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# Roles of N<sub>2</sub> gas in etching of platinum by inductively coupled Ar/Cl<sub>2</sub>/N<sub>2</sub> plasmas

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Recently, much effort has been expended on etching platinum film, which is the candidate electrode material for the capacitor structure of future dynamic random access memory and ferroelectric random access memory. One of the most critical problems in the etching of platinum was generally considered to be the gradual character of the etch slope. Therefore, the addition of N<sub>2</sub> gas into the Ar/Cl<sub>2</sub> gas mixture, which had been proposed as the optimized platinum etching gas combination in our previous article, was performed. The selectivity of platinum to oxide as an etch mask increased with the addition of N<sub>2</sub> gas, and a steeper etch slope, over 75°, could be obtained. These phenomena were interpreted as the result of a blocking layer, such as Si–N or Si–O–N, on the oxide mask. Compositional analysis was carried out by x-ray photoelectron spectroscopy and secondary ion mass spectrometry. Moreover, the higher etch rate of the Pt film and a steeper profile without residues (such as Pt–Cl and Pt–Pt) could be obtained by the addition of 20% N<sub>2</sub> gas in the Ar(90)/Cl<sub>2</sub>(10) plasma. The plasma characteristics were extracted from optical emission spectroscopy. © 2000 American Vacuum Society. [S0734-2101(00)09404-5]

## I. INTRODUCTION

In the development of highly integrated memory devices, small-feature-size dynamic random access memory (DRAM) devices require capacitors of larger capacitance. This has resulted in more complicated device structures, such as cylinders or trenches, which involve many difficult process steps. To avoid the stringent process requirements associated with conventional capacitor structures, high dielectric materials, such as barium strontium titanate (BST) and lanthanum-doped lead zirconium titanate (PLZT), have been proposed as the materials of capacitor cells in future DRAMs. The deposition of these metal oxides over bottom electrodes often requires high-temperature processing; in an oxygen-containing ambient, the materials of the bottom electrode (such as doped poly-Si and RuO<sub>2</sub>) are easily oxidized and undergo decreased electrical conductivity. Pt film is used as an electrode material because platinum does not oxidize during high-temperature processing. Also, it is known that the leakage current of Pt film is lower than that of other electrodes. However, dry etching of Pt film is difficult with conventional tools since etch products are nonvolatile and produce unwanted sidewall redeposits. Sidewall redeposits must be removed because these residues can cause shorts in the ferroelectric random access memory (FRAM) and inconsis-

tent capacitance due to the change of the dielectric layer thickness on the electrode sidewall of the DRAM.<sup>1</sup> Therefore, to fabricate capacitors in high-density DRAM and FRAM, an etch process for Pt films with a vertical profile and no sidewall residues must be developed.

To realize this object, research was performed using Ar/Cl<sub>2</sub>/O<sub>2</sub> and Ar/Cl<sub>2</sub>/SiCl<sub>4</sub> gas plasmas.<sup>2,3</sup> A good etch profile was obtained using Ar/Cl<sub>2</sub>/O<sub>2</sub> plasmas with a low etch rate and some redeposits (such as PtCl<sub>x</sub> and PtOCl<sub>x</sub>) remaining on the mask sidewall. Therefore, to eliminate redeposits, subsequent cleaning with HCl was necessary after removing the mask. The etch slope of Pt film fabricated with Ar/Cl<sub>2</sub>/SiCl<sub>4</sub> gas plasma still was inadequate for high-density memory devices. Consequently, the need remained to develop an etch process with a good profile, a high etch rate, and no residue.

In this study, a Pt film was etched with inductively coupled plasmas (ICPs) by varying the content of N<sub>2</sub> gas in Ar(90)/Cl<sub>2</sub>(10) plasma, which was optimized as described in the previous article.<sup>4</sup> But, we did not experiment with a Si<sub>3</sub>N<sub>4</sub> mask because it was generally known that the etch rate of Si<sub>3</sub>N<sub>4</sub> is higher than that of SiO<sub>2</sub> by energetic ion bombardment.<sup>5</sup> In order to study the role of N<sub>2</sub> in Pt etching, the etched surface was investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). The etch profile of the Pt film was examined by scanning electron microscopy (SEM).

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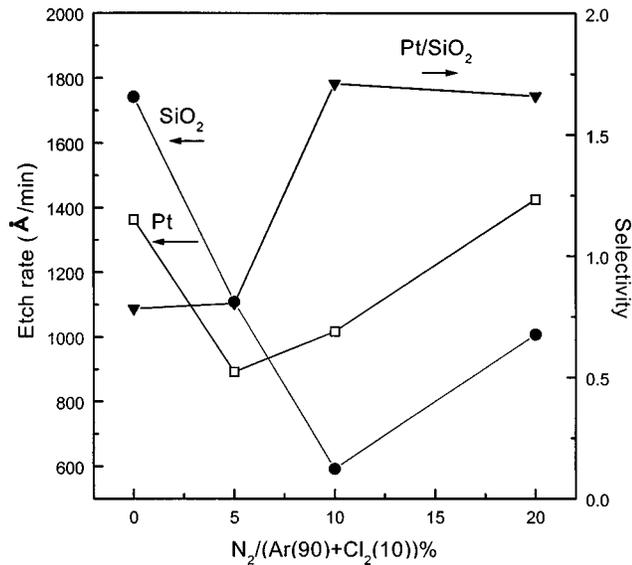


FIG. 1. Etch rate of Pt and SiO<sub>2</sub> and selectivity of Pt to SiO<sub>2</sub> as a function of N<sub>2</sub> gas added to the Ar(90)/Cl<sub>2</sub>(10) plasma (rf source power: 500 W; dc-bias voltage: -300 V; substrate temperature: 40 °C; and chamber pressure: 10 mTorr).

## II. EXPERIMENTAL DETAILS

For this study, the samples of Pt films were made as follows: Silicon wafers were doped with boron (0.85–1.15 Ω cm), oriented (100), and chemically etched for 60 s using 1% HF:H<sub>2</sub>O prior to chemical-vapor deposition (CVD) growth. The samples were coated with a 2000-Å-thick layer of SiO<sub>2</sub> grown by low-pressure CVD. A 500-Å-thick Ti film was deposited prior to Pt deposition. These Ti films were used to improve the adhesion of their overlying platinum films. Pt films were deposited by a Varian 3180 dc sputtering system. The final thickness of the sputtered Pt film was 2000 Å. Also, 3000-Å-thick SiO<sub>2</sub> films were deposited by the plasma-enhanced CVD (PECVD) method. To research the etch rate of Pt film and the selectivity of Pt films to SiO<sub>2</sub>, both Pt film and SiO<sub>2</sub> films on blanket wafers, were etched. We cannot expect differences when etching patterned wafers. The etch rates of both Pt and SiO<sub>2</sub> were measured with a Tencor Model α-step 200 surface profiler. To observe the etch profile, a 3000-Å-thick SiO<sub>2</sub> film was deposited by the PECVD method onto 500-Å-thick TiW, which had been deposited to improve the adhesion of the Pt film. These SiO<sub>2</sub> films were patterned with photoresist etching masks, for the subsequent etching of the Pt films. The lines and spaces of the pattern were from 0.6 to 1.2 μm in a structure. Plasma etching of these samples was performed using an ICP etching system. To generate inductively coupled plasmas, 13.56 MHz rf source power was applied to a planar spiral copper coil wound with 3.5 turns. Another 13.56 MHz rf power was also applied to the bottom electrode to induce bias voltage to the substrate. The Pt films in this study were etched by varying, from 0% to 20%, the amount of N<sub>2</sub> gas added to Ar(90)/Cl<sub>2</sub>(10) plasma, which was optimized as discussed in the previous article. In this study, the optimized condition was a rf power of 500 W, a dc bias voltage of -300 V, a

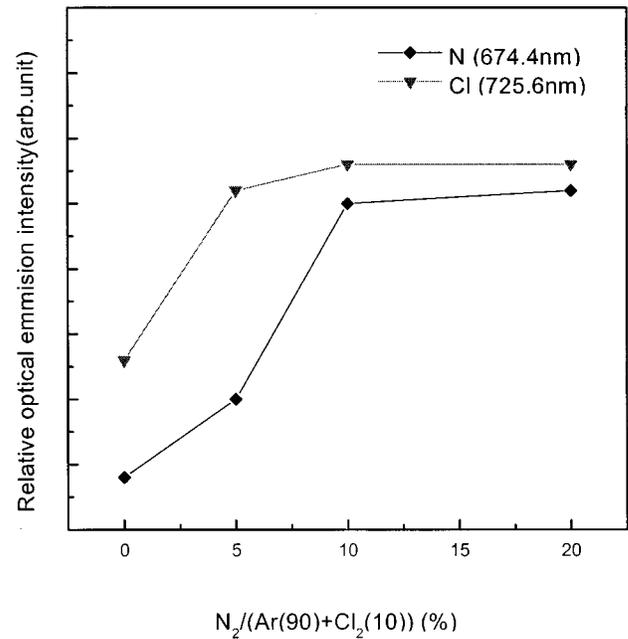


FIG. 2. Relative plasma species density as a function of N<sub>2</sub> gas added to the Ar(90)/Cl<sub>2</sub>(10) plasma (rf source power: 500 W; dc-bias voltage: -300 V; substrate temperature: 40 °C; and chamber pressure: 10 mTorr).

chamber pressure of 10 mTorr, and a substrate temperature of 40 °C. The etched samples were exposed to the atmospheric environment for approximately 24 h prior to XPS and SIMS analysis. Compositional analysis of the Pt and SiO<sub>2</sub> surface was investigated using a VG Scientific ESCALAB 220-IXL and a CEMECA IMS6F. The XPS Al

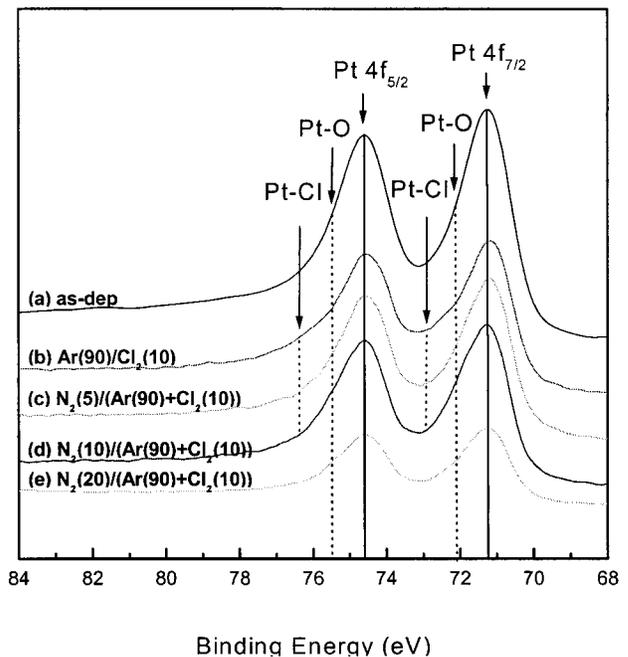


FIG. 3. Pt 4f narrow scan spectra of the etched Pt film as a function of N<sub>2</sub> gas added to the Ar(90)/Cl<sub>2</sub>(10) plasma (rf source power: 500 W; dc-bias voltage: -300 V; substrate temperature: 40 °C; and chamber pressure: 10 mTorr).

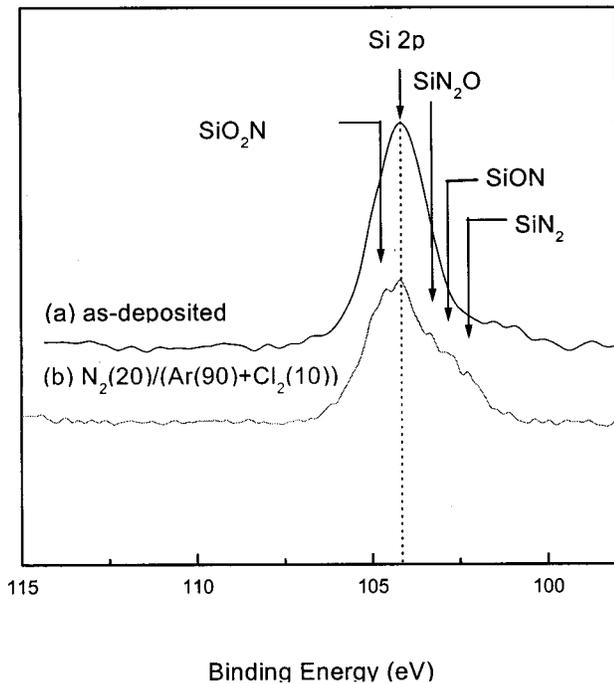


FIG. 4. Si 2*p* narrow scan spectra of the etched SiO<sub>2</sub> film with the addition of 20% N<sub>2</sub> gas in the Ar(90)/Cl<sub>2</sub>(10) plasma (rf source power: 500 W; dc-bias voltage: -300 V; substrate temperature: 40 °C; and chamber pressure: 10 mTorr).

K $\alpha$  source provides chromatic x rays at 1486.6 eV. Narrow scan spectra of all interested regions were recorded with 20 eV pass energy in order to qualify the surface composition and to identify the chemical binding state. SIMS measured the molecular weight of particles released from the surface of the material by bombardment of ions. A Cs<sup>+</sup> ion beam of 1.11 kV and 10.68–10.92 nA was used by the SIMS source. The Hitachi S-800 SEM photograph showed the profile of the etched samples, and the plasma characteristics were diagnosed by optical emission spectroscopy (OES).

### III. RESULTS AND DISCUSSION

Figure 1 shows the etch rates of Pt and SiO<sub>2</sub>, and the selectivity of Pt to SiO<sub>2</sub> as a function of N<sub>2</sub> gas added to the Ar(90)/Cl<sub>2</sub>(10) plasma. The samples were etched using ICP at a chamber pressure of 10 mTorr, a rf power of 500 W, a dc-bias voltage of -300 V, and a substrate temperature of 40 °C. As up to 20% N<sub>2</sub> gas was added to the Ar(90)/Cl<sub>2</sub>(10) plasma, the etch rate of Pt increased from 1363 to 1425 Å/min. The selectivity of Pt to SiO<sub>2</sub> increased from 0.782 to 1.66.

Figure 2 shows the intensity of the Cl radical as a function of additive N<sub>2</sub> gas in Ar/Cl<sub>2</sub> plasma. As shown in Fig. 2, Cl radicals increased with the addition of N<sub>2</sub> gas, in spite of the decreasing partial pressure of Cl<sub>2</sub>. When the plasma includes an added 5% or 10% of N<sub>2</sub>, Cl and N radicals increase. If the chemical reaction were dominant in the Pt etching, the etch rate of the Pt film would increase. However, when 5% or 10% N<sub>2</sub> is added to the plasma, the etch rate of the Pt film remains low. This means that the Cl radical does not enhance

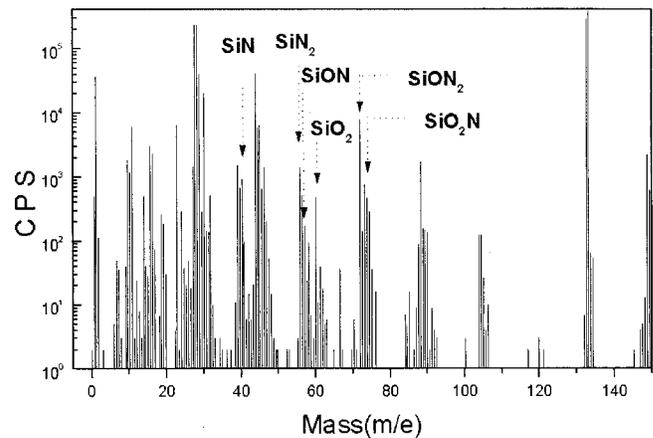


FIG. 5. Mass analysis of the etched SiO<sub>2</sub> surface with the addition of 20% N<sub>2</sub> gas in the Ar(90)/Cl<sub>2</sub>(10) plasma.

Pt etching. This is confirmed by our previous research.<sup>4</sup> It was hypothesized that the N<sub>2</sub> dissociated into the N<sup>+</sup> ion and the N radical. The decrease of the etch rate of SiO<sub>2</sub> would then be due to a blocking layer, such as Si-N or Si-O-N, produced by the process.

Figure 3 shows Pt 4*f* narrow scan spectra as a function of N<sub>2</sub> gas added to the Ar/Cl<sub>2</sub> plasma. The Pt 4*f* peaks at 71.2 and 74.4 eV binding energies can be resolved into Pt 4*f*<sub>7/2</sub> and Pt 4*f*<sub>5/2</sub> of the original Pt 4*f* peak. As shown in Fig. 3(a), the binding-energy peaks at 72 and 75.4 eV binding energies correspond to Pt-O resulting from exposure to the atmospheric environment. In Figs. 3(b)–3(d), the Pt shapes decrease and broaden. However, the peak intensities at 73 and 76.4 eV increase. These peaks correspond to the bond of Pt-Cl. However, in Fig. 3(e), the low peak intensity of the Pt-Cl bond can be presented.

Figure 4 shows Si 2*p* narrow scan spectra as a function of added N<sub>2</sub> gas in the Ar/Cl<sub>2</sub> plasma. The Si 2*p* peak in SiO<sub>2</sub>

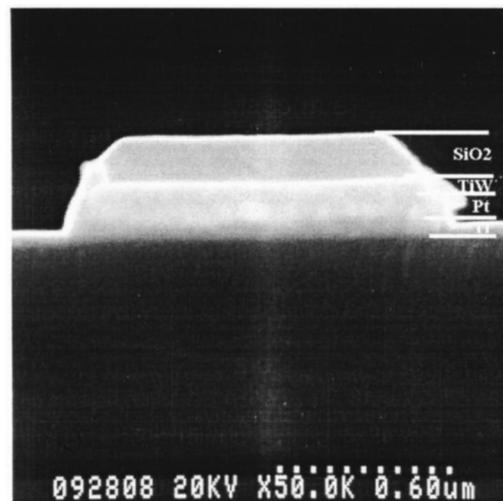


FIG. 6. Cross-sectional SEM photograph of a Pt film etched with the addition of 20% N<sub>2</sub> gas in the Ar(90)/Cl<sub>2</sub>(10) plasma (rf source power: 500 W; dc-bias voltage: -300 V; substrate temperature: 40 °C; and chamber pressure: 10 mTorr).

appears at 104.1 eV binding energy. The peaks at 102.8 and 103.3 eV correspond to SiN<sub>x</sub> and SiO<sub>x</sub>N<sub>y</sub> in Fig. 4(b). This confirms that N interacts with the SiO<sub>2</sub> mask and produces a blocking layer, resulting in a decreased etch rate of SiO<sub>2</sub> and an enhanced Pt/SiO<sub>2</sub> selectivity.

Figure 5 shows the mass analysis of the etched surface of SiO<sub>2</sub> film at 20% additive N<sub>2</sub> gas in Ar(90)/Cl<sub>2</sub>(10) plasma by SIMS. As shown in Fig. 5, the existence of SiN<sub>2</sub>, SiN, of SiO<sub>2</sub>N, and SiON<sub>2</sub> was proven.

Figure 6 shows the SEM photograph of a Pt pattern etched with 20% additive N<sub>2</sub> gas in the Ar(90)/Cl<sub>2</sub>(10) plasma. The etch profile was over 75° and free of residues, such as Pt-Cl and Pt-Pt bonds.

#### IV. CONCLUSION

The role of N<sub>2</sub> gas in etching Pt film was studied by using ICP. The etch rate of Pt film is the highest with 20% additive N<sub>2</sub> gas in the Ar(90)/Cl<sub>2</sub>(10) plasma. The maximum etch

rates of the Pt film and selectivity of Pt to SiO<sub>2</sub> are 1425 Å/min and 1.71, respectively. Moreover, this process can achieve a good profile (over 75°, and free of residue) at 20% additive N<sub>2</sub> gas in the Ar(90)/Cl<sub>2</sub>(10) plasma because N<sub>2</sub> plays the role of increasing ion density and forming a blocking layer, such as Si-N or Si-O-N onto the SiO<sub>2</sub> mask.

#### ACKNOWLEDGMENT

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