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Effect of additive gases on the selective etching of tungsten films using inductively coupled halogen-based plasmas

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Abstract

In this study, the effect of additive gases such as N_2, Ar and O_2 on the selective etching of tungsten (W) films relative to that of poly-Si films was investigated using inductively coupled CF_4/Cl_2-based plasmas. When CF_4/Cl_2 gas mixtures were used to etch W films and poly-Si, due to the formation of volatile etch products, the etch rates of W and poly-Si were very high. However, because the poly-Si etch product is more volatile than the W etch product, the etch selectivity of W over poly-Si was lower than 0.3. When Ar or N_2 was added to a CF_4/Cl_2 gas mixture, the etch rates of both W and poly-Si were increased, however, the etch selectivity of W over poly-Si remained similar. When O_2 was added to a CF_4/Cl_2 gas mixture, not only higher W etch rates (approx. 350 nm/min) but also higher etch selectivity of W over poly-Si (approx. 2.4) could be obtained by suppressing the poly-Si etch rate. The increase of W etch rates and etch selectivity by the oxygen addition to the CF_4/Cl_2 appears from the formation of volatile tungsten halogen oxide on the W surface and involatile silicon oxide on the poly-Si surface.

Keywords: Additive gas; Selective etching; Tungsten

1. Introduction

Tungsten (W) is currently used as a material for vias, gates and interconnects for the fabrication of integrated circuits (IC) and it is one of the most promising materials for gate and interconnection of next generation thin film transistor liquid crystal display (TFT-LCD) devices due to its thermal stability and low sheet resistance [1,2]. To apply W to next generation TFT-LCD devices, W should be patterned by dry etching because wet etching of W causes low etch rates, the reduction of line width and the presence of post-etch residues even though wet etchings are used for patterning many materials for TFT-LCDs.

For some of the next generation TFT-LCD devices, a poly-Si film or an amorphous silicon (a-Si) film is located under the W film and not only high W etch rates but also high etch selectivities of W over the underlying materials such as a-Si and poly-Si are required. Many researchers have investigated dry etching of W using fluorine-based gases such as SF_6 [2–4], CF_4 [2] and $CBrF_3$ [2,5] for the application of TFT-LCD devices. However, the etch selectivities of W over underlying materials were not high enough (lower than two) because of higher vapor pressures of halogen compounds of a-Si and poly-Si compared to those of W in fluorine-based gas chemistry and, in these etching conditions, the etch rates of W were lower than 150 nm/min.

In this study, W film etching was carried out using inductively coupled halogen (CF_4/Cl_2)-based plasmas and, to obtain higher etch selectivities of W over underlying materials together with high W etch rates, the effect of various additive gases such as N_2, O_2 and Ar was investigated. These additive gases were carefully selected to investigate the effects of ion bombardment by Ar and the formation of various compounds such as nitrides and oxides by O_2 and N_2 on the enhancement of W etching and the etch selectivity of W over poly Si. Also, the mechanism obtaining the etch selecitivity was also investigated.

2. Experimental

W thin films were etched using a home-made inductively coupled plasma (ICP) equipment. The ICP source

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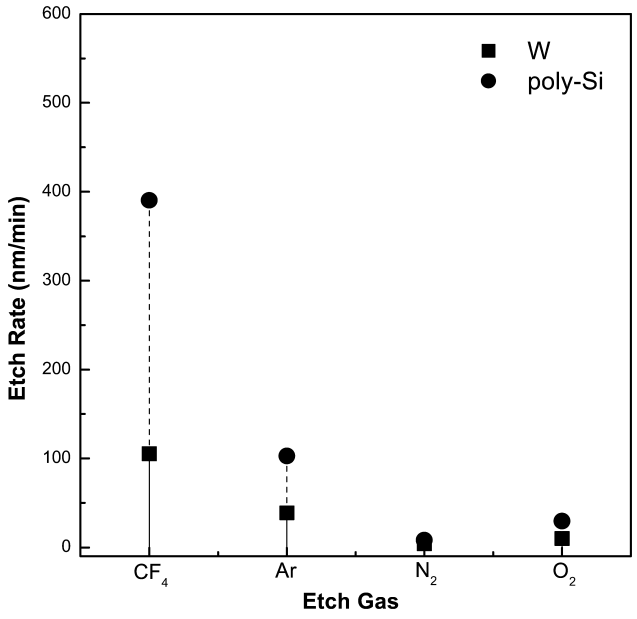

Fig. 1. Etch rates of W and poly-Si as a function of pure CF_4, Ar, N_2 and O_2. (process condition: inductive power (500 W), d.c. bias voltage (−150 V) and operating pressure (2 Pa)).

was consisted of a 3.5-turn-spiral copper coil located on the top of the process chamber separated by a 1-cm thick quartz window. To generate the inductively coupled plasmas, 13.56 MHz r.f. power was applied to the coil. Separate 13.56 MHz r.f. power was supplied to the bottom electrode to provide a d.c. bias voltage to the sample. The distance between the quartz window and the substrate was 7 cm. Substrate cooling was provided by chilled water; therefore, the substrate temperature was kept constant at near room temperature. Details of the ICP equipment used in the experiment are described elsewhere [6].

W and poly-Si thin films were deposited on LCD-grade glass substrates by r.f. sputtering and plasma enhanced chemical vapor deposition (PECVD), respectively. CF_4/Cl_2 gas mixtures were used to etch W and poly-Si thin films. Other etch parameters such as the inductive power, the d.c. bias voltage, and the operating pressure were kept at 500 W, −150 V and 2 Pa, respectively. Additive gases such as Ar (0–35 sccm), N_2 (0–35 sccm) and O_2 (0–35 sccm) were varied to a CF_4/Cl_2 gas mixture (5 sccm CF_4/3 sccm Cl_2) to study the effect of additive gases on the etch characteristics.

The etch rates were estimated by measuring the step heights of the films before and after the etching with a stylus profilometer. X-Ray photoelectron spectroscopy (XPS) was also used to analyze the etch products on the etched W surfaces.

3. Results and discussion

Fig. 1 shows the effect of various gases such as CF_4, N_2, Ar and O_2 on the etch rates of W and poly-Si. Inductive power, d.c. bias voltage, operating pressure and substrate temperature were maintained at 500 W, −150 V, 2 Pa and 25 °C, respectively. The flow rates of CF_4, N_2, Ar and O_2 to obtain 2 Pa of operating pressure were 8.4 sccm, 12.5 sccm, 15 sccm and 14 sccm, respectively. As shown in the figure, when CF_4 was used to etch W and poly-Si, the etch rates of both W and poly-Si were relatively high. However, when Ar, N_2 or O_2 was used to etch W and poly-Si, the etch rates were very low. The etch selectivities of W over poly-Si were lower than one for all of the cases and, especially, the etch selectivity for pure CF_4 was the lowest at 0.27.

Fig. 2 shows the effect of CF_4/Cl_2 gas mixtures on the etch rates of W, ploy-Si, and the etch selectivities of W over poly-Si. The etch parameters such as inductive power, d.c. bias voltage, operating pressure and substrate temperature were maintained the same as those in Fig. 1. The flow rates of CF_4 and Cl_2 were varied to maintain 2 Pa of operating pressure. As shown in the figure, the etch rates of W and poly-Si showed maximums at the CF_4/Cl_2 gas mixtures of 20% Cl_2 and of 80% Cl_2, respectively. However, the etch selectivities of W over poly-Si were less than 0.3, therefore, the etch selectivity was not improved significantly.

Table 1 shows the melting points and boiling points of W and Si compounds related to the gases used in the experiment [7]. It is difficult to obtain vapor pressure data of various compounds, however, because the compounds having low melting points and boiling points generally show high vapor pressures, the data on the melting points and boiling points of various compounds were used as the indication of relative vapor pressures instead. As shown in the table, fluorides and chlorides

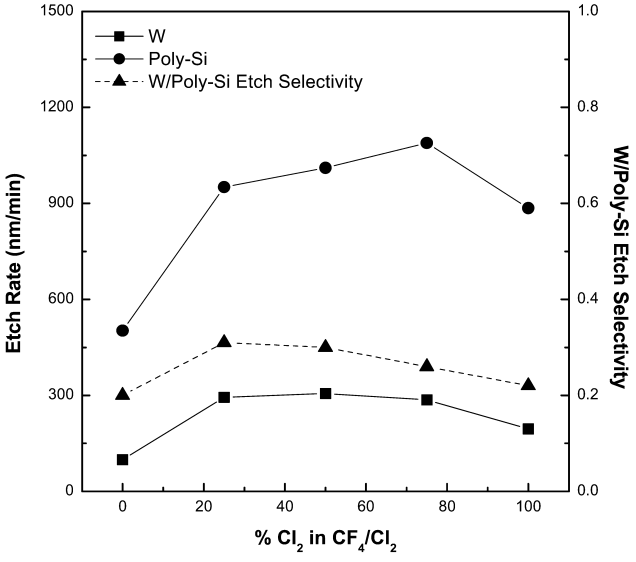

Fig. 2. Etch rates of W and poly-Si and the etch selectivities of W over poly-Si as a function of CF_4/Cl_2 gas mixture. (process condition: inductive power (500 W), d.c. bias voltage (−150 V) and operating pressure (2 Pa)).

Table 1
Boiling points and melting points of the compounds of W and poly-Si related to the gases used in the experiment

Compound	Melting point (°C)	Boiling point (°C)
WF_4	800	–
WF_6	2	17
WOF_4	108	186
WCl_4	Dec 300	–
$[WCl_5]_2$	242/248	286
WO_2	1500	1730
WO_3	1473/1470	1837
SiF_4	−90	−86
$SiCl_4$	−69	58
SiO_2	1710	2590
Si_3N_4	1900	–

of W and Si generally show low melting points and boiling points, therefore, the etch rates of W and poly-Si by CF_4 and Cl_2 are expected to be high due to the high vapor pressures of their etch products. The high etch rates of W and poly-Si with CF_4 shown in Fig. 1 are due to the formation of these volatile halides during the etching by CF_4, therefore, the etching is enhanced by the chemical reaction. However, the etchings by Ar, N_2 and O_2 form involatile etch products, therefore, the etchings occur only by physical sputtering. Also, as shown in the table, the melting points and boiling points of W halides are higher than those of Si halides. The low etch selectivities of W over poly-Si shown in Fig. 2 are attributed to the differences in the vapor pressures of etch products formed during the etchings by CF_4/Cl_2. Even though we were not able to find the data on F–Cl compounds of W and Si, the maximum etch rates of W and poly-Si shown in the certain mixture of CF_4/Cl_2 in Fig. 2 also appear related to the high vapor pressures of these etch products.

Fig. 3 shows the effect of additive gases such as Ar (a), N_2 (b) and O_2 (c) to 5 sccm CF_4/3 sccm Cl_2 gas mixture on the etch rates of W and poly-Si and etch selectivities of W over poly-Si. Ar, N_2 and O_2 were varied from 0 to 35 scccm. The other etch parameters such as inductive power, d.c. bias voltage, operating pressure and substrate temperature maintained the same conditions as those in Fig. 1. As shown in Fig. 3a, the addition of Ar showed the increase of W etch rates and poly-Si etch rates until 10 sccm of Ar was added to the CF_4/Cl_2 gas mixture and the further increase of Ar flow rate decreased the etch rates of both W and poly-Si. The etch selectivity of W over poly-Si was low and did not change significantly with Ar addition. The addition of N_2 to the CF_4/Cl_2 shown in Fig. 3b also showed the increase of the etch rates of W and poly-Si when a small amount of N_2 was added to the CF_4/N_2, however, the further increase of N_2 decreased the etch selectivity. Fig. 3c shows the effect of O_2 addition to the CF_4/Cl_2 gas mixture on the etch rates of W and poly-Si and the etch selectivities. As shown in the figure, the addition of oxygen increased poly-Si etch rate when 5 sccm of oxygen was added, however, the further increase of oxygen decreased poly-Si etch rate. In the case of W, the addition of oxygen increased W etch rate until approximately 23 sccm of oxygen was added and the further increase of oxygen also decreased the W etch rate. The etch selectivity of W to poly-Si increased sharply to 2.4 by the addition of 23 sccm oxygen. At that condition, the W etch rate higher than 300 nm/min could be obtained. The further increase of oxygen, however, decreased the etch selectivity significantly.

The increase of the etch rates of W and poly-Si with the small amount (5–10 sccm) of Ar shown in Fig. 3a appears to be from the increase of plasma density by Ar addition and by the increase of physical bombardment as discussed by other researchers [8–10]. The further increase of Ar appeared to decrease the etch rates by the decreasing the residence time of reactive halides and by diluting the chemically active species. Not the changes in the vapor pressures of etch products but the changes only in plasma density, concentration of chemical species and physical sputtering by Ar addition appeared to result in the insignificant change of etch selectivity. The addition of N_2 to CF_4/Cl_2 is known to increase the dissociation of CF_4 and Cl_2 [11], therefore, the increase of the etch rates of W and poly-Si with the small addition of N_2 shown in Fig. 3b appears to be from the increased chemical reaction. The decrease of the etch rates with the further increase of N_2 also appears to be from the increased dilution and the decrease of residence time of active chemical species with the excessive N_2 addition similar to the case of Ar addition. Also, the etch selectivity was not significantly changed with N_2 similar to the case of Ar addition. Even though the etch selectivities are similar for both Ar addition and N_2 addition, the etch rates of W and poly-Si for the N_2 addition were lower than those for the Ar addition possibly due to the involatile nitride formation on the surfaces of both W and poly-Si in addition to lower ion bombardment effect. The initial increase of the etch rates and the final decrease of the etch rates of poly-Si with the addition of oxygen shown in Fig. 3c appears to be similar to the case of N_2 addition in Fig. 3b. That is, when the addition of oxygen was small, oxygen dissociates more halides such as CF_4, therefore, the poly-Si etch rate is increased and, due to the high vapor pressure of silicon halides as shown in Table 1, the etch rates of poly-Si is generally high [12]. However, as the oxygen is added more, the formation of involatile oxide on the poly-Si surface by the oxygen atom blocks the poly-Si etching and decreases the etch rate significantly. In the case of W etching, the initial increase of W etch rate with O_2 up to 23 sccm appears to be not only from the increased dissociation of halide, but also from the formation of relatively volatile etch products composed of oxyhalide as shown in Table 1. Also, the decrease of W etch rate at

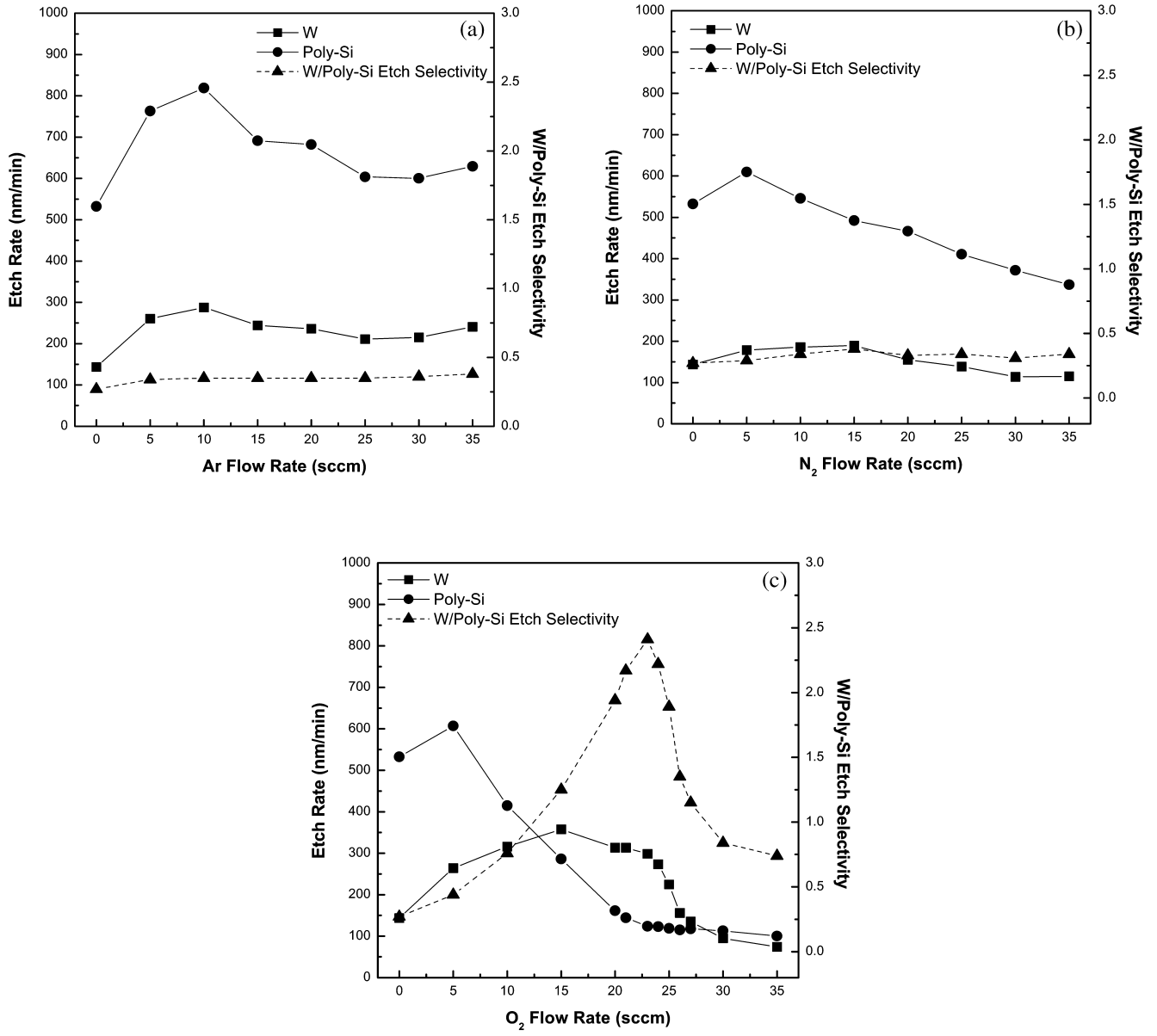

Fig. 3. Etch rates of W and poly-Si and the etch selectivities of W over poly-Si as a function of additive gases such as (a) Ar, (b) N_2 and (c) O_2, to the 5 sccm CF_4/3 sccm Cl_2 gas mixture. (process condition: inductive power (500 W), d.c. bias voltage (−150 V) and operating pressure (2 Pa)).

the oxygen flow rate higher than 23 sccm appears to be not only from the dilution of reactive chemical species but also from the formation of involatile W oxides as shown in Table 1 [1]. The differences in the etch rates with the addition of oxygen changed the etch selectivity of W over poly-Si as shown in Fig. 3c.

The etch products mentioned above could be estimated by observing the chemical binding status of W surfaces etched by CF_4/Cl_2-based gas mixtures. Fig. 4 shows the XPS narrow scan data of W4f peaks for the W surfaces etched by CF_4(5 sccm)/Cl_2(3 sccm), CF_4(5 sccm)/Cl_2(3 sccm)/Ar(23 sccm), CF_4(5 sccm)/Cl_2(3 sccm)/N_2(23 sccm) and CF_4(5 sccm)/Cl_2(3 sccm)/O_2(23 sccm) gas mixtures. Blank W samples deposited on the glass substrates were etched with the above gas mixtures for 30 s. The other etch parameters were the same as the conditions in Fig. 1. In the case of clean W, $W4f_{7/2}$ peak was observed at 31.54 eV as shown in the figure. But when the W was etched with the CF_4/Cl_2 gas mixture, $W4f_{7/2}$-halogen peak instead of $W4f_{7/2}$ peak was observed at 32.15 eV possibly due to the formation of W halide on the W surface during the etching with CF_4/Cl_2. Also, when Ar was added to the CF_4/Cl_2, the position of $W4f_{7/2}$ was similar to that of $W4f_{7/2}$ peak for CF_4/Cl_2 suggesting no differences in the etch products by the addition of Ar. Therefore, the

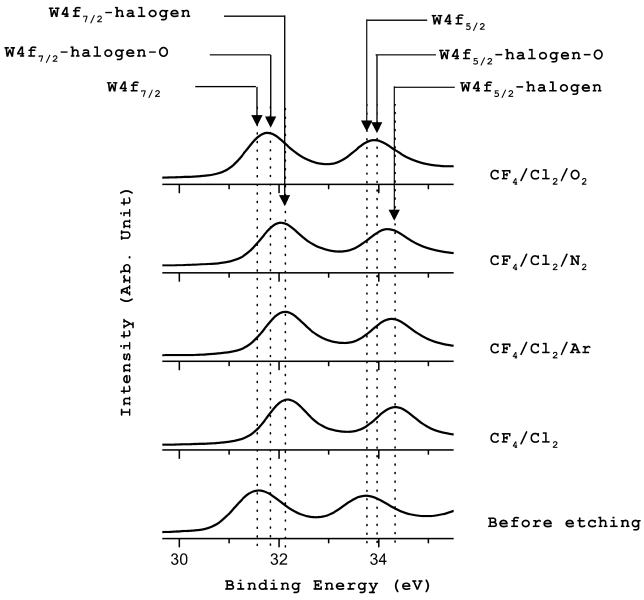

Fig. 4. W4f XPS W4f narrow scan spectra of W film surfaces exposed to CF_4/Cl_2, $CF_4/Cl_2/N_2$, $CF_4/Cl_2/Ar$ and $CF_4/Cl_2/O_2$ plasma. (process condition: inductive power (500 W), d.c. bias voltage (−150 V) and operating pressure (2 Pa)).

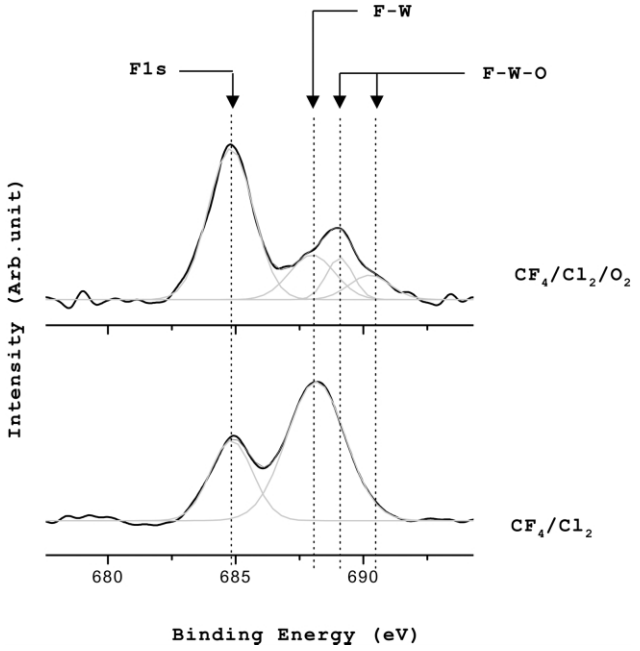

Fig. 5. F 1s XPS F1s narrow scan spectra of W film surface exposed to CF_4/Cl_2 and $CF_4/Cl_2/O_2$ plasma. (process condition: inductive power (500 W), d.c. bias voltage (−150 V) and operating pressure (2 Pa)).

change of the W etch rate with Ar is believed to be from the change of halogen radicals in the plasma as mentioned before. However, in the cases of the addition of N_4 and O_2, there was a definite change in the peak position of $W4f_{7/2}$ approximately 0.13 eV (32.02 eV) and 0.34 eV (31.81 eV), respectively. The peak position located at 31.81 eV with $CF_4/Cl_2/O_2$ was identified as the peak related to W oxyhalide even though the peak position located at 32.02 eV with $CF_4/Cl_2/N_2$ is not clear. From this result, the increase of W etch rate with $CF_4/Cl_2/O_2$ appears to be from the formation of relatively volatile W oxyhalide.

To confirm the possibility of oxyhalide formation on W during the etching, XPS F1s narrow scan data were also investigated for CF_4/Cl_2 and $CF_4/Cl_2/O_2$ gas mixtures shown in Fig. 4 and the results are shown in Fig. 5. As shown in the figure, when the CF_4/Cl_2 gas mixture was used to etch W, in addition to the original F1s peak at 684.9 eV, an additional peak at 688.23 eV originated from the F–W bonding could be observed. Also, when the $CF_4/Cl_2/O_2$ gas mixture was used to etch W, the additional peak was moved approximately 0.83–689.06 eV indicating the formation of F–W–O bonding, that is, the formation of W oxyhalide [13].

4. Conclusions

In this study, inductively coupled CF_4/Cl_2-based plasmas were used to etch W and the effect of additive gases such as Ar, N_2 and O_2 on the W etch rates and the etch selectivities over poly-Si was investigated.

When W and poly-Si were etched using pure halogen gas mixtures such as CF_4/Cl_2, due to the formation of etch products with high vapor pressures, high W etch rates could be obtained, however, due to the higher vapor pressures of poly-Si etch products, the etch selectivities of W over poly-Si were generally lower than 0.3. The addition of Ar or N_2 to CF_4/Cl_2 did not improve the etch selectivity because Ar and N_2 did not change the vapor pressures of etch products significantly between W and poly-Si. However, when the small quantity of O_2 was added to CF_4/Cl_2, the etch rates of W were increased and the etch selectivities over poly-Si were also increased by the simultaneous decrease of poly-Si etch rates with oxygen. The increase of W etch rates with oxygen to CF_4/Cl_2 appears to be not only from the increased dissociation of halogen molecules but also from the formation of relatively volatile W oxyhalide while the decrease of poly-Si etch rate is related to the formation of involatile silicon oxide. In this experiment, by adding 23 sccm of oxygen to 5 sccm CF_4/3 sccm Cl_2 gas mixture, the W etch selectivity over poly-Si higher than 2.4 could be obtained while maintaining the W etch rates higher than 300 nm/min.

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