical ion bombardment, leading to the increase in the etch rate of TiO_2 thin films. As a result, the increase of RF power increases the etch rate of TiO_2 thin films [6,10].

Figure 4 shows the etch rate of TiO_2 thin films as a function of the DC-bias voltage in $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm) plasma. The RF power was maintained at 700 W, and the process pressure was 2 Pa. As the DC-bias voltage increases from -50 to -250 V, the

Fig. 3. Etch rate of TiO_2 thin films as a function of the RF power. The $\text{N}_2/\text{CF}_4/\text{Ar}$ gas mixture was maintained at 6:16:4 sccm, the DC-bias voltage was -150 V, and the process pressure was 2 Pa.

Fig. 4. Etch rate of TiO_2 thin films as a function of the DC-bias voltage. The $\text{N}_2/\text{CF}_4/\text{Ar}$ gas mixture was maintained at 6:16:4 sccm, the RF power was 700 W, and the process pressure was 2 Pa.

etch rate of TiO_2 thin films gradually increases from 64.2 nm/min to 200.6 nm/min, and the selectivity of TiO_2 to SiO_2 increases from 0.35 to 0.50. These results with increasing the DC-bias voltage can be explained by ion-assisted chemical reaction. With an increase in the DC-bias voltage, the ion bombarding energy increases through the increase of the mean ion energy. The increase of the ion bombarding energy enhanced the sputtering yields on the surface of TiO_2 thin films leading to the sputtering removal of etch by-products. As a result, the increase of DC-bias voltage increases the etch rate of TiO_2 thin films.

Figure 5 shows the etch rate of TiO_2 thin films as a function of the process pressure in $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm) plasma. The RF power was maintained at 700 W, and the DC-bias voltage was -150 V. As the process pressures increase from 1 to 3 Pa, the etch rate of TiO_2 thin films decreases from 136 nm/min to 106.3 nm/min, whereas the selectivity of TiO_2 to SiO_2 increases from 0.36 to 0.43. As the process pressure increases, the ion bombardment effect decreases due to the increased probability of collision and charge transfer in the substrate sheath region. On the other hand, the increase of the process pressure enhances the density of chemically neutral active species, leading to acceleration of the chemical reactions. Therefore, the etch by-product on the surface of TiO_2 thin films increases due to the acceleration of chemical reactions. As a result, the etch rate of TiO_2 thin films was decreased due to the decrease of the ion bombardment ef-

Fig. 5. Etch rate of TiO_2 thin films as a function of the process pressure. The $\text{N}_2/\text{CF}_4/\text{Ar}$ gas mixture was maintained at 6:16:4 sccm, the RF power was 700 W, and the DC-bias voltage was -150 V.

fect and the increase of chemical reactions. [6,11,12].

To analyze the variation of surface composition with the addition of N_2 to CF_4/Ar plasma, the chemical state on the surface of TiO_2 thin films was investigated by XPS. The chemical state on the etched surfaces was compared with that of the as-deposited sample. Figure 6 shows the XPS narrow scan spectra of (a) Ti and (b) O, which were obtained from the surfaces of TiO_2 thin films after etching in CF_4/Ar plasma and $\text{N}_2/\text{CF}_4/\text{Ar}$ plasma.

Figure 6(a) shows the photoelectron peak of Ti 2p from the as-deposited and etched TiO_2 thin films as a function of gas mixture. The Ti 2p peak of the as-deposited films was observed at 458.8 eV. After the etching of TiO_2 thin films in CF_4/Ar (= 16:4 sccm) plasma, the peak of Ti 2p was shifted to a lower binding energy and the maximum deviation was about -0.2 eV. This peak shift was caused by changes in chemical composition of the surface of TiO_2 thin films. We supposed that Ti chemically reacted with F radicals, which led to the formation of Ti-F bonds on the surface by ion bombardment. In other words, the chemical reaction of F radicals was increased on the surface, leading to the formation of Ti-F bonds attributed to the physical sputtering of Ar ions. After the etching of TiO_2 thin films in $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm) plasma, the peak of Ti 2p at 458.8 eV was shifted to a lower binding energy, and the maximum deviation was about -0.6 eV. This peak shift indicates that Ti chemically reacted with F radicals as well as N radicals, which led to the formation of Ti-N and Ti-F bonds on the surface by ion bombardment. In other words, the chemical reaction of N radicals was increased on the surface of TiO_2 , and the formation of Ti-F bonds and Ti-N bonds was attributed to the physical sputtering of Ar ions [4,13]. Figure 6(b) shows the photoelectron peak of O 1s from the as-deposited and etched TiO_2 thin films as a function of gas mixture. The O 1s peak of the as-deposited films was observed at 530.2 eV. After the etching of TiO_2 thin films in CF_4/Ar (= 16:4 sccm) plasma, the peak of O 1s at 530.2 eV was shifted to a higher binding energy, and the maximum deviation was about +0.2 eV. This peak shift was caused by changes in chemical composition on the surface of TiO_2 thin films. It is supposed that the Ti-O bonds were dissociated by ion bombardment, and the O 1s peak was decreased due to the formation of F-O bonds [4]. After the etching of TiO_2 thin films in $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm) plasma, the peak of O 1s at 530.2 eV was shifted to a lower binding energy and the maximum deviation was about -0.4 eV. This peak shift indicates that the formation of F-O bonds increases on the surface through the effective dissociation of the Ti-O bonds by ion bombardment. As a result, Ti and O were removed by the chemical reactions with the F radicals and the physical bombardment of Ar ions. Figure

Fig. 6. The XPS narrow scan spectra of the etched TiO_2 thin films. The RF power was maintained at 700 W, the DC-bias voltage was -150 V, and the process pressure was 2 Pa. (a) Ti 2p, (b) O 1s, and (c) F 1s.

6(c) shows the photoelectron peak of F 1s from the as-deposited and etched TiO_2 thin films as a function of gas mixture. The F 1s peak of the as-deposited film was not observed. After the TiO_2 thin films were exposed to the CF_4/Ar (=16:4 sccm) plasma, the peak of F 1s was observed at 686 eV. After the TiO_2 thin films were exposed to the $\text{N}_2/\text{CF}_4/\text{Ar}$ (=6:16:4 sccm) plasma, the core F 1s peak was decreased significantly, the peak of F 1s was shifted to a lower binding energy, and the maximum deviation was about -0.5 eV. This is due to the less volatile Ti-F. The strength of the Ti-F chemical bond (272 kJ/mol) is higher than that of the Ti-O bond (383 kJ/mol). As a result, the core F 1s peak of the TiO_2 in CF_4/Ar plasma was higher than that of the TiO_2 thin films in $\text{N}_2/\text{CF}_4/\text{Ar}$ plasma, as demonstrated by the decrease in the number of Ti-F bonds on the etched surface of TiO_2 thin films in $\text{N}_2/\text{CF}_4/\text{Ar}$ plasma due to the increase of F-O bonds [13-15].

To understand the surface state of TiO_2 thin film, the surface morphology and roughness of TiO_2 thin films were investigated

Fig. 7. The surface morphology and roughness of TiO_2 thin films. The RF power was maintained at 700 W, the DC-bias voltage was -150 V, and the process pressure was 2 Pa. (a) As-deposited, (b) CF_4/Ar = 16:4 sccm, (c) $\text{N}_2/\text{CF}_4/\text{Ar}$ = 3:16:4 sccm, (d) $\text{N}_2/\text{CF}_4/\text{Ar}$ = 6:16:4 sccm, and (e) $\text{N}_2/\text{CF}_4/\text{Ar}$ = 9:16:4 sccm.

by atomic force microscopy (AFM). We compared the surface morphology and root mean square values between the as-deposited and etched TiO_2 thin films as a function of gas mixture.

Figure 7 shows the surface morphology of TiO_2 thin films from as-deposited and etched TiO_2 thin films as a function of gas mixture. As shown in Fig. 7(a), the surface morphology of as-deposited TiO_2 thin films is a little rough, and the root mean square (RMS) roughness is about 36.5 Å. Figure 7(b) shows the surface morphology of TiO_2 thin films as a function of CF_4/Ar (= 16:4 sccm), and the RMS roughness is about 59.8 Å. Figures 7(c), (d), and (e) show the surface morphology of TiO_2 thin films as a function of $\text{N}_2/\text{CF}_4/\text{Ar}$ gas mixture, and the RMS roughness was 37.3 Å, 22.3 Å, and 40.5 Å, respectively. As the N_2 gas increases from 0 to 6 sccm in CF_4/Ar plasma, the RMS roughness of TiO_2 thin films decreases from 59.8 Å to 22.3 Å, and the surface morphology of TiO_2 thin films becomes fine and compact. On the other hand, with a further increase in N_2 (= 9 sccm) gas, the RMS roughness of TiO_2 thin films increases from 22.3 Å to 40.5 Å, and the surface morphology of TiO_2 thin films shows rough features. The changes in the RMS roughness as a function of $\text{N}_2/\text{CF}_4/\text{Ar}$ gas mixture may be explained by the following. After the etching of TiO_2 thin films in CF_4/Ar (= 16:4 sccm) plasma, the formation of etch by-products was enhanced and accumulated gradually on the etched surface of TiO_2 thin films. However, when N_2 was added to CF_4/Ar plasma, the N_2 gas in combination with etch by-products was evaporated from the etched surface of TiO_2 thin films. Therefore, as the N_2 gas increased from 3 to 6 sccm, it is supposed that the surface morphology of TiO_2 thin films became fine and compact by addition of N_2 gas. However, with a further increase in N_2 (= 9 sccm) gas, it induces an adsorption of N on the etched surface, and then partially interrupts the etching process. Therefore, nonvolatile residues were increased and the etch rate was decreased. As a result, as the N_2 gas increases from 6 to 9 sccm, the roughness of etched TiO_2 thin films increases. So, compared with the as-deposited TiO_2 thin films, the surface morphology of TiO_2 thin films in $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm) plasma became fine and compact [16,17].

4. CONCLUSIONS

We investigated the dry etching characteristics of the TiO_2 thin films in $\text{N}_2/\text{CF}_4/\text{Ar}$ plasma as functions of the etching parameters, such as the gas mixture, RF power, DC-bias voltage, and process pressure. The maximum etch rate and selectivity of TiO_2 thin films was 111.7 nm/min and 0.37 in $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm) plasma, respectively. The RF power was maintained at 700 W, the DC-bias voltage was - 150 V, and the process pressure was 2 Pa.

As the N_2 gas in CF_4/Ar plasma increases from 0 to 6 sccm, it enhances the effect of ion bombardment as well as the concen-

tration of the F radicals, leading to an increase in the etch rate of TiO_2 thin films. However, the etch rate of TiO_2 thin films decreases with further increases in N_2 gas ratio to 9 sccm. The chemical state on the etched surface of TiO_2 thin films was investigated by XPS. The Ti interacted with the F radicals in the N_2 containing plasmas, and Ti-F bonds evaporated on the etched surface. However, Ti-N bonds remained on the etched surface, due to the low volatility of Ti-N bonds. These etch by-products on the surface can be effectively removed with the help of ion bombardment. Therefore, the TiO_2 thin film etching in $\text{N}_2/\text{CF}_4/\text{Ar}$ plasma is not a simple sputter etching but a chemically assisted sputter etching. The surface morphology and roughness of etched TiO_2 thin films were investigated by AFM. After the etching of TiO_2 thin films in $\text{N}_2/\text{CF}_4/\text{Ar}$ (= 6:16:4 sccm), the RMS roughness was decreased, and the surface morphology of TiO_2 thin films became fine and compact.

REFERENCES

- [1] J. Yan, D.C. Gilmer, S.A. Campbell, W.L. Gladfelter, P.G. Schmid. *J. Vac. Sci. Technol. B* 14 (1996) 1706.
- [2] S.A. Campbell, D.C. Gilmer, X. Wang, M.T. Hsieh, H.S. Kim, W.L. Gladfelter, J. Yan. *IEEE Electron Devices*. 44 (1997) 104.
- [3] G.D. Wilk, R.M. Wallance, J.M. Anthony. *J. Appl. Phys.* 89 (2001) 5243.
- [4] J.C. Woo, Y.H. Joo, C.I. Kim, *Jpn J. Appl. Phys.* 50 (2011) 08KC02.
- [5] R. d'Agostino, F. Fracassi, C. Pacifico, P. Capezzuto. *J. Appl. Phys.* 71 (1992) 462.
- [6] N.M. Muthukrishnan, K. Amberialdis, A.E. Riad, *J. Electrochem. Soc.* 144 (1997) 1780.
- [7] G.H. Kim, C.I. Kim, *J. Vac. Sci. Technol. A* 24 (2006) 1514.
- [8] J.K. Jung, W.J. Lee, *Jpn J. Appl. Phys.* 40 (2001) 1408.
- [9] D.R. Lide : *CRC Handbook of Chemistry and physics* (CRC Press, Boca Raton, 1994) 75th ed.
- [10] T. Smith, *Surf. Sci.* 32 (1972) 527.
- [11] X. Yang, J.C. Woo, D.S. Um, C.I. Kim, *Trans. Electr. Electron. Mater.* 11 (2010) 202.
- [12] A.M. Efremov, D.P. Kim, C.I. Kim, *Thin Solid Films*. 435 (2003) 83.
- [13] I. Bertoti, M. Mohai, J.L. Sullivan, S.O. Saied, *Appl. Surf. Sci.* 84 (1995) 357.
- [14] S. Norasetthekul, P.Y. Park, K.H. Baik, K.P. Lee, B.S. Jeong, V. Shishodia, E.S. Lambers, D.P. Norton, S.J. Pearton, *Appl. Surf. Sci.* 185 (2001) 27.
- [15] R. d'Agostino, F. Fracassi, C. Pacifico, *J. Appl. Phys.* 72 (1992) 4351.
- [16] G. Chiarello, R. Barberi, A. Amoddeo, L.S. Caputi, E. Colavita, *Appl. Surf. Sci.* 99 (1996) 15.
- [17] Z.H. Liu, N.M.D. Brown, A. Mckinley, *Appl. Surf. Sci.* 108 (1997) 319.