



Surface Etching of TiO₂ Thin Films Using High Density Cl₂/Ar Plasma

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Received October 21, 2015; Revised November 11, 2015; Accepted November 16, 2015

In this study, we carried out an investigation of the etch characteristics of TiO₂ thin films and the selectivity of TiO₂ to SiO₂ in adaptive coupled Cl₂/Ar plasma. The maximum etch rate of the TiO₂ thin film was 136±5 nm/min at a gas mixing ratio of Cl₂/Ar (75%:25%). The X-ray photoelectron spectroscopy (XPS) analysis showed the efficient destruction of oxide bonds by the ion bombardment as well as the accumulation of low volatile reaction products on the etched surface.

Keywords: Etching, TiO₂, High density plasma, X-ray photoelectron spectroscopy

1. INTRODUCTION

Recently, the high density memory has been developed by scaling down feature size. In order to increase the density and the speed while decrease the operating power of memory devices, methods to compensate for the decrease of gate width with high-dielectric materials must be explored. The reduction of the gate dielectric, commonly a SiO₂ material, as the insulator layer of transistors causes serious problems in terms of leakage current and reliability. Therefore, a high-k material such as the TiO₂ thin film has been studied to provide a substitute for SiO₂ as the insulator layer of transistors. High-k thin films can be used as insulators for metal-insulator-metal (MIM) capacitors to increase the packing density of integrated circuits by increasing the dielectric constant of the insulators [1-3]. However, among new insulator candidates, TiO₂ can achieve a high etch rate and a high selectivity for the sake of the throughput and reliability of the MIM capacitor.

Until now, the etch characteristics of TiO₂ in inductively coupled plasma (ICP) and capacitively coupled plasma are not understood completely. The ICP source shows characteristics of high etch rate and high plasma density, as well as its own unique

characteristics. Some of the basic properties and the process performance were previously reported [4-6]. However, new insulator candidates must comply with the device processing procedure. Among the high-k materials, TiO₂ is good candidate because a high etch rate and high selectivity can be achieved for the necessary high throughput and reliability of the MIM capacitor.

In this study, TiO₂ thin films were etched in an adaptively coupled plasma (ACP) system with various Cl₂/Ar gas ratios. The etch characteristics of the TiO₂ thin films were investigated in terms of the etch rate and the selectivity. The morphologies on the surface of the etched TiO₂ thin films were investigated by atomic force microscopy (AFM). The chemical binding states on the surface of the etched TiO₂ thin films were investigated by X-ray photoelectron spectroscopy (XPS). Field emission-scanning electron microscopy (FE-SEM) was used to investigate the etch profile.

2. EXPERIMENTS

The TiO₂ thin films used in this work were deposited by plasma enhanced atomic layer deposition (PEALD). The substrate was a 6-in *p*-type Si (100) with resistivity was in the range of 5-30 ohm-cm deposited on the substrate at a temperature of 200 °C. The RF power was 13.56 MHz, process pressure, and Ar gas flow rate, were maintained at 500 W, 11 mTorr, and 200 sccm, respectively. The deposited TiO₂ thin films were post annealed at 650 °C. The final thickness of the TiO₂ thin films was about 100 nm. The

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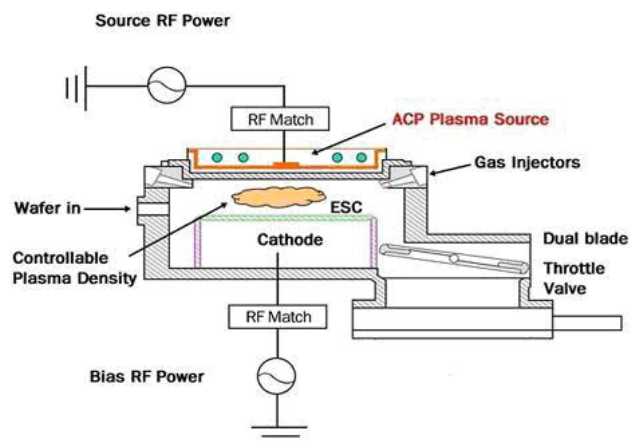


Fig. 1. Schematic diagram of the adaptively coupled plasma system.

SiO₂ thin films used in this work were deposited by the plasma enhanced chemical vapor deposition (PECVD) system. The deposition temperature was fixed at 400 °C. The other process conditions, viz. the RF power at 13.56 MHz, process pressure and SiH₄ and N₂O gas flow rate were maintained at 300 W, 3 Torr, 60 sccm, and 1,200 sccm, respectively. The final thickness of the SiO₂ thin films was about 400 nm. And, the etching experiments were performed in a planar ACP system (Selex 200, APTC Co.).

As shown in Fig. 1, the system consisted of multi-spiral coils and a bushing, and the coil antenna was located above a thick horizontal ceramic window. A 12.56 MHz RF power generator in the source power was connected to a coil antenna to generate the plasma. Another 13.56 MHz RF power generator in bias power was connected to the electrostatic chuck (ESC: 1500 V) to control the ion energy. This plasma source shows characteristics of both traditional sources of inductively coupled plasma (ICP) and capacitively coupled plasma (CCP), as well as its own unique characteristics [7,8]. The etch characteristics of the TiO₂ thin films were investigated as a function of the Cl₂/Ar gas mixing ratio. In addition, the etching of the TiO₂ thin films was investigated by changing the etching parameters. The etch rate was measured by a surface profiler (KLA Tencor, α -step 500). The compositional changes on the surface of the etched TiO₂ thin film were investigated using XPS (SIGMA PROBE, Thermo VG Scientific). The spectra were plotted by counting the photo electrons at kinetic energy intervals of 0.1 eV. The surface images of the etched TiO₂ thin films was confirmed by using AFM (Dimension 3100, Veeco). All of the samples for the XPS and AFM analysis were bare TiO₂ thin films that did not have any photoresist (PR) patterns, and the size of the samples was 1×1 cm². The etching time was 10 sec. The etching profile of the cross-section was characterized using FE-SEM (Sirion 400, FEI). The TiO₂ thin films used for measuring the etch rate and etching profile did have a PR (SS03A9) pattern. The width and thickness of the PR pattern were 1.5 μm and 1.02 μm, respectively.

3. RESULTS AND DISCUSSION

For the etch characterization of the TiO₂ thin film in the ACP system, the etch characteristics of the TiO₂ thin film was systematically investigated as a function of the Cl₂/Ar gas mixing ratio, source power, bias power, and process pressure. Generally, the combination of Cl₂ and Ar enhances the etch rate of metal-oxide materials by forming volatile etch by-products, such as ClO_x and metal-chlorides. Otherwise, the etch rate is decreased by forming

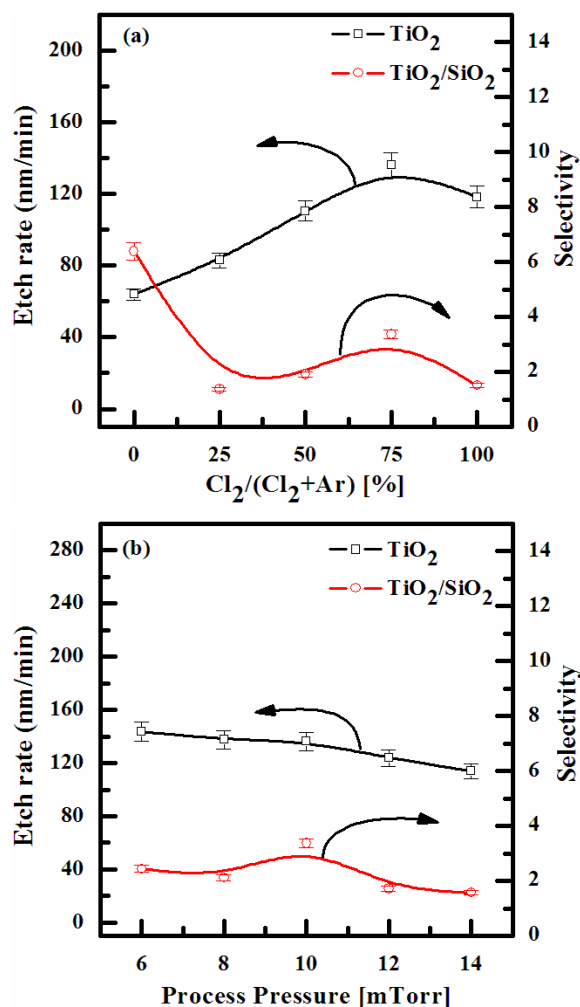


Fig. 2. The etch rate of TiO₂ thin film and the selectivity of TiO₂ to SiO₂ as a function of (a) the Cl₂/Ar gas mixing ratio and (b) the process pressure, respectively.

non-volatile etch by-products of ClO [9-10]. If Cl₂O₃ is accumulated on the surface, this layer precludes any chemical reactions between Cl and metals [11]. The steady-state rate of the chemical etch pathway (ER_{ch}) is equal to (1-θ)γ_{ch}S_{Cl}Γ_{Cl}+ (1-θ)YSF_{Ar}⁺ [12], where Γ is fluxes of species to the etched surface, γ_{ch} is the probability of chemical interaction, S_{Cl} is the sticking probability of atoms. θ is the fraction of surface active sites occupied by non-reactive species and determined by the balance between the rates of the chemical reaction (which fills the surface with low volatility reaction products) and the ion stimulated desorption [12].

Fig. 2(a) shows the etch rate of the TiO₂ thin film as a function of the Cl₂/Ar gas mixing ratio was measured when the total flow rate was fixed at 100 sccm. The other process parameters condition was maintained as shown in the Table 1, respectively. As the Cl₂ content in the Cl₂/Ar gas plasma increases from 0% to 75%, the etch rates of the TiO₂ thin films increase from 64±5 nm/min to 136±5 nm/min. When the Cl₂ content increased over 75%, the etch rate of TiO₂ thin film decreases. As the Cl₂ content in the Cl₂/Ar gas plasma increases from 0% to 75%, the selectivity, which is the etch rate ratio, of TiO₂ to SiO₂ decreases from 6.4 to 3.37. The effect is because SiO₂ is reacts better than TiO₂ when Cl₂ contents increased. Cl₂-based plasma etching shows SiO₂ to be more effective than TiO₂ in etching. The maximum etch rate of the TiO₂ thin film was 136 nm/min, at a Cl₂/(Cl₂+Ar) ratio of

Table 1. The input plasma parameters.

Process parameter	Parameter
Source power	400 W
Bias power	100 W
Process pressure	10 mTorr
Substrate Temperature	45 °C

75%. The comparisons on etch rates of the TiO₂ thin film in Cl₂-based plasma shows that chemical etching is more effective than physical sputtering [13]. TiO₂ thin film etching in chlorine-based plasma is well known to produce highly volatile by-products such as Ti-Cl₄. The evident enhancement on etch rate of the TiO₂ thin film in the pure Cl₂ plasmas suggests that the chemical etch pathways provided by the Cl-atoms are the dominant mechanism for the given set of input process parameters. In the case of physical sputtering of TiO₂ thin films, we expect the contribution of this pathway to be much lower than ion-assisted chemical reactions. In Cl₂-based plasma, increasing Cl₂ content up to 75% increases etch rate via two different mechanisms: (1) accelerated chemical reactions by the ion-stimulated desorption of the reaction products and (2) increasing the contribution of physical sputtering. Nevertheless, when the Cl₂ content exceeds 75%, the etch rate begins to decline due to the interruption of physical sputtering. For a given range of experimental conditions, chemical reactions were more effective than the physical etch pathway [11,12]. Fig. 2(b) shows the etch rate of TiO₂ thin film as a function of the process pressure in the Cl₂/Ar (75%:25%) plasma. As the process pressures increased from 6 mTorr to 14 mTorr, the etch rates of the TiO₂ thin film decreased from 144±5 nm/min to 114±5 nm/min. As the process pressure increases from 6 mTorr to 14 mTorr, the selectivity (or the etch rate ratio) of TiO₂ to SiO₂. O₂ tends to be maintained in all sections. The effect of process pressure may be explained as follows: An increase in process pressure at fixed Cl₂/Ar mixing ratio leads to an increase in both density and flux of fluorine atoms on the etched surface, but causes a decrease in ion flux and mean ion energy. As a result, the chemical etch pathway tends to accelerate, however, ion stimulated desorption of reaction products results due to a decreased fraction of free surface acceptable for chemical reaction. Similar to the effect of the gas mixing ratio discussed above, these two opposing factors produce non-monotonic behavior of the etch rate.

We hypothesize that molecular bonds were broken by ion bombardment on the surface of the TiO₂ thin film. Frequent chemical reactions in the plasma were facilitated by the higher ion density and the increased number of broken molecular bonds. This conclusion is in good agreement with the data shown in Fig. 2(a) and Fig. 2(b) [9-12].

For more detailed investigation of the chemical reaction on the etched surfaces, XPS analysis was carried out. We compared the differences between the chemical reactions on the surface of the etched TiO₂ thin film and on the surface of the as-deposited TiO₂ thin film. We also compared the differences between the peaks from the as-deposited TiO₂ thin film and the etched TiO₂ thin films in order to evaluate the changes of the chemical shift. The input plasma parameters were as follows at the Table 1.

Figure 3 shows the Ti 2p and O 1s XPS narrow-scan spectra on the surface of the etched TiO₂ thin film as a function of the Cl₂/Ar gas mixing ratio. As shown in Fig. 3(a), there are strong peaks at 464.34 eV and 458.8 eV, which correspond to Ti 2p_{1/2} and Ti 2p_{3/2} in the TiO₂ thin film. These peaks were shifted toward a low binding energy and the maximum deviation was about Δ 0.3 eV when the TiO₂ thin films were exposed in Cl₂/Ar plasma. This chemical shift indicates that Ti chemically reacted with Cl radi-

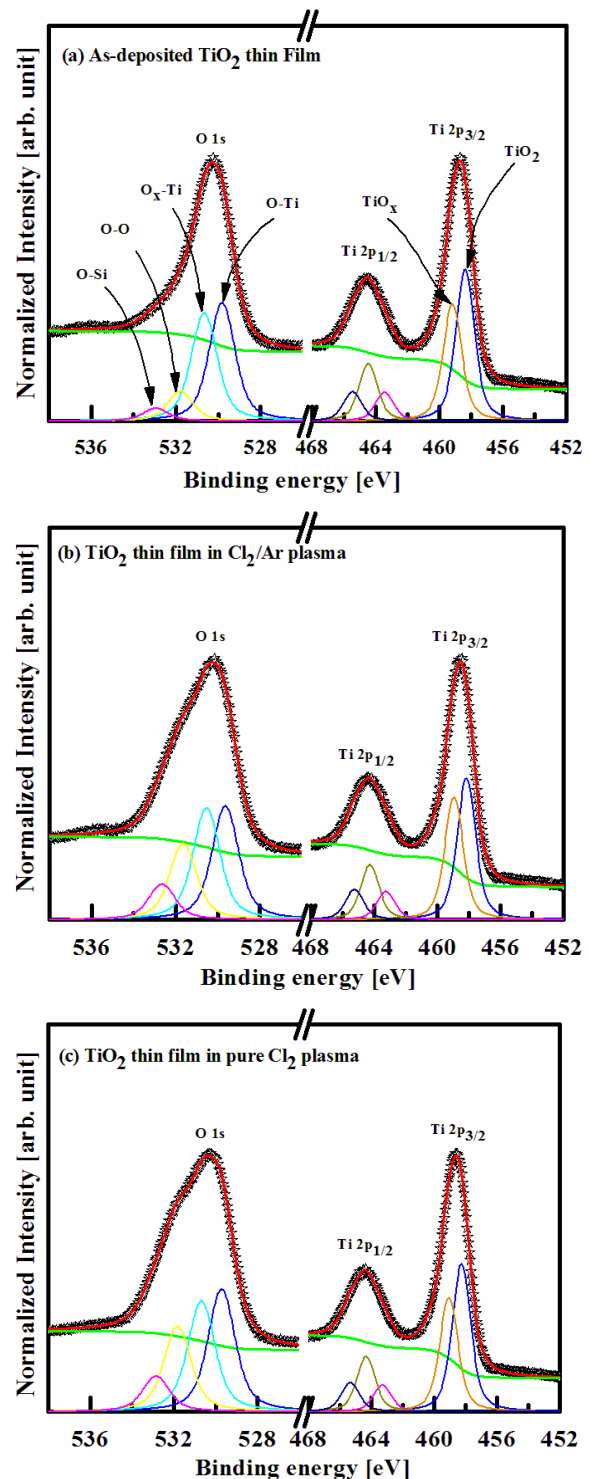


Fig. 3. The Ti 2p and O 1s XPS spectra with peak deconvolution results on the surface of the etched TiO₂ thin films as a function of gas mixing ratio, respectively. (a) As-deposited, (b) Cl₂/Ar (75%:25%), and (c) pure Cl₂.

cal at the surface [13-15]. The intensity of this peak increases slightly with the Cl₂/Ar (75%:25%) plasma, as shown in Fig 3(b), this changes of intensity can be related to the signal from the Ti-O_x bond, which was deconvoluted as shown in Fig. 3. These peaks were shifted toward the higher binding energy and the maximum deviation was about Δ 0.1 eV when TiO₂ thin films

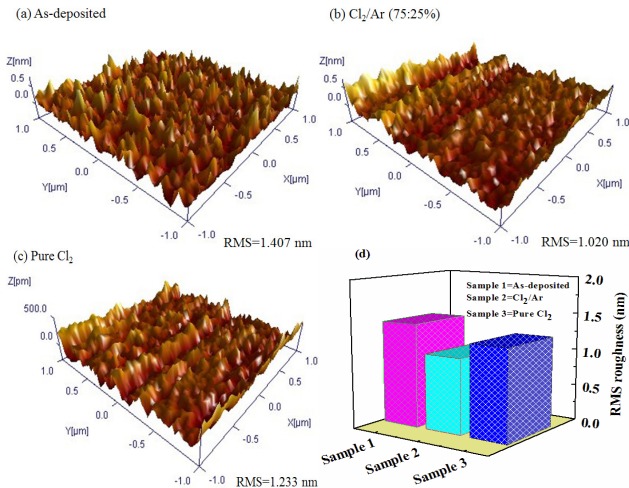


Fig. 4. AFM images on the surface of the etched TiO₂ thin film as a function of the etch chemistry.

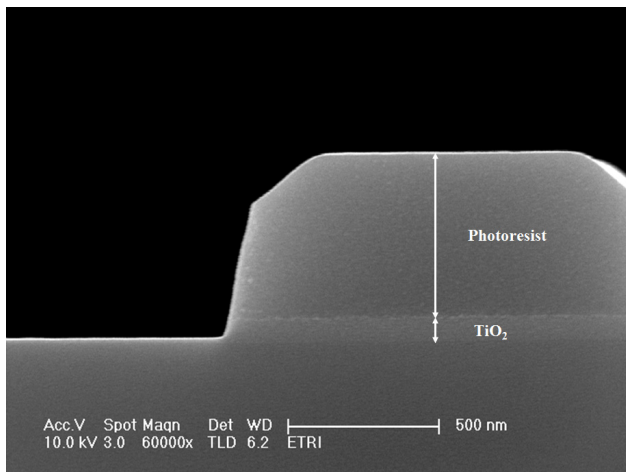


Fig. 5. The cross-wall sectional SEM image of the etched TiO₂ thin film in the Cl₂/Ar (75:25%) plasma.

were exposed in pure Cl₂ plasma, as shown in Fig. 3(c). From these facts, we can conclude that the Ti-O bonds are effectively destroyed by the Cl⁺ ion bombardments, which is in good agreement with the etch mechanism proposed above and the O 1s XPS narrow-scan spectra on the surface of the etched TiO₂ thin film as function of the Cl₂/Ar gas mixing ratio. As shown in Fig. 3(a) as-deposited, there is a strong peak at 530.2 eV, which corresponds to the O 1s in TiO₂ thin film. The O 1s peak of as-deposited TiO₂ thin film showed a single peak. This peak was composed of four maximums at 533 (O-Si), 531.8 (O-O), 530.65 (O_x-Ti) and 529.8 eV (O-Ti). In order to investigate the chemical states of the surface, the O 1s peaks were deconvoluted. As shown in Fig. 3(b) and (c), the O 1s peak was deconvoluted into four peaks, which were determined to correspond to the oxygen and/or hydroxyl group on the surface in the Cl₂/Ar plasma and the pure Cl₂: O-Si bond (532.7±0.3 eV), O-O bond (531.65±0.15 eV), O_x-Ti bond (530.55±0.1 eV), and O-Ti bond (529.65±0.15 eV). The confirmation of this is that the intensity of the peak centered at 530.2 eV was constant and was not dependent on the film treatment conditions [13,14].

As shown in Fig. 4, in order to clarify the etch mechanism further in terms of surface morphology, the etched TiO₂ thin films

by the pure Cl₂ and the Cl₂/Ar (75%:25%) plasma were investigated by AFM observation as function of the Cl₂/Ar gas mixing ratio. The input plasma parameters were as follows as shown in the Table 1. For comparison, on the surface of the as-deposited TiO₂ thin film is also measured and exhibits a roughness of about 1.407 nm (Fig. 4(a) as-deposited). For the pure Cl₂ plasma and etching by Cl₂/Ar (75:25%) plasma, the roughness is approximately 1.233 nm and 1.020 nm, respectively, [Fig. 4(b) Cl₂/Ar (75%:25%) and (c) pure Cl₂] due to the re-deposition effect. From the summarized roughness result shown in Fig. 4(d), decreasing the Cl₂ content in the Cl₂/Ar mixture brought about the formation of a coarse surface.

Figure 5 shows the cross sectional SEM images of the TiO₂ thin film after etching in Cl₂/Ar (75%:25%) plasma at a fixed condition shown in the Table 1 and the etching time was 30 sec. As shown in Fig. 5, the cross-sections of the PR and TiO₂ thin films were obtained with a PR mask. The experimental results showed that the vertical etching profile after plasma etching of the TiO₂ thin film was associated with Cl-radicals, due to the high etch rate of the TiO₂ thin film.

4. CONCLUSIONS

In this paper, the etch characteristics of TiO₂ thin films were investigated by measuring the etch rates under the varying input parameters using an ACP system. The maximum etch rate of the TiO₂ thin film was 136.4 nm/min at a Cl₂/(Cl₂+Ar) gas ratio of 75%. As the fraction of Cl₂ in the Cl₂/Ar plasma was increased from 0% to 75%, the etch rate of the TiO₂ thin film increased. However, the etch rate of the TiO₂ thin film decreased with the further addition of Cl₂ gas. The etch rates of the TiO₂ thin films increased with increasing source power and bias power, but decreased with increasing process pressure. Ion bombardment was required, due to the relatively high volatility of the by-products formed during etching by the Cl₂/Ar plasma. The chemical states on the surface of the etched TiO₂ thin films were investigated using XPS. The etch characteristics of the TiO₂ thin film can be explained as follows: Ti interacted with the Cl-radicals in the Cl₂ containing plasmas to form the high volatile TiCl_x by-products, which can be effectively removed with the help of ion bombardment. The results agreed well with the general energy dependency of the ion-enhanced chemical etching yields.

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