

ETCHING OF PLATINUM THIN FILMS BY HIGH DENSITY Ar/Cl₂/HBr PLASMA

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ABSTRACT

Platinum is widely researched as the electrode material for capacitor of high dielectric films in dynamic random access memory (DRAM) application. However, the dry etching of Pt is difficult because of its chemical stability. So, the dry etching of Pt remains at the preliminary work.

In this work, Pt etching mechanism was investigated by using inductive coupled plasma (ICP) with Ar/Cl₂/HBr gas.

The peaks were found due to brominated Pt as well as chlorinated Pt in the XPS (X-ray photoelectron spectroscopy) narrow scan. Ion bombardment effects on the etched surface decreased with increasing HBr/(HBr+Cl₂) gas mixing ratio. The maximum etch rate of Pt was 105 nm/min at the HBr/(HBr+Cl₂) ratio of 0. And selectivity to SiO₂ was good in all samples with various HBr/(HBr+Cl₂) gas mixing ratios. These results are consistent with XPS and OES (optical emission spectrometry) and single Langmuir probe.

INTRODUCTION

As highly integrated memory devices develop above giga bit, dynamic random access memory (DRAM) requires the capacitor of high dielectric films. Some of metal oxides such as Pb(Zr_{1-x}Ti_x)O₃, Ba_{1-x}Sr_xTiO₃ and Sr_xTiO₃ have proposed material of capacitor cells in future DRAM.^{1,2,3} Because they have much higher dielectric constant compared with conventional silicon-oxide or silicon-nitride.

In order to preserve the high dielectric constant, the crystal structure of dielectric materials has to be perovskite structure of substrate materials and requires non-oxidized surface of substrate materials.⁴

Platinum is most promising material as bottom electrode because of its chemical stability and good crystallinity. In spite of this merits of platinum, the technology for patterning of platinum thin films didn't much be developed due to property of platinum not to be produce volatile compounds with any etching gas at room temperature.

Anyway, for the purpose of highly integrated memory device by higher dielectric capacitor, it is the first priority to develop the technology for plasma etching of platinum.

Plasma process used inductively coupled plasma (ICP) has emerged as a promising technique to meet the increasingly stringent requirements in microelectronics fabrication.^{5,6} The high density of plasma produced by ICP sources is particularly attractive for DRAM application. Some advantages in using this technique for etching is included high etch rate and lower ion bombardment energies compared with conventional reactive ion etching (RIE).

We presented in our previous paper that addition of Cl₂ gas into Ar gas helped etch rate of platinum thin films improve at 0.1 of Cl₂/(Ar+Cl₂) ratio. That's the reason of chemical effect of Cl radicals.⁷

In this study, we make research in the influence of HBr gas additive to Ar/Cl₂ plasma using ICP. X-ray photoelectron spectroscopy (XPS) was used for the investigation into surface reaction of platinum etching with Ar/Cl₂/HBr plasmas. The effects of HBr plasma in platinum thin films etching can be known by the investigations of plasma characteristics using optical emission spectroscopy (OES) and ion current density of mixed plasmas using single Langmuir probe.

EXPERIMENT

The 5-inch Si substrates used for this study were doped with B (0.85-1.15 μm), oriented (100), and chemically etched for 60 sec using 1% HF:H₂O prior to chemical vapor deposition (CVD) growth. The substrates were coated with a 600 nm-thick layer of SiO₂ grown by low-pressure-CVD (SiH₄ + O₂, 420 °C, 240 mTorr). To enhance the adhesion of Pt on the oxide layer, a 75 nm-thick TiW(90%) was deposited prior to Pt deposition. Deposition of the Pt films was performed using a Varian 3180 d. c. sputtering system equipped with a 7-inch conical magnetron sputtering source. The Pt sputtering target was specified at 99.999 % purity. Sputtering was performed in research-grade Ar at a pressure of 8 mTorr, and the distance from source to substrate was \sim 3.3 inch. Typical sputtering power was 9.6 kwatts. These conditions resulted in a nominal deposition rate of \sim 1,000 nm/min. During deposition, the substrate was grounded and the substrate temperature was held at 200 °C using a gas conduction heating. The final thickness of the sputtered Pt film was \sim 200 to 300 nm, and \sim 95 % uniform across the surface of the 5-inch wafers. Film thickness was measured using a Tencor Model -step 200 surface profiler.

Plasma etching of the Pt films was performed using a home-made ICP mode etching system. Fig. 1 is schematic diagram of experimental apparatus. A planar inductively coupled plasma (ICP) etching equipment having a 3.5-turn spiral copper coil on the top of the chamber separated by a 1cm-thick quartz window was used in this experiment. 13.56MHz rf power was applied to the coil to induce inductively coupled plasma. Another 13.56MHz rf power was applied to the substrate to induce bias voltage to the wafer. Wafers were placed on a bottom electrode. Substrate holder temperature during the Pt etch was held at \sim 50 °C using the circulation of cooling water. A Balzers turbo pump reduced residual gas pressure to below 5×10^{-5} Torr before the processing step. The HBr/(HBr+Cl₂) mixing ratio was changed from 0 to 1. ICP source power was constant at 600 watts. Bias voltage was at -125 volts and bias power was controlled to maintain the constant bias voltage. Etch rate was measured using a 4-point probe and thin film thickness measuring system. To observe the etch profile, a \sim 300 nm thick plasma enhanced chemical vapor deposition (PECVD) film was deposited as a masking layer during Pt etching. The etch profiles were examined by using scanning electron microscopy (SEM; Hitachi S-800).

After removing the plasma etched samples from the etching system, the samples had been exposed to the atmospheric environment for approximately 1 day prior to XPS analysis. Compositional analysis of the Pt surface was performed using a VG Scientific ESCALAB 200R XPS with Mg K (1253.6 eV) radiation operating at 250W. A narrow scan spectra of all regions of interest were recorded with 20 eV pass energy in order to quantify the surface composition and identify the chemical binding state.

The plasma characteristic was extracted from OES and single Langmuir probe. A optical emission spectrometry (OES) located at the sidewall of the process chamber was used to monitor species such as dissociated radicals in the plasma. The hole of 1mm-diameter was formed to the wall of etching chamber and connected to the differential pumped system. Single Langmuir probe was also inserted at the center of the chamber to measure the ion current density in the plasma. Ion current was saturated at approximately \sim 20 volts and was extracted at \sim 40 volts. Ion current density was calculated by dividing ion current into probe area.

RESULTS AND DISCUSSION

The plasma species densities were obtained by OES. Fig. 2 shows the relative intensity of plasma species with various HBr/(HBr+Cl₂) gas mixing ratio at 50% Ar gas. In this figure, Br radicals increase with increasing HBr/(HBr+Cl₂) ratio. This seems to be due to the increase of HBr partial pressure in the plasma. At the same time, Cl radicals density decrease with increasing HBr/(HBr+Cl₂) ratio. These indicate that variation of etch characteristic is dominated by Br and Cl radicals when other parameters are

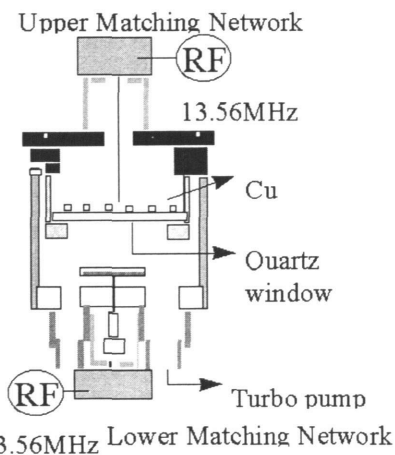


Figure 1. Schematic diagram of ICP etcher

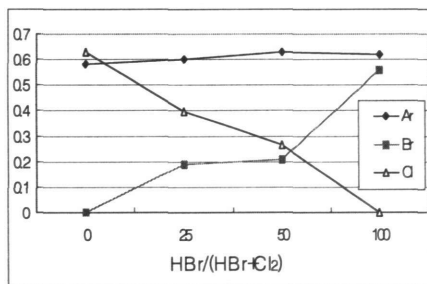


Figure 2. The relative plasma species density with various HBr/(HBr+Cl₂) mixing ratio

maintained.

Table 1 represents the XPS atomic counts of the Pt surface with HBr/Cl₂ gas mixing ratio at 50% Ar gas. Pt, O, C, Cl and Br atoms were detected on the etched surface. However, Ar did not exist on the etched surface. O and C were observed which is caused by air exposure of the etched samples prior to XPS analysis. In the table 1, Br was observed on the etched surface at HBr/(HBr+Cl₂) ratio of 1 and Cl was observed on the surface at HBr/(HBr+Cl₂) ratio of 0.

XPS narrow scan analysis was carried out to examine the chemical binding states of each element on the Pt surface with HBr/(HBr+Cl₂) ratio. Fig. 3 shows Pt narrow scan spectra. Fig. 3 (a) and (b) represent the Pt 4f spectra on the etched surface with Ar only and HBr/(HBr+Ar) ratio of 0.5 (i. e., HBr/(HBr+Cl₂) ratio of 1 at 50% Ar), respectively. Fig. 3 (a) shows that the Pt 4f spectrum can be resolved into 2 chemical components as Pt-Pt and Pt-O. The peaks at 71 eV and 74.4 eV binding energies correspond to Pt 4f_{7/2} and Pt 4f_{5/2} of elemental Pt, respectively. At the same time, The peaks due to oxidized Pt is also found at the binding energy of 72 eV and 75.5 eV for normal Pt-O bond in PtO and PtO₂, respectively.⁸ This implies that Pt atoms on the surface mainly exists the chemical state of elemental Pt. It is also found in this figure that the peak intensities of Pt-O bonds are small. This seems to be resulted from the chemical stability of Pt.⁷ In comparison to fig. 3 (a), it is found that the peak intensities corresponding to 72.5 eV and 76 eV were increased in fig. 3 (b). These peak increases seem to be resulted from brominated Pt.

Fig. 4 represents the ion current density with various gas mixing ratio by single Langmuir probe. This figure shows that the ion current density decrease with increasing HBr/(HBr+Cl₂) ratio. This implies that ion bombardment effects on the etched sample are decreased with increasing HBr/(HBr+Cl₂) ratio.

Fig. 5 represents Pt and oxide etch rates as a function of HBr/(HBr+Cl₂) gas mixing ratio. This figure shows that Pt etch rate decreases with increasing HBr/(HBr+Cl₂) gas mixing ratio. Therefore, it is confirmed that the decreased Pt etch rate with increasing HBr/(HBr+Cl₂) gas mixing ratio is resulted from the decreased chemical reaction between Pt and Cl radicals and the decreased ion bombardment effects as mentioned. Oxide etch

atom HBr/(HBr+Cl ₂)	atom				
	Pt	O	C	Br	Cl
0%	34.2	44.5	18.2	-	7.11
50%	34.6	46.7	18.9	-	-
100%	34.4	44.2	16.8	4.6	-

Table 1. The XPS atomic counts of Pt surface with HBr/(HBr+Cl₂) gas mixing ratio

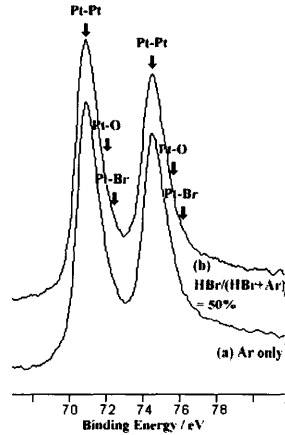


Figure 3. Pt 4f narrow scan spectra at HBr/(HBr+Ar) ratio of (a) 0 (b) 0.5

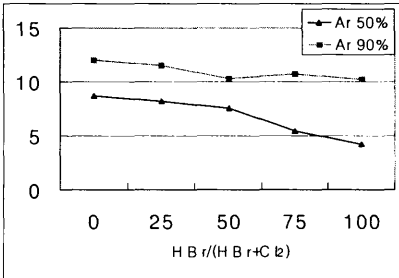


Figure 4. Ion current density as a function of various HBr/(HBr+Cl₂) gas mixing ratio and Ar fraction

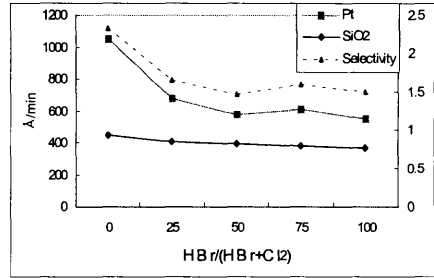
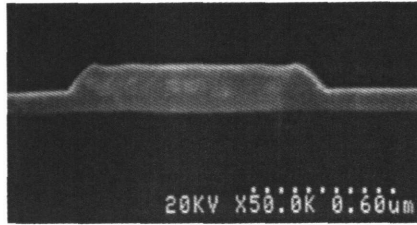


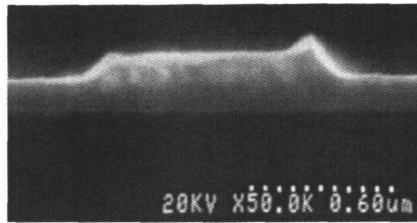
Figure 5. Pt and oxide etch rates as a function of HBr/(HBr+Cl₂) gas mixing ratio and the selectivity to SiO₂

rate is decreased with increasing HBr/(HBr+Cl₂) gas mixing ratio. The decrease of oxide etch rate seems to be resulted from the decrease of Cl₂ partial pressure. Therefore, selectivity to SiO₂ also decreased as a function of HBr/(HBr+Cl₂) gas mixing ratio.

Fig. 6 shows SEM photographs of Pt film after etching in 90% Ar/5% HBr/5% Cl₂ and in 90% Ar/10% Cl₂. In 90% Ar/10% Cl₂ (Fig. 6(b)), etch residues were deposited on the sidewall of the film.



(a)



(b)

Figure 6. SEM micrograph of Pt patterns after etching in (a) 90% Ar + 5% HBr + 5% Cl₂ (b) 90% Ar + 10% Cl₂

CONCLUSIONS

The chemical binding states of etched surface with various HBr/(HBr+Cl₂) gas mixing ratios were investigated by using XPS. The peaks were found due to brominated Pt and chlorinated Pt in the XPS narrow scan. Single Langmuir probe results showed that ion bombardment effects on the etched surface decreased with increasing HBr/(HBr+Cl₂) gas mixing ratio. The maximum etch rate of Pt was 105nm/min at the HBr/(HBr+Cl₂) ratio of 0. And the minimum was 55nm/min at HBr/(HBr+Cl₂) ratio of 1. Selectivity to SiO₂ was good in all samples with various HBr/(HBr+Cl₂) gas mixing ratios. Etch profile was better at HBr/(HBr+Cl₂) ratio of 0.5 than at HBr/(HBr+Cl₂) ratio of 0 or 1.

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