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Chemical Dry Etching of Platinum Using Cl_2/CO Gas Mixture

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In this study, we have developed a novel method for Pt etching using a chemical dry etching (CDE) system. A volatile etching product was formed during the reaction of Pt with Cl_2 and CO. The etch rate was abruptly increased above 210 °C, which corresponds to the sublimation temperature of platinum dicarbonyl chloride, $PtCl_2(CO)_2$. The maximum etch rate was obtained at the Cl_2/CO mole ratio of 1/2, which agrees with the stoichiometric ratio of Cl_2 to CO to form platinum dicarbonyl chloride. The large enhancement in etch rate above 210 °C might be attributed to the formation of a volatile platinum carbonyl compound on the Pt surface. A relatively high etch rate above 100 nm/min and high selectivity toward Pt against sublayers such as SiO_2 and TiN were obtained under various etching conditions. Chemical analysis of the etched surface with XPS showed that surface Pt atoms were converted to a volatile compound. XPS and SEM studies of the Pt surface treated with Cl_2 and/or CO indicated that volatile platinum carbonyl compounds were formed in the reaction of CO with Pt surface pretreated with Cl_2 above 210 °C.

Introduction

Ferroelectric thin film capacitors that have a large capacitance arising from the high dielectric constant and a hysteresis behavior including spontaneous and remanent polarization have attracted much attention because of increasing demands for highly integrated memory devices, such as DRAM (dynamic random access memory) beyond 1 gigabyte density or nonvolatile ferroelectric random access memory of the future generation.[1,2] In future DRAM devices, a simple ferroelectric capacitor of planar structure will be used to simplify the processing to form a capacitance layer, because ferroelectric materials have a dielectric constant much higher than conventional ONO (oxide−nitride−oxide) capacitors.[3] Furthermore, ferroelectric materials for nonvolatile memory have such advantages as high-density integration, high speed, and low operating voltage, enabling us to design a compatible system-on chip memory soon. However, several problems were raised in applications for integrated ferroelectrics.[4] One of them is the difficulty in achieving the fine patterning of ferroelectric structures because pattern resolution is reduced by the formation of nonvolatile residues during dry etching.

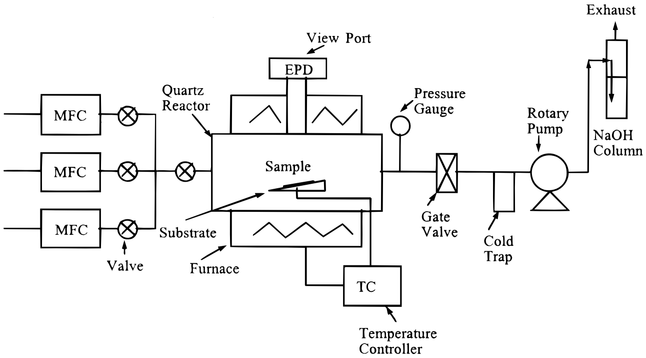

Figure 1. Schematic diagram of the chemical dry etching.

Platinum films show a high electrical conductivity and low leakage current. Therefore, it has been used as an important electrode material in ferroelectric capacitors. Since platinum is chemically stable, it is difficult for Pt atoms to be converted to volatile products. Recently, several studies have been reported on the dry etching of platinum films using halogen-containing gases, such as CF_4/Ar,[5] Cl_2/O_2,[6,7] Cl_2/C_2F_6,[8] and H_2S/HBr.[9] However, there has been little study on dry etching using the chemical reaction of Pt with etchants to form a volatile product, despite the importance of solving the practical problems associated with formation of the nonvolatile residues during etching process. The conventional etching process done by ion sputtering using high bias voltage and low pressure has such disadvantages as residue deposition at the pattern sidewall during etching and a sloped etch profile resulting from

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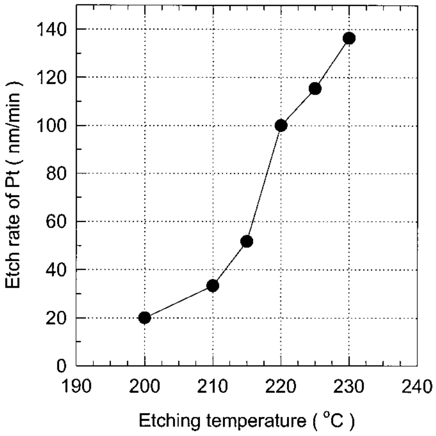

Figure 2. Dependence of the etch rate of Pt films on etching temperature (percentage Cl_2 in CO = 22% and total flow rate = 255 sccm).

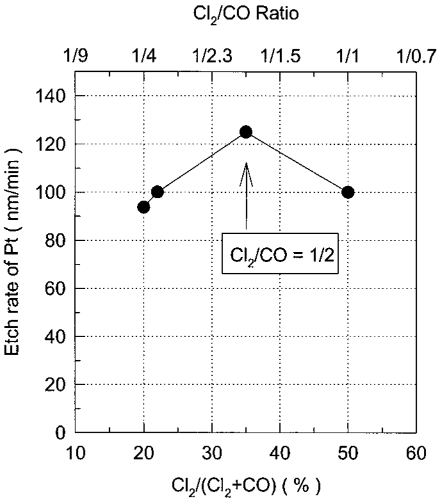

Figure 3. Dependence of the etch rate of Pt films on Cl_2/CO ratio (etching temperature = 220 °C and total flow rate = 255 sccm).

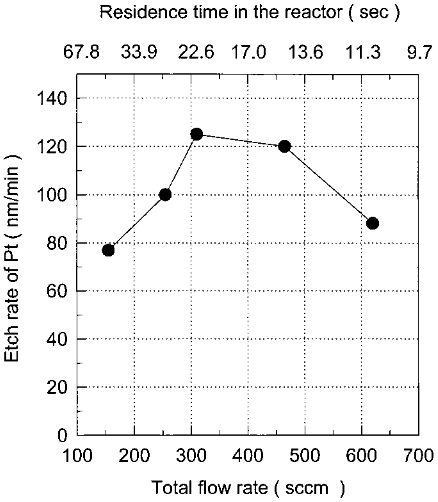

Figure 4. Dependence of the etch rate of Pt films on total flow rate (etching temperature = 220 °C and percentage Cl_2 in CO = 22%).

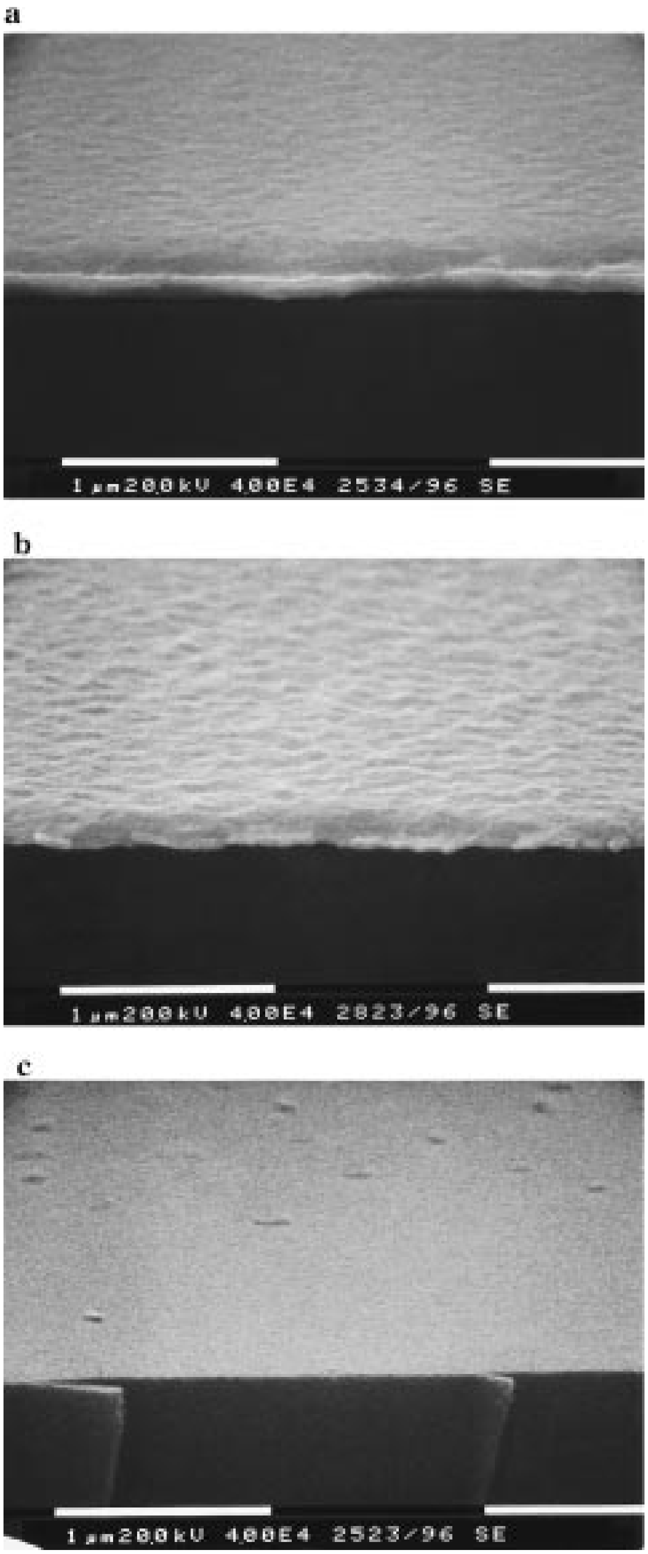

Figure 5. Tilt view of cross sectional SEM photographs of the etched Pt films on SiO_2/Si: (a) before etching, (b) after partial etching, and (c) over-etching at 220 °C and 1 atm in an atmosphere of 22% Cl_2 in CO.

bad selectivity against pattern mask and sidewall deposits. Hence, it was not easy to achieve fine patterning at the resolution of 0.25 μm or less. To adopt ferroelectric capacitors in highly integrated circuits, high etch resolution of Pt is needed. The etching process in which volatile etching products can be formed should be developed for the etching of platinum.

In this work, we report a novel method for etching of Pt. By using the chemical reaction of Pt with CO and Cl_2 at suitable temperature, a volatile chloro–carbonyl Pt complex was produced at the reaction temperature. The effects of the composition of the Cl_2/CO mixture gas

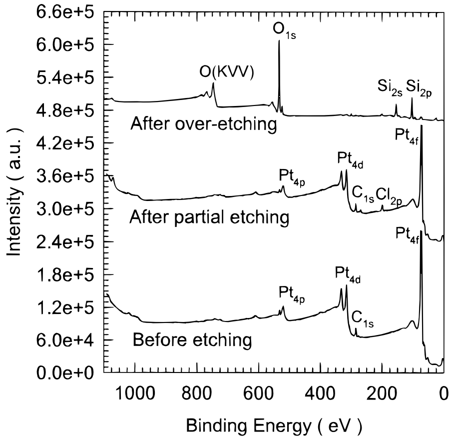

Figure 6. XPS wide scan of the Pt film surface before and after the CDE process (etching temperature = 220 °C, percentage Cl_2 in CO = 22%, and total flow rate = 255 sccm).

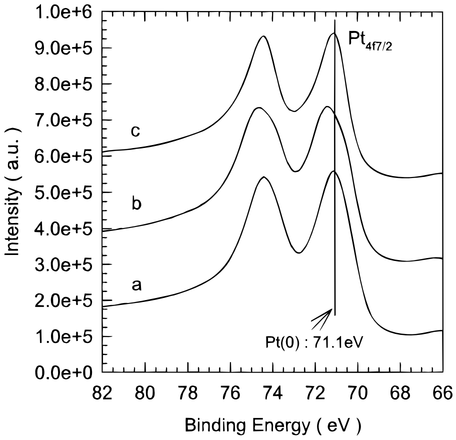

Figure 7. XPS binding energy of the $Pt_{4f7/2,5/2}$ doublet of the Pt film surface partially etched with the Cl_2/CO gas mixture: (a) before etching, (b) etched at 200 °C, and (c) etched at 220 °C (percentage Cl_2 in CO = 22%, 1 atm, total flow rate = 255 sccm).

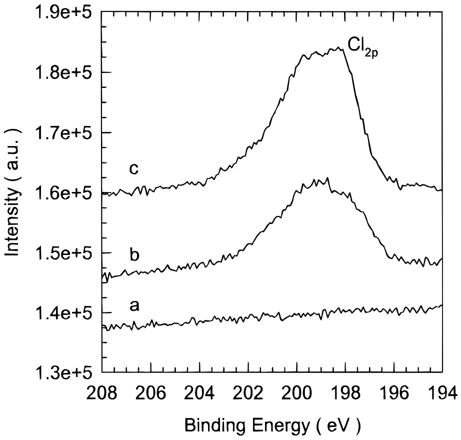

Figure 8. XPS binding energy of the Cl_{2p} of the Pt film surface partially etched with the Cl_2/CO gas mixture: (a) before etching, (b) etched at 200 °C, (c) etched at 220 °C (% Cl_2 in CO = 22%, 1 atm, total flow rate = 255 sccm).

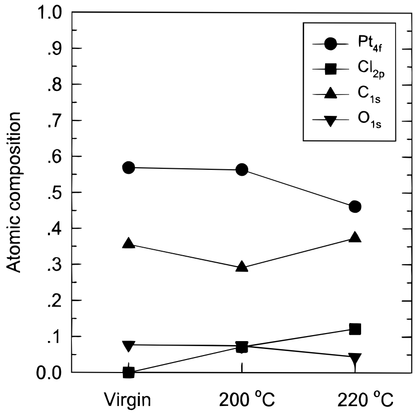

Figure 9. Variations of the surface atomic composition of Pt films partially etched at 200 and 220 °C.

and reaction temperature on the etch rate and selectivity against the mask film were investigated. Furthermore, the etching residue and the chemical state on the etched surface were determined by using XPS. The surface analysis of etched Pt after controlled treatments with XPS and SEM allowed us to propose an etching mechanism and a rate-determining step for the chemical dry etching process of Pt films.

Experimental Section

To evaluate the etch rate of Pt and selectivity against SiO_2, the 250 nm thick platinum thin films were prepared by sputtering platinum onto 500 nm thick SiO_2/Si (bulk) at 430 °C in a conventional argon gas sputtering unit. The 500 nm thick SiO_2 films used to evaluate selectivity were thermally grown in a furnace.

The chemical dry etching apparatus utilized to etch Pt films is shown schematically in Figure 1. This system consists of a quartz reactor, a furnace, the sample to be etched, which is positioned on the quartz substrate connected to a thermocouple, a gas supply system, and a NaOH column to be neutralized. The quartz reactor of 24 mm diameter and 250 mm length can be heated to 800 °C.

The etching reaction using the Cl_2/CO gas mixture was carried out at 1 atm, at an etching temperature of between 200 and 230 °C, at a gas ratio (Cl_2/CO) of 1/1 to 1/4, and at a total flow rate of the Cl_2/CO mixture between 155 and 625 sccm. The etch rate of Pt was determined by visual detection when the SiO_2 layer under the Pt film completely appeared on the sample. This endpoint of etching was confirmed by SEM and a four-point probe system. The surfaces of Pt films etched partially or totally were analyzed by SEM and XPS. The experimental errors of XPS were within 3% because the samples have a flat surface and a conducting film of Pt.

To understand the etching mechanism, various surface treatments were carried out on Pt films at 220 °C and 1 atm for 5 min with Cl_2 and CO gas, respectively. The surface morphology and atomic composition of the surface after treatments were analyzed by SEM and XPS.

Results and Discussion

Characteristics of Chemical Dry Etching Using Cl_2/CO Gas Mixture. The influence of various etching conditions on the etch rate was studied for Pt films on SiO_2. The investigations included the effect of etching temperature, the Cl_2/CO gas ratio, and the total gas flow rate of the feeding gas.

Figure 2 shows the effect of etching temperature on the etch rate of Pt films at 1 atm in Cl_2/CO (1/3.6) and the total gas flow rate of 255 sccm into the reactor. The etch rate increased with increase in etching temperature between 200 and 230 °C. A large enhancement in etch rate occurred between 210 and 220 °C. However, the enhancement rate was gradually reduced above 220 °C. This result indicates that a volatile platinum compound that sublimated between 210 and 220 °C was produced

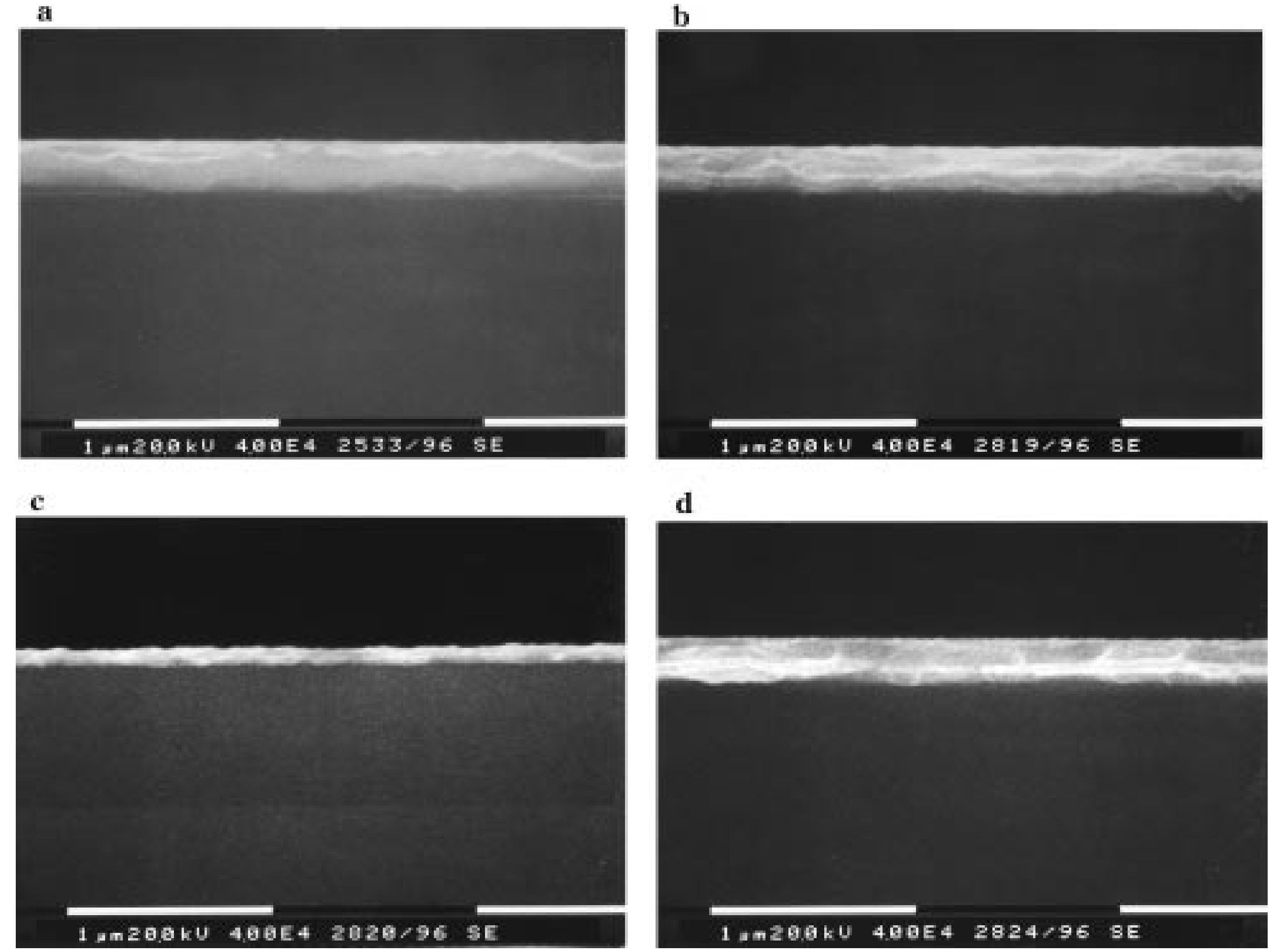

Figure 10. Cross sectional SEM photographs of Pt films treated under various conditions: (a) virgin film and film treated with (b) Cl_2, (c) Cl_2 and CO sequentially, and (d) CO only at 220 °C and 1 atm.

after reaction of Cl_2/CO with Pt. The sublimation temperature of platinum dicarbonyl chloride is 210 °C.[10] Thus, it can be suggested that the etching product may be a kind of volatile platinum carbonyl compound generated by exposing CO to platinum chloride.[11]

The dependence of the etch rate of Pt films on Cl_2/CO ratio is shown in Figure 3. The maximum etch rate was obtained at 33% Cl_2 in CO (Cl_2/CO ratio = 1/2). This ratio agreed with the stoichiometric ratio of Cl_2 and CO for platinum dicarbonyl chloride, $PtCl_2(CO)_2$, which has a sublimation temperature of 210 °C. This compound is not decomposed as easily as other platinum carbonyl compounds;[10,12] therefore, it can be considered as a plausible etching product.

Figure 4 shows the dependence of the etch rate of Pt films on the total flow rate into the quartz reactor. The etch rate of Pt has a maximum value between 300 and 400 sccm. The etch rate increased from 77 to 120 nm/min as the flow rate increased from 155 to 300 sccm. This indicates that the etching reaction is in the region of mass transfer control. The higher flow rate increased the mass transfer of CO and Cl_2 to the Pt surface and of volatile Pt compounds to the bulk phase of gas. The etching reaction above the flow rate of 400 sccm is in the region of surface reaction control. The etch rate decreased because the residence time of Cl_2/CO with Pt decreased as the flow rate increased.

Additionally, the selectivity of Pt against a sublayer such as SiO_2 and TiN under the various etching conditions was very high. The thickness of SiO_2 and TiN before and after etching did not change within experimental error. Therefore, it indicates that the reaction between Cl_2/CO and the sublayer did not occur in this temperature range. Thus, it can be expected that the SiO_2 film can be utilized as a good mask material for a pattern etching of Pt films.

Surface Analysis of Etched Pt Film. To confirm the morphology change of the surface and the kind of etching residue before and after the etching process, the etched Pt films were investigated with SEM, as shown in Figure 5. After a partial etching to the extent of half of the 250 nm thick Pt film at 220 °C and 1 atm in the atmosphere of 22% Cl_2 in CO, the roughness of the surface increased as shown in Figure 5b. As shown in Figure 5c, the Pt film disappeared completely and the etched surface is SiO_2 after overetching. These SEM photographs show that the isotropic etching resulting from the chemical reaction was occurred along the grain boundary of the Pt film.

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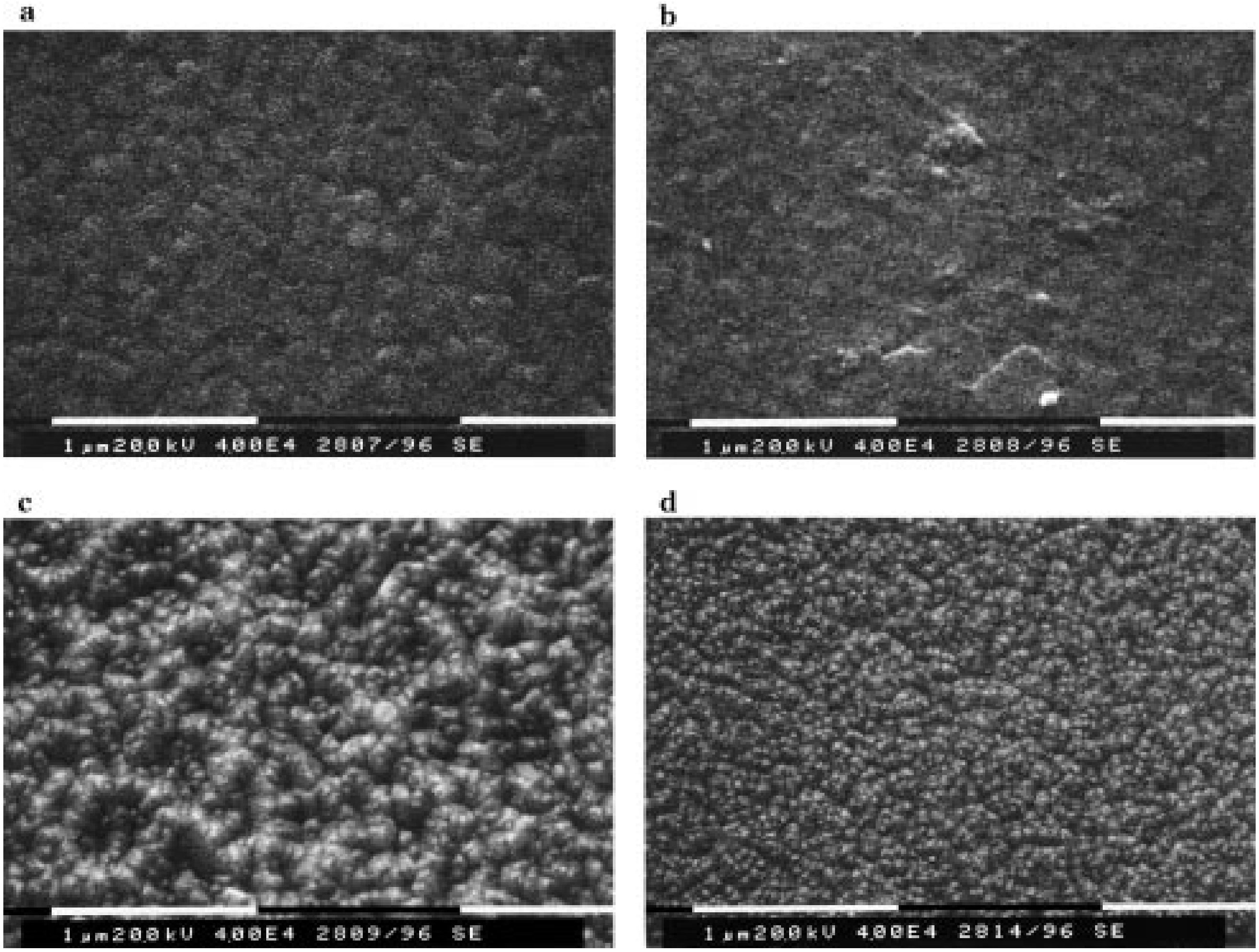

Figure 11. Tilt view of SEM photographs of Pt films treated under various conditions: (a) virgin film and film treated with (b) Cl_2, (c) Cl_2 and CO sequentially, and (d) CO only at 220 °C and 1 atm.

The XPS wide scans revealed the atomic composition of the etched surface before and after chemical dry etching of Pt films, as shown in Figure 6. Etched samples were exposed to air before XPS analysis. However, any significant contaminations were not observed. No residual Pt compounds were present on the SiO_2 surface after overetching and the etched surface was completely changed to a SiO_2 surface. On the other hand, the Cl_{2p} peak newly appeared after partial etching but was removed at the end of etching process. Hence, it can be concluded that Pt films were converted to volatile Pt compounds after reaction with the Cl_2/CO gas mixture.

Figure 7 shows the XPS Pt_{4f} doublet of the Pt film surface partially etched at 200 and 220 °C. The Pt_{4f} doublet revealed the effect of etching temperature below and above the sublimation temperature of platinum dicarbonyl chloride, $PtCl_2(CO)_2$, 210 °C. The partial etchings were carried out in an atmosphere of 22% Cl_2 in CO at 200 and 220 °C for 7.5 and 1.5 min. When the Pt film was etched at 200 °C, the binding energy of the Pt was higher than that of Pt(0), as shown in Figure 7b, indicating that Pt was not perfectly converted to a volatile compound with Cl_2 and CO at 200 °C but remained as a $PtCl_x$ compound. However, at 220 °C, the binding energy is that of Pt(0), as shown in Figure 7a,c. Therefore, these results indicate that the Pt etching process should be take place above 210 °C to produce a volatile compound without formation of a nonvolatile residue during etching. The intensity of the Cl_{2p} peak at 220 °C is higher than that of the Cl_{2p} peak at 200 °C. In comparison with Figure 7, the Cl atom identified by the XPS Cl_{2p} peak of Figure 8c did not change and did not influence the binding energy of the Pt(0) peak at 220 °C, indicating that the Cl atom does not bond to Pt. This Cl originates from the $C-Cl_x$ bond formed by the reaction of CO/Cl_2 because the surface atomic composition of C was increased at 220 °C, as shown in Figure 9. The surface atomic composition was calculated by normalizing with atomic sensitivity factors.[13] However, the Cl atom identified by the Cl_{2p} peak of Figure 8b shifted the zerovalent Pt binding energy by +1.1 eV. Hence, it can be concluded that the platinum chloride remained on the surface and was not completely converted to volatile carbonyl compounds at 200 °C. However, platinum chloride was completely removed by carbonylation at 220 °C. Thus, the etch rate was greatly increased above 210 °C, as shown in Figure 2.

Etching Mechanism. To suggest an etching mechanism, we tried to investigate the variation of surface composition and of the thickness of the Pt films after

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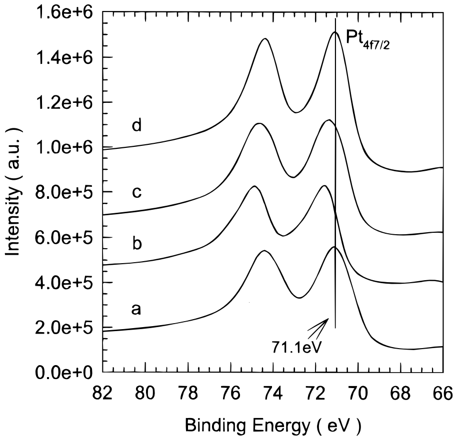

Figure 12. XPS binding energy of the $Pt_{4f7/2,5/2}$ doublet of the Pt film surface treated under various conditions: (a) virgin film and film treated with (b) Cl_2 at 220 °C, (c) CO at 170 °C on Pt preexposed to Cl_2, and (d) CO at 220 °C on Pt preexposed to Cl_2.

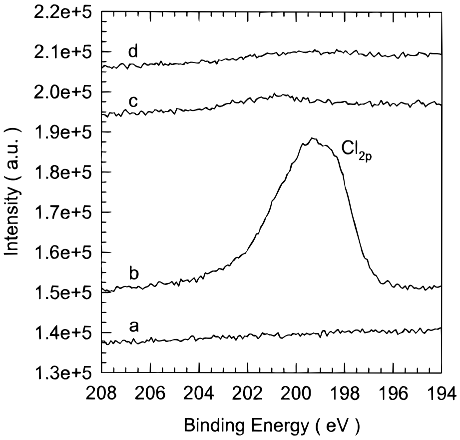

Figure 13. XPS binding energy of the Cl_{2p} of the Pt film surface under various conditions: (a) virgin film and film treated with (b) Cl_2 at 220 °C, (c) CO at 170 °C on Pt preexposed to Cl_2, and (d) CO at 220 °C on Pt preexposed to Cl_2.

treatment with Cl_2 and/or CO. These treated samples were analyzed by SEM and XPS.

Figure 10 shows SEM photographs of Pt films treated with Cl_2 and CO at 220 °C and total gas pressure of 1 atm. The large decrease in Pt thickness was observed after CO treatment of Pt film preexposed to Cl_2. However, the thickness of Pt films treated with Cl_2 or CO is nearly the same as that of the virgin sample. In the case of Cl_2 treatment of chlorinated Pt film, the thickness of Pt was also nearly the same as that of the virgin sample according to the measurement of the four-point probe system. This result indicates that a volatile Pt compound is formed via carbonylation of platinum chloride with CO gas. The surface morphology change after various treatments was studied with SEM, as shown in Figure 11. When the Pt surface was treated with Cl_2 at 220 °C, surface morphology is almost the same as that of the virgin sample, as shown in Figure 11a,b. However, after addition of CO treatment, the Pt surface became rougher along the grain boundary, as shown in Figure 11c. When the Pt surface was treated with CO only at 220 °C, the roughness of the Pt surface increased, as shown in Figure 11d. However, the Pt thickness did not greatly decrease, as shown in Figure 10d. These results indicate that chlorination of the Pt surface is required before carbonylation with CO to form a volatile compound in the etching process. Thus, it can be suggested that the Pt etching is dominated by carbonylation of platinum chloride.

Figure 12 shows the XPS Pt_{4f} doublet of the Pt film surface treated under various conditions. It was founded that $PtCl_x$ was formed after Cl_2 treatment at 220 °C. The binding energy of the $Pt_{4f7/2}$ peak of $PtCl_2$ typically appears at 73.5 eV.[14] Since the temperature of Cl_2 treatment (220 °C) is much lower than that of formation of $PtCl_2$ (500 °C),[15] the polycrystalline $PtCl_2$ phase was not made at 220 °C. The binding energy of $Pt_{4f7/2}$ after treatment of Cl_2 at 220 °C is at about 71.6 eV, which is 0.5 eV higher than the binding energy of Pt(0) of the virgin sample. This XPS result indicates that nonstoichiometric $PtCl_x$ was formed. The binding energy of Pt_{4f} of PtO_{ads} was also lower than that of the platinum(II) oxide.[16] In the case of CO treatment at 170 °C of chlorinated Pt film, the binding energy of $Pt_{4f7/2}$ appears at 71.4 eV, as shown in Figure 12c. After treatment of CO at 220 °C, the binding energy returned to 71.1 eV, as shown in Figure 12d. The treatment of CO under the sublimation temperature of a volatile Pt compound maintains $PtCl_x$ on the surface because carbonylation of the platinum chloride is not fully proceeded. However, in the case of CO treatment above 210 °C, $PtCl_x$ is sublimated as a chloro−carbonyl Pt compound. The XPS binding energy of Cl_{2p} is shown in Figure 13. The Cl_{2p} peak is strong after Cl_2 treatment at 220 °C. A very small amount of Cl remains on the surface, when chlorinated Pt film was treated with CO at 170 °C. The surface atomic composition of Pt films after various treatments is shown in Figure 14. From these results, it can be proposed that the etch rate of platinum using Cl_2 and CO be limited by the rate of formation of the chloro−carbonyl Pt compound and by the sublimation rate of this volatile platinum compound.

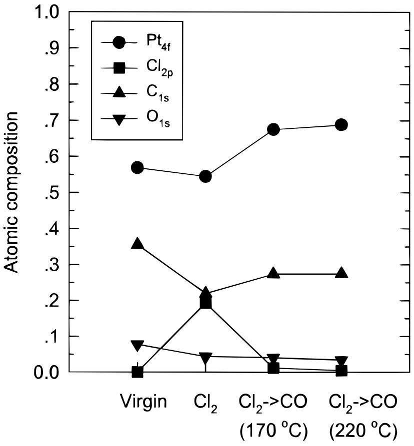

Figure 14. Variations of the surface atomic composition after various treatments.

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Conclusion

A novel chemical dry etching method of Pt films using Cl_2/CO gas mixtures was created. The large enhancement in the etch rate occurred near the sublimation temperature of platinum dicarbonyl chloride, $PtCl_2(CO)_2$. Additionally, the maximum etch rate was obtained at the molar Cl_2/CO ratio of 1/2, which agrees with the stoichiometric ratio of Cl_2 and CO for $PtCl_2(CO)_2$. The XPS analysis of the etched surface showed that the binding energy of Pt_{4f} during etching at 220 °C was equal to that of Pt(0). Nonvolatile etching residue including platinum was completely removed after overetching. XPS and SEM study allowed us to propose that Pt etching is proceeded via the formation of a volatile chloro−carbonyl Pt compound and its sublimation at the etching temperature.

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