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Etch Characteristics of Pt Using $Cl_2/Ar/O_2$ Gas Mixtures

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Inductively coupled plasma etching of platinum with $Cl_2/O_2/Ar$ gas chemistries was examined. Plasma characteristics were investigated with increasing O_2 ratios using a Langmuir probe and a quadrupole mass spectrometer. The chemical reaction during the platinum etching was also examined from the chemical binding states of the etched surface by X-ray photoelectron spectroscopy. Additional characterization employed a four-point probe, thin-film thickness measuring system, and scanning electron microscopy. The relationship between plasma characteristics and etch results with various O_2-gas mixing ratios was also studied. It was confirmed that small additions of oxygen into the Cl_2/Ar gas mixtures lead to high selectivity and a good sidewall profile without a fence, also referred to as a bull-ear.

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Gigabit dynamic random access memory (DRAM) and ferroelectric random access memory (FRAM)[1] need films with a high dielectric constant. Many researchers have been interested in the formation of high dielectric thin films[2-4] such as $Pb(Zr_{1-x}Ti_x)O_3$, $Ba_{1-x}Sr_xTiO_3$, and $SrTiO_3$. In order to preserve the high dielectric constant, it is important to use substrate materials which are inert and minimize surface oxidation. A promising candidate with such properties is Pt, which has been widely used for the formation of high-dielectric films because of its chemical stability and good crystallinity.[5] Therefore, the development of Pt etching technology is required. However, little work has been done in developing the etch technology for patterning Pt.[6-8] In a previous report,[8] we investigated the etch characteristics of Pt in Cl_2/Ar plasmas using inductively coupled plasma (ICP). From the results, the selectivity of Pt to silicon dioxide was as low as 1.7 and a fence (also referred to as a bull-ear) on the etched sidewall was formed, so to improve this low selectivity and to remove the fence, we introduced O_2 to the gas mixtures.

In this study, the effects of additive O_2-gas to Ar/Cl_2 plasma on the Pt etch characteristics were investigated. The plasma characteristics and chemical surface reaction and Pt etch characteristics with $Ar/Cl_2/O_2$-gas chemistries are discussed.

Experimental

The 5 in. Si substrates were doped with B (0.85-1.15 Ω cm), oriented (100), and chemically etched for 60 s using 1% $HF:H_2O$ prior to chemical vapor deposition (CVD) growth. The substrates were coated with a 600 nm thick layer of SiO_2 grown by low-pressure CVD ($SiH_4 + O_2$, 420°C, 240 mTorr). To enhance the adhesion of Pt to the oxide layer, a 75 nm thick $Ti_{0.1}W_{0.9}$ layer was deposited prior to the Pt deposition which was performed using a Varian 3180 dc sputtering system. Plasma etching of the Pt films was performed using a homemade ICP mode etching system. Target materials, process conditions, the thickness of Pt film, and the ICP[9,10] system used for this study were described in detail in a previous report.[8] The ratio of Cl_2/Ar gas mixture was kept constant at 1/9. The O_2-mixing ratio was controlled by partial pressure and changed from 0 to 0.5. Etch rate was measured using a four-point probe and thin-film thickness measuring system (Leitz Co., MPV-SP). To observe the Pt etch profile, a dioxide film was deposited to a thickness of ~300 nm by plasma-enhanced chemical vapor deposition (PECVD) as a masking layer during Pt etching.

After etching, the samples were exposed to the atmospheric environment for approximately 1 day prior to X-ray photoelectron spectroscopy (XPS) analysis. Compositional analysis of the Pt surface was performed using a VG Scientific ESCALAB 200R XPS with Mg Kα (1253.6 eV) radiation operating at 250 W. A narrow scan spectra of all regions of interest were recorded with 20 eV pass energy.

A quadrupole mass spectrometer (QMS, Balzers QMG/E 125) was used to monitor species such as dissociated radicals in the plasma. A single Langmuir probe was also inserted into the plasma to measure the ion current density. Ion current was extracted at −40 V and its density was calculated by dividing the ion current into the probe area.[11] To examine the Pt etch characteristics, a Hitachi scanning electron microscope (SEM) was used.

Results and Discussion

Plasma characteristics.—We investigated plasma characteristics with additive O_2 ratio by the quadrupole mass spectrometer (QMS). Figure 1 shows the relative values of the reactive species. Cl^+ and Ar^+ species were abruptly decreased with the addition of O_2, and both species showed the same trend. Up to 20% of O_2 addition, the Ar^+ and Cl^+ species abruptly decreased. Then, beyond 20% they were nearly saturated. Meanwhile, O^+ species increased linearly, which resulted from the increase of O_2 partial pressure. The ion current density with the addition of O_2 was also measured with a Langmuir probe, and is shown in Fig. 2. It was also found that the ion current density decreased with adding the O_2 gas.

Surface reaction.—XPS analyses were carried out to investigate surface reactions on Pt films with the addition of O_2. Samples were

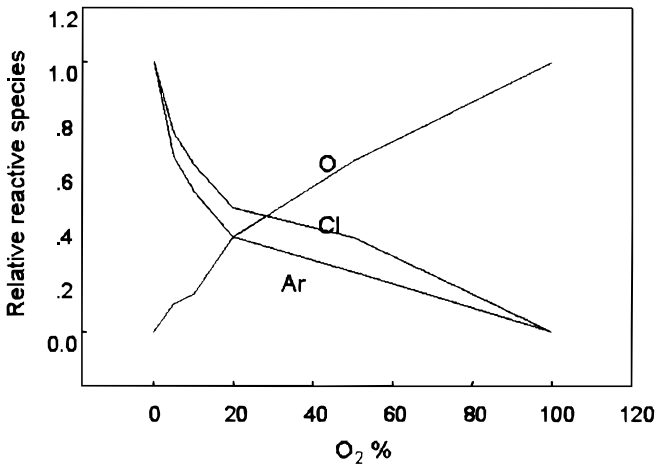

Figure 1. The relative values of the reactive species with various O_2 ratios.

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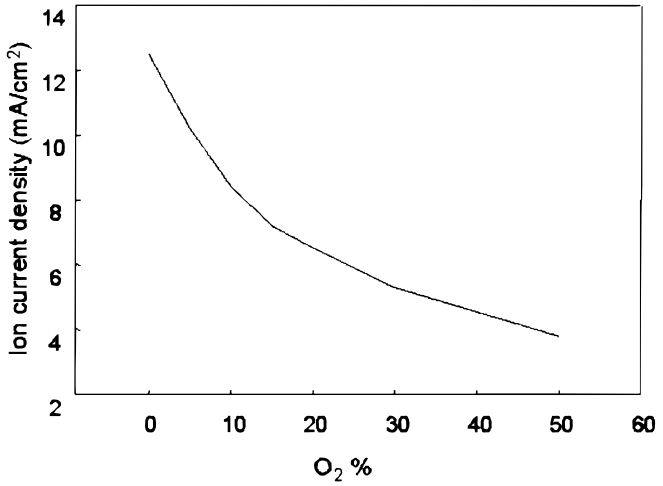

Figure 2. The ion current density with the addition of O_2.

analyzed at the take-off angle of 15°. Figure 3 shows the atomic percent of each element detected on the etched surface after being etched with various gas-mixing ratios. For comparison, the data on a pure Pt film are also plotted. On the pure Pt film, the atomic percentage of platinum, carbon, and oxygen were 41.8, 41.9, and 16.3%, respectively. The carbon and the oxygen detected on the pure Pt film was a result of air exposure. The atomic percentage of carbon is generally about 10% at the take-off angle of 90°. Such a high value of the atomic percent of carbon obtained in this study is due to the measurement at the low take-off angle. In the case of using only Ar/Cl_2 gases, a chlorine content of 28.84% was detected. This indicates that the layer of Cl-containing compound was formed on the etched film.[8] A small addition of O_2 made the atomic content of Cl abruptly decrease. This means that the small addition of O_2 largely contributes to the removal of Cl-containing compound.

The atomic percentages of Cl, Pt, and O increased but that of C decreased with increasing the addition of O_2 above 5%, which is consistent with the QMS data shown in Fig. 1. However, in spite of the decrease of Cl_2 partial pressure in the plasma, the atomic content of Cl was slightly increased.

From the binding states of each element after etch, we can infer the surface reaction. To do this, the binding state of each element on the etched surface was examined by using narrow scan analyses of XPS. Carbon peaks were detected at the binding energy of 284.5 eV and had the typical shape of graphitic carbon.[12] This carbon peak results from air contamination.

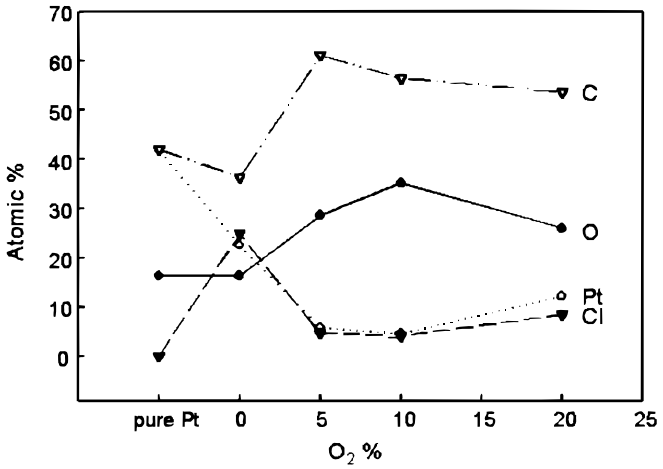

Figure 3. The atomic percent of each element with various O_2-gas mixing ratios.

Figure 4 shows Pt 4f spectra depicting the surface reaction. In the case of the pure Pt, the binding energy of metallic Pt $4f_{7/2}$ and $4f_{5/2}$ were 70.8 and 74.1 eV, respectively, and the difference was 3.3 eV, which is consistent with the reported value.[12] On the other hand, the full width at half maximum (fwhm) of the Pt 4f spectrum of Cl_2/Ar etched samples was wider than that of the pure Pt, and the peak position shifted to a higher binding energy. The Pt $4f_{7/2}$ peak that was formed on the Cl_2/Ar etched sample seems to be a grouping of a metallic Pt peak and the other peak at 72 eV, which is thought to result from subchlorinated Pt's. However, the spectrum of the Pt peak at the O_2 ratio of 5% is very similar to that of the metallic Pt. This means that most Pt-Cl bonds were removed by the addition of O_2. From this result, we can explain the phenomenon described in Fig. 3. That is, in Fig. 3, a small addition of O_2 gas to Cl_2/Ar plasma contributes to the removal of Cl-containing compounds and finally reduces the atomic content of Cl on the etched surface. Generally, the shapes of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks in metallic Pt spectra are symmetric.[12] However, it is also observed that the peak of Pt with increasing of O_2 ratio is not symmetric and the valley between Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks changes shape. This means that another peak around 72.5 eV is present and this peak grows larger with increasing O_2 ratio. This binding energy corresponds to a suboxidized bond. Generally, the peak of Pt-O is detected at the higher binding energy than that of Pt-Cl because the electronegativity of oxygen is higher than that of chlorine.

Figure 5 shows the Cl 2p spectra. Generally, the doublet in a Cl 2p spectrum is observed. The binding energies of Cl $2p_{3/2}$ and Cl $2p_{1/2}$ are 198.5 and 200.1 eV, respectively. At the O_2 ratio of 0%, the peak corresponds to the typical Cl-metal bonds. This implies that chlorine mainly bonds to platinum. However, a small trace of Cl was detected at the O_2 ratio of 10%. This means that the content of Cl formed on the etched surface is very small. This low content of Cl results from the interactions with oxygen on the etched surface. This oxygen interaction can be explained as follows: oxygen with Cl forms $PtCl_xO_y$ compounds on the Pt surface and these $PtCl_xO_y$ compounds are easily removed. So in Fig. 3 and 4, the content of Cl at the O_2 ratio of 5% was very low. With increasing O_2, the Cl peak intensity increased and the peak position shifted to a lower value. As the O_2 partial pressure increases, the ion-bombardment effect was also decreased due to lower ion densities as mentioned in Fig. 2. In this case, the decrease of ion bombardment may have an effect on the removal of $PtCl_xO_y$ from the surface. Therefore, in spite of the decrease of Cl radical density with increasing O_2 ratio as mentioned in Fig. 1, the content of Cl formed on the etched surface increases with the O_2 ratios.

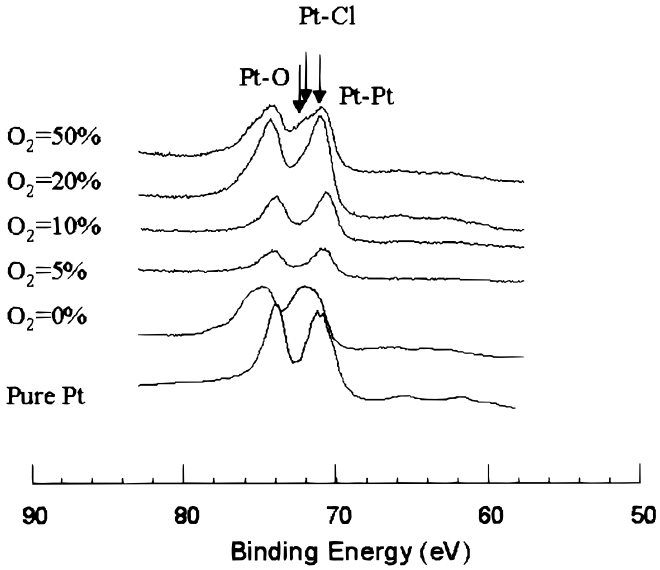

Figure 4. Pt 4f narrow scan spectra at various O_2-gas mixing ratios.

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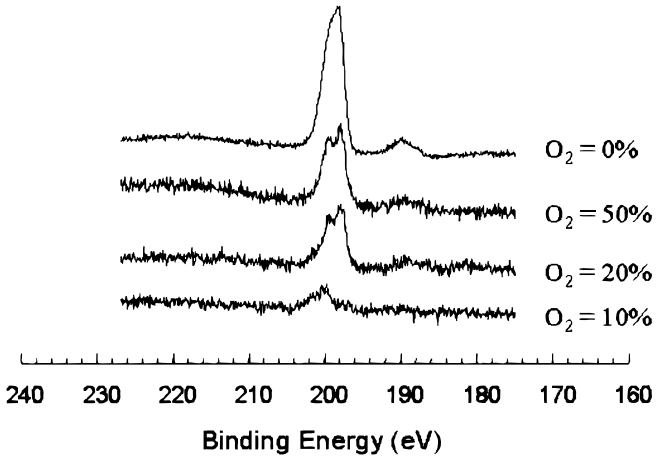

Figure 5. Cl 2p narrow scan spectra at various O_2-gas mixing ratios.

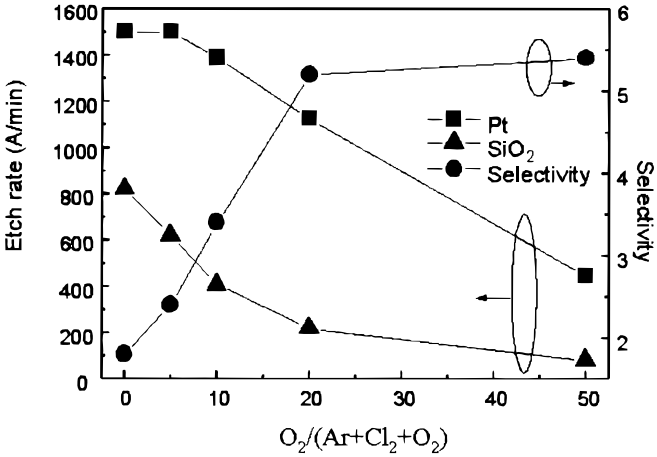

Figure 6. The change of the etch rate and selectivity by the addition of O_2.

Etch characteristics.—The change of the etch rate and the selectivity by the addition of O_2 were examined and plotted in Fig. 6. The etch rate of oxide abruptly decreased with increasing O_2 ratio. However, the slope of the Pt etch rate is lower than that of oxide. Therefore, the selectivity increased linearly up to 20% of O_2 addition but saturated over that value. It can be explained that the addition of O_2 will reduce the relative density of chlorine, lower the ion current density, and then finally decrease the etch rate of silicon dioxide. This explanation can also be applied to the change of the Pt etch rate. However, the decrease in the Pt etch rate is lower than that of the oxide. This difference can be explained by O_2 interactions on surface with the Pt. Since PtO_xCl_y compound is more easily removed than $PtCl_x$, the decrease in Pt etch rate with the addition of O_2 is slower than that of dioxide.

The etch profile after etch with various gas mixtures was examined by SEM and is shown in Fig. 7. Figure 7a shows a profile etched with Cl_2/Ar gas. A fence on the pattern sidewall was observed. Figure 7b shows an SEM image with the addition of 5% O_2. The thin layer, about 5 nm, on the Pt was a mask layer. The mask layer on the Pt was not entirely removed compared to that of Cl_2/Ar plasma. That is, the selectivity was increased. On the other hand, in the case of Cl_2/Ar gas mixtures (1:9), sputtering of the surface formed the fence, but it was not formed in the case of the 5% O_2 condition. A subchlorinated Pt layer was formed after the etch by using

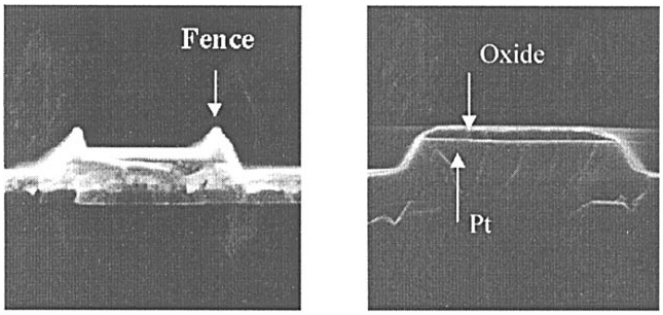

Figure 7. The profile after etch with various gas mixtures: (a, left) 0% O_2 and (b, right) 5% O_2.

the Cl_2/Ar gas mixture. This can be sputtered and redeposited on the sidewall. However, with the addition of O_2, such residue layers did not form. That is, the presence of O radicals easily removes the subchlorinated Pt layer, as discussed.

Conclusion

In this study, the effects of additive O_2 gas to Ar/Cl_2 plasma on the Pt etch characteristics were investigated. The plasma characteristics and chemical reaction on the etched surface, and Pt etch characteristics with Ar/Cl_2/O_2 gas chemistries were examined by a Langmuir probe, QMS, XPS, SEM, and a four-point probe. From XPS analysis, it was found that the O_2 addition to Cl_2/Ar plasma resulted in a decrease of Cl content on the etched surface. This implies that O_2 contributes to the removal of Cl compounds on the etched Pt surface. It was also found by the Langmuir probe measurement that as the O_2 partial pressure increases, the ion current density was decreased. In this case, the change of ion current density may have an effect on the removal of $PtCl_xO_y$ from the surface. Therefore, in spite of the decrease of Cl radical density with increasing O_2 ratio, the content of Cl formed on the etched surface increases with O_2 ratio.

At the same time, it was found that the Pt etch rate more slowly decreased compared to that of dioxide with O_2 gas mixing ratio. Therefore, the Pt to dioxide selectivity increased and an improved Pt etch profile was obtained with the O_2 addition. This can also result from the formation of $PtCl_xO_y$.

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