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Mass spectrometry studies of resist trimming processes in HBr/O₂ and Cl₂/O₂ chemistries

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In a previous article, a parametric study of HBr/O₂ and Cl₂/O₂ resist trimming processes correlated to x-ray photoelectron spectroscopy (XPS) analyses has been performed. The present article confirms the preliminary results obtained by XPS. Mass spectrometry experiments have established that the slow resist erosion rate measured in Cl₂/O₂ trim chemistries is attributed to a competitive etching of the resist by atomic chlorine and oxygen, while in HBr/O₂ trim chemistries, atomic oxygen is the main etching species, bromine playing only a minor role. The etching of the resist by the oxygen species originating from the dissociation of HBr/O₂ and Cl₂/O₂ plasmas generates the formation of volatile resist-etch-by-products such as CO and CO₂, while the etching of the resist by halogen (bromine or chlorine) generates less volatile and heavier resist-etch-by-products such as C_xH_yBr_z with bromine and C_xH_yCl_z with chlorine. Mass spectrometry has also shown that plasma conditions leading to a higher concentration of halogen-resist-etch-by-products in the plasma gas phase are also the conditions inducing the lower trim rates. This confirms the assumption that the deposition of heavy resist-etch-by-products on the resist sidewalls controls the trim rates. © 2005 American Vacuum Society. [DOI: 10.1116/1.1839915]

I. INTRODUCTION

The requirements imposed by the roadmap for front-end processes is becoming more and more challenging at each new technological node. For instance, the physical gate dimension targeted for the 45 nm technological node is 18 nm, while the lithographic processes used in manufacturing with 193 nm exposure can only achieve at best 60 nm. Nowadays, the strategy developed to overcome the lithography limitation is to introduce a “resist trimming” step prior to all the other classical gate etching steps [bottom anti-reflective coating (BARC) and hard mask opening steps and gate etching]. This step generates a lateral erosion of the photoresist mask in order to decrease its critical dimension defined by the lithography. Thanks to this resist trimming step, the final transistor gate length can be adjusted to reach the transistor speed imposed at each new technological node. In manufacturing, this technique is now currently used to address the 90 nm node requirements and in research and development, resist trimming processes are currently used to generate sub-40 nm silicon gates using 193 nm exposure scanners.^{1,2} A detailed study of resist trimming processes using HBr/O₂ or Cl₂/O₂ chemistries has already been carried out in another study.³ In this work, we have shown the effect of plasma parameters such as plasma chemistry, bias power, and reactor pressure on the trimming process performance (vertical resist etch rates and trim rates). The trend is similar with both

chemistries: an increase of the atomic oxygen concentration in the plasma (obtained by increasing the oxygen flow in the gas mixture or by increasing the source power) leads to an increase of the trim rates, while an increase in bias power and in pressure in the plasma lead to a decrease of the trim rates. This parametric study has also been correlated with XPS analyses of the resist patterns after trim processes using an experimental procedure described in detail in Ref. 4. This study has allowed the determination of the chemical composition and thickness of the reactive layers that are formed both on tops and sidewalls of the resist patterns during the resist trimming process. We have been able to correlate the chemical modifications occurring on the resist sidewalls in HBr/O₂ and Cl₂/O₂ plasmas with the trim rates.

We have shown that HBr/O₂ chemistries lead to faster trim rates than Cl₂/O₂ plasmas, and we have also determined by measuring the chlorine and bromine coverage on the resist sidewalls by x-ray photoelectron spectroscopy (XPS) that the trim rate is directly correlated to the reactivity of bromine or chlorine with the resist. Indeed, XPS analyses show that in HBr/O₂ trim plasmas, the reactive layers formed on the resist sidewalls are mainly composed of carbon and oxygen while very small bromine concentrations are detected in all the conditions investigated (less than 5% of bromine is detected in the reactive layers formed on the resist sidewalls in all the plasma conditions investigated). On the other hand, the reactive layers formed on the sidewalls in Cl₂/O₂ are mainly composed of carbon and chlorine (around 40% depending on the plasma conditions). Moreover,

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HBr/O₂ plasmas lead to the formation of very thin reactive layers on the sidewalls (less than 1 nm), whereas Cl₂/O₂ plasmas generate the formation of thicker reactive layers (about 2 nm). The chemical composition and thickness of the reactive layers indicate that HBr/O₂ trim plasmas react with the resist essentially through spontaneous chemical reactions between the atomic oxygen present in the discharge and the polymer resist, generating fast trim rates. In contrast, in Cl₂/O₂ chemistries, there is a competitive adsorption between chlorine and oxygen atoms on the resist surface leading to the formation of thick perturbed layers on the sidewalls inducing slower trim rates than with HBr/O₂ chemistries.

Thanks to these XPS analyses, we have been able to explain the correlations between Cl₂/O₂ plasma parameters and the measured trim rates. A decrease in trim rate is directly correlated with an increase of the reactive layer thickness on the sidewalls and an increase of the chlorine concentration in the layer. We have suggested that the chemical modifications of the resist sidewalls are attributed to the deposition of low volatile chlorine rich carbon resist products (such as CCl_x) on the resist sidewalls, directly correlated with the decrease in trim rates. Conversely, with HBr/O₂, it was difficult to draw clear conclusions on the relation between the reactive layers formed on the sidewalls and the trim rates, because the variation of the chemical composition and thickness of the reactive layers (as measured by XPS) as a function of the plasma parameters was within the accuracy of the XPS experiments.

In the present article, we have used mass spectrometry to confirm the hypothesis suggested in the previous article,³ concerning the deposition of resist-etch-by-products on the resist sidewalls directly correlated with the low trim rates measured in Cl₂/O₂ plasmas. Moreover, as XPS analyses are not relevant to explain the trim rate variation with the plasma parameters in HBr/O₂ chemistries, mass spectrometry can be an interesting source of information to progress in the understanding of trim mechanisms using this chemistry.

The aim of these mass spectrometry measurements is to determine the reactive species present in the plasma discharge using either Cl₂/O₂ or HBr/O₂ trim chemistries and also to provide some information on the chemical nature of the resist-etch-by-products.

II. EXPERIMENTAL SETUP

Experiments are carried out in an inductively coupled industrial plasma (DPS from Applied Materials Inc.) accepting 200-mm-diam silicon wafers. The reactor has been described in detail elsewhere.^{5,6}

Mass spectrometry experiments are carried out while exposing either SiO₂ or resist blanket wafers to resist trimming plasmas. The plasma chemistries used in this study are either pure Cl₂, HBr, and O₂ gas or a mixture of HBr/O₂ and Cl₂/O₂. In all the experiments, the total gas flow rate is kept constant at 100 sccm. Feed gas ratio, bias power, source power, and pressure are the four parameters investigated.

Mass spectrometry experiments are performed with a Hiden HAL-EQP 500 quadrupole mass spectrometer connected to the DPS chamber wall. A detailed description of this spectrometer can be found in other articles.^{7,8} This apparatus is composed of five sections: an extractor, an ionization source (for neutral analysis), a 45° sector field energy analyzer, a quadrupole mass analyzer and detectors (channeltrons). The spectrometer is differentially pumped with its own turbo-molecular pump backed by a primary pump, thus maintaining a low background pressure of 10⁻⁸ Torr with no gas flow in the reactor and a maximum of 2 × 10⁻⁷ Torr with 16 mT of gas in the reactor chamber.

By biasing the extractor, analyses of either ions or neutrals extracted from the plasma is, in principle, possible. However, because neutral detection by mass spectrometry requires careful attention and specific differentially pumped systems,^{9,10} we have only used the mass spectrometer in the ion analysis mode. In this mode, the positive ion Bohm flux leaving the plasma is sampled through a 50-mm-diam sampling orifice (located at the reactor wall), behind which the extractor is placed. The extractor is polarized at -2 V in order to extract the positive ions from the plasma and the voltage of the different electrostatic lens of the system is set in order to optimize the output signal. When working in the ion mode, the most important parameter to set is the pass energy through the energy analyzer. This energy is usually obtained from a preliminary acquisition of the ion energy distribution function (IEDF) at a given mass. The energy value corresponding to the maximum intensity of the IEDF is set as the pass energy for all the ions present in the plasma. This approach is valid only if the IEDF of all ions is single peaked (around the dc value of the plasma potential).¹¹

Then, before acquiring a mass spectrum, it should be checked that the maximum of the IEDF is obtained at the same energy value for all the ions. If this is not the case, a mass could be underestimated compared to another one. Indeed, in some cases (when ions are sensitive to the rf auto-polarization or when the plasma potential is sensitive to the rf power), the IEDF can present two maxima for one particular mass while there is only one maximum for another mass. In these conditions, it can be unreliable to make some quantitative analyses from the mass spectra recorded.

The mass spectrometer transmission is a function of the mass. We have shown in a previous article⁵ that the sensitivity of this spectrometer decreases when the analyzed mass increases. The transmission function has been calibrated in another paper⁵ which shows that below the mass 40, the sensitivity of the spectrometer is constant and equal to 1, and that for masses above 40, the sensitivity decreases exponentially with the mass.

The aim of this study is not to calculate the absolute concentration of a species under particular plasma conditions, but to determine if its concentration changes as a function of the plasma conditions. We have only treated the ion mass analysis, but we can assume that the presence of an M⁺ ion in the plasma gas phase is the signature of the corresponding neutral molecule M.

Mass spectrometry experiments have been performed on SiO₂ and resist-blanket wafers. A SiO₂ wafer exposed to resist trimming plasmas using either HBr/O₂ or Cl₂/O₂ chemistries is not etched. Thus, the detected masses with the SiO₂ wafer represent the species that are present in the gas phase when there are no etching reactions with SiO₂, and that are the reactive species responsible for the etching of the resist.

Exposing a resist-blanket wafer to trimming processes results in the formation of numerous resist-etch-by-products in the plasma gas phase. Mass spectrometry experiments have then been performed on resist wafers to determine the chemical nature of resist-etch-by-products. To determine the contribution of a particular mass M^+ present in the plasma, noted $[M^+]$, we have simply calculated the peak area corresponding to the mass M^+ , named, A_M , and we divided it by the sum of all the peak areas corresponding to all the species present in the plasma, named A_{total} : $[M^+] = A_M/A_{total} * 100$ (1). We have used Eq. (1) in Sec. III C only to determine an evolution of the concentration of the different resist-etch-by-products with the plasma parameters. The isotopes of chlorine- or bromine-based species have been taken into account.

Before studying the trim plasma chemistries HBr/O₂ or Cl₂/O₂, we have first studied by mass spectrometry the simplest cases (cf. Sec. III A), i.e., when the gas phase is composed of one gas only, either pure O₂, or Cl₂ or HBr, the other plasma parameters being similar to those used for trim process conditions. In Sec. III B, we have studied particular plasma conditions for both trim chemistries. And in Sec. III C, we have studied the influence of the plasma parameters on the chemical nature of the resist-etch-by-products in HBr/O₂ and Cl₂/O₂ chemistries.

III. EXPERIMENTAL RESULTS

A. Study of pure O₂, Cl₂ and HBr plasmas by mass spectrometry

In this section, mass spectrometry experiments have been carried out on SiO₂ and resist-blanket wafers. The plasma conditions investigated are the following: for 100 sccm of pure O₂, Cl₂, or HBr, the source power is fixed at 500 W, the bias power at 50 W, and the plasma pressure at 10 mT. For each wafer, mass spectra of the ionic species are recorded. The mass spectra performed on a SiO₂ blanket wafer (which should not be etched under these plasma conditions) give some information on the reactive species present in the discharge, and those performed on blanket resist wafers are used to determine the chemical nature of the resist-etch-by-products.

1. O₂ plasma chemistry

Figure 1 compares the mass spectra of ionic species obtained on an oxide [cf. Fig. 1(a)] and resist [cf. Fig. 1(b)] wafers exposed to a pure O₂ plasma.

The ionic species detected on a SiO₂ wafer are O₂⁺ and O⁺, which are representative of the corresponding neutral species O₂ and O. In a pure oxygen plasma, the reactive species that are involved in the resist etching are O₂ and O, as expected.

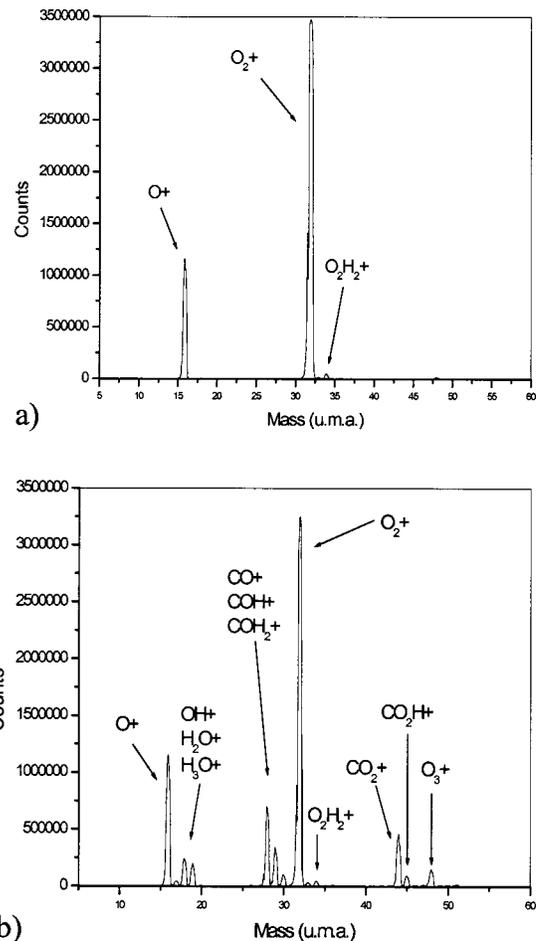


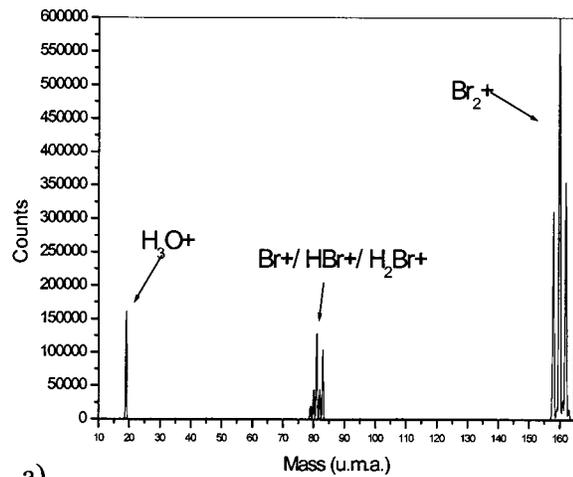
Fig. 1. Mass spectra of ionic species achieved (a) on a SiO₂-blanket wafer and (b) on a resist-blanket wafer, both exposed to the following plasma conditions: O₂(100 sccm)/bias(50 W)/source(500 W)/pressure(10 mT).

If we study the mass spectra obtained with a blanket resist wafer [see Fig. 1(b)], we notice that new masses are present in the discharge representing the resist-etch-by-products:

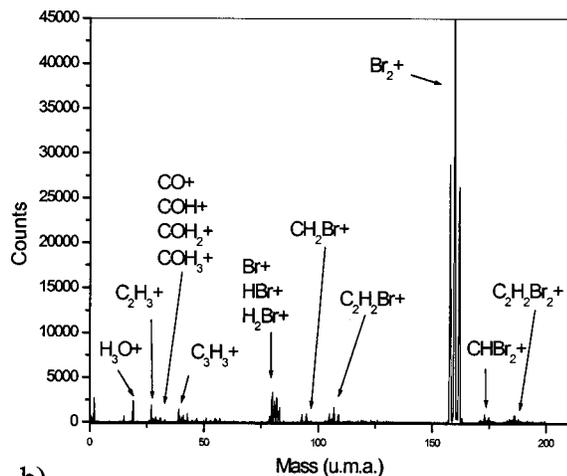
- products such as OH⁺, H₂O⁺ and H₃O⁺ which are representative of the neutral species OH, and H₂O. These products are formed from the hydrogen contained in the resist and the oxygen of the plasma; and
- products such as CO⁺, COH⁺, COH₂⁺ and CO₂⁺, CO₂H⁺ which are, respectively, the signature of resist-etch-by-products such as CO and CO₂.

It can be noticed that ionic species resulting from the etching of the resist tend to undergo protonic attachment. Thus the neutral species CO is represented by the ionic species CO⁺, COH⁺, COH₂⁺, and H₂O by H₂O⁺ and H₃O⁺.

Moreover, all the resist-etch-by-products formed with pure oxygen chemistry are very volatile. The vertical-etch rate measured under this plasma condition is 10 nm/s (measured by ellipsometry measurements), confirming the strong reactivity of pure oxygen plasma towards the resist.



a)



b)

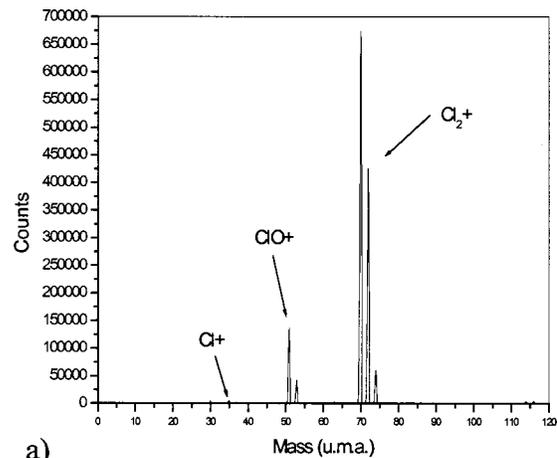
FIG. 2. Mass spectra of ionic species achieved (a) on a SiO₂-blanket wafer and (b) on a resist-blanket wafer, both exposed to the following plasma conditions: HBr(100 sccm)/bias(50 W)/source(500 W)/pressure(10 mT).

2. HBr plasma chemistry

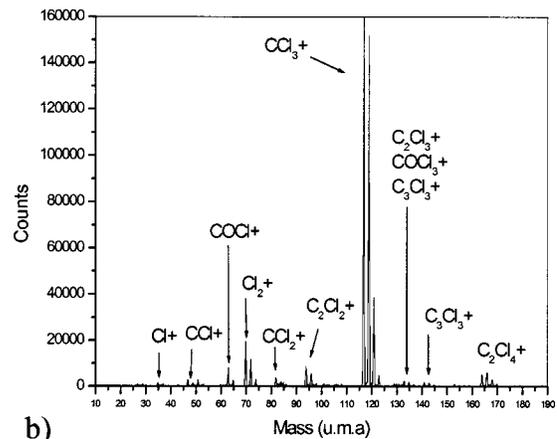
Figure 2 compares the mass spectra of ionic species obtained on oxide [cf. Fig. 2(a)] and resist [cf. Fig. 2(b)] wafers exposed to a pure HBr plasma.

The ionic species detected on a SiO₂ wafer are Br₂⁺, Br⁺, HBr⁺, H₂Br⁺, H₃O⁺ representative of the neutral species Br₂, Br, HBr, H₂O. The presence of H₃O⁺ is surprising since no source of oxygen has been introduced in the reactor. A mass spectrum of the ionic species present in the gas phase has been performed on a silicon-blanket wafer under the same plasma conditions (not shown here) and no H₃O⁺ is detected, while Br₂⁺, Br⁺, HBr⁺, H₂Br⁺ are present. We attribute the presence of H₃O⁺ on the mass spectrum to the slow ion assisted etching of the SiO₂ wafer by the hydrogen introduced with the HBr molecule. Br₂, HBr and Br are the reactive species present in the plasma discharge when using a pure HBr plasma.

The mass spectrum performed on the resist blanket wafer [cf. Fig. 2(b)] shows very few new masses. Indeed, the vertical etch rate of the resist measured under these plasma con-



a)



b)

FIG. 3. Mass spectra of ionic species achieved (a) on a SiO₂-blanket wafer and (b) on a resist-blanket wafer, both exposed to the following plasma conditions: Cl₂(100 sccm)/bias(50 W)/source(500 W)/pressure(10 mT).

ditions is about 0.4 nm/s, typical etch rates of a sputtering regime. This confirms the poor reactivity of bromine with respect to the resist that has been already demonstrated by the XPS analyses in a previous article.³

The mass spectrum of ionic species reveals the formation of three types of resist-etch-by-products:

- bromine-based products such as C_xH_yBr_z represented by CH₂Br⁺, C₂H₂Br⁺, C₂H₂Br₂⁺, CHBr₂⁺...
- products such as C_xH_y represented by the ionic species CH₃⁺, C₂H₃⁺... and
- oxygen-based products such as COH_x⁺ and H₃O⁺. These products are formed from the oxygen present in the resist, since no source of oxygen is introduced in the reactor.

When using a pure HBr plasma chemistry, the majority of resist-etch-by-products detected are quite heavy (C_xH_yBr_z) and less volatile than the products obtained with a pure oxygen plasma.

3. Cl₂ plasma chemistry

Figure 3 compares the mass spectra of ionic species obtained on an oxide [cf. Fig. 3(a)] and resist [cf. Fig. 3(b)] wafers exposed to a pure Cl₂ plasma.

TABLE I. Summary of the main characteristics of the etching of the resist when using 100 sccm of O₂, HBr, or Cl₂ with the following plasma conditions: Bias (50 W)/source (500 W)/pressure (10 mT).

Plasma chemistry	Resist-vertical-etch rate (nm/s)	Majority resist-etch-by-products	Characteristics of the etching
100 sccm of O ₂	10	CO, CO ₂	Chemical etching
100 sccm of HBr	0.4	C _x H _y Br _z	Sputtering
100 sccm of Cl ₂	2.3	CCl ₄	Chemical and physical etching

The ionic species present in the discharge when a SiO₂ wafer is used are mainly Cl₂⁺ and Cl⁺ [cf. Fig. 3(a)]. ClO⁺ is also detected while no source of oxygen has been introduced. It has been checked that these species are formed from the spontaneous etching of the SiO₂ wafer by chlorine atoms. Indeed, a mass spectrum achieved on a silicium-blanket wafer does not reveal the presence of this species (not shown here).

The plasma gas phase of a pure chlorine discharge is then composed of Cl₂ and Cl and their ionic equivalents.

The mass spectrum obtained on a resist wafer [cf. Fig. 3(b)] is rich with new masses compared to the spectrum obtained on a SiO₂ wafer. The etching of the resist by chlorine leads to the formation of numerous chlorine-rich carbon resist products. Ionic species such as CCl₃⁺, C₂Cl₄⁺, C₂Cl₂⁺, CCl₂⁺, CCl⁺ are mainly detected. These species are the signature of neutral species such as CCl₄, CCl₃, C₂Cl₄, CCl and CCl₂. The chlorine plasma chemistry leads to a vertical-etch rate of the resist of 2.3 nm/s, almost six times faster than with the HBr plasma under the same conditions. Both the large amount of resist-etch-by-products detected by mass spectrometry and the high vertical-etch rate confirm that chlorine is much more reactive towards the resist than bromine. This has already been shown in Ref. 3.

Table I summarizes the main characteristics of the etching of the resist with pure O₂, Cl₂, or HBr plasmas.

B. Study of HBr or Cl₂/O₂ chemistries

In this section, we have carried out mass spectrometry experiments on oxide-and-resist wafers exposed to a particular plasma condition for either HBr/O₂ or a Cl₂/O₂ trim chemistry: HBr or Cl₂ (70 sccm)/O₂ 30 sccm/source power: 500 W/bias power: 50 W/pressure: 10 mT.

The aim of these experiments is to determine the reactive species (with oxide wafer) and the chemical nature of the resist-etch-by-products (with resist wafer) present in the gas phase.

1. HBr/O₂ plasma chemistry

Figure 4 compares the mass spectra of ionic species obtained on an oxide [cf. Fig. 4(a)] and resist [cf. Fig. 4(b)] wafer. With 30% of oxygen introduced in the gas phase, the oxide wafer is not etched.

The plasma gas phase obtained with a mixture of HBr and O₂ is completely different from the gas phase of pure O₂ or HBr plasmas. The main ionic species detected in a HBr/O₂ plasma is H₃O⁺ representative of the neutral molecule H₂O.

Very few O₂⁺ and O⁺ are detected, showing that the oxygen introduced in the reactor is mainly transformed into water (certainly by recombination with hydrogen on the chamber wall or on the wafer surface). The recombination of atomic oxygen and hydrogen on the surface is a very easy reaction and besides we have noticed in Fig. 2(a) that H₃O⁺ is spontaneously formed on the oxide wafer exposed to a HBr plasma, while this wafer is hardly etched (etch rate inferior to 0.1 nm/s). The bromine species can be found as Br₂⁺, Br⁺ and HBr⁺, representative of Br₂, Br and HBr. A new species is also formed with a significant amount, BrO⁺.

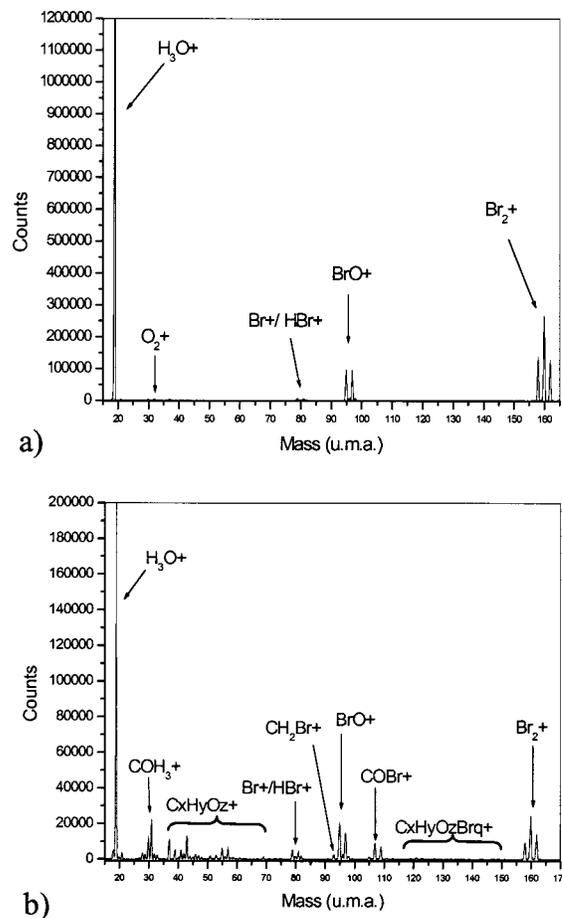


FIG. 4. Mass spectra of ionic species achieved (a) on a SiO₂-blanket wafer and (b) on a resist-blanket wafer exposed to the following plasma conditions: HBr(70 sccm)/O₂(30 sccm)/bias(50 W)/source(500 W)/pressure (10 mT).

The mass spectrum obtained on a blanket resist wafer shows that the exposition of the resist to HBr/O₂ plasmas results in the formation of four different types of resist-etch-by-products.

- Products such as C_xH_y [which represent 10% of the total amount of resist-etch-by-products]: C₂H₂⁺ and C₂H₃⁺ are the signature of carbon resist-etch-by-products. These species were also present in weaker concentrations when etching the resist with a pure O₂ or HBr plasma.
- Products such as C_xH_yO_z (40% of the total amount of resist-etch-by-products). This category can be divided into two groups:

— Species with only one atom of carbon ($x=1$) that represent 25% of the total amount of resist-etch-by-products.

These products are those obtained with a pure oxygen plasma: CO and CO₂ represented by the ionic species CO⁺, COH⁺, COH₂⁺, CO₂⁺, CO₂H₃⁺, CO₂H₂⁺, CO₂H⁺. It should be noticed that the major ionic species in this category detected are COH₃⁺ and CO₂H₃⁺ and not CO⁺ and CO₂⁺ because of the great reactivity between oxygen and hydrogen present in large amount in the gas phase. These resist-etch-by-products are very volatile.

— Species with longer carbonated chain ($x > 1$) that represent 15% of the total amount of resist-etch-by-products: the presence of C₂H₃O⁺, C₃H₃O⁺, C₃H₅O⁺ and C₂HO⁺ is detected in the plasma gas phase.

- Products such as C_xH_yBr_z (22% of the total amount of resist-etch-by-products): these products have already been detected when etching the resist with a pure HBr plasma. Among them, we can find C₂H₂Br⁺, CH₂Br⁺, CBr⁺, CHBr₂⁺, C₂H₂Br₂⁺. These products are heavy and low volatile molecules.
- Products such as C_xH_yOBr (28% of the total amount of resist-etch-by-products): these are products that have not already been obtained with a pure HBr or O₂ plasma. Among them, we detect a large amount of COBr⁺ representative of COBr, which is the main species of this category. The other species such as C₂OBr, C₂H₂OBr, C₂H₄OBr, C₃OBr, are detected in a less important amount.

H₂O (H₃O⁺) must also be a resist-etch-by-product, but it is difficult to estimate its contribution to the total amount of products because it is also a reactive species present in the plasma gas phase.

2. Cl₂/O₂ plasma chemistry

Figure 5 shows the mass spectra of ionic species obtained on oxide [cf. Fig. 5(a)] and resist [cf. Fig. 5(b)] blanket wafers exposed to the same plasma conditions. As shown in Fig. 5(a), the main ionic species is ClO⁺ and not Cl₂⁺ and O₂⁺ as obtained, respectively, for pure Cl₂ and O₂ plasmas. As for the HBr/O₂ chemistry, very few O₂⁺ and O⁺ are detected and the oxygen introduced in the plasma is mainly transformed into ClO. The formation of this species is due to the recombination of atomic chlorine and oxygen on the reactor walls and wafer surface. The formation of this species is easy to obtain since we have observed that a SiO₂ wafer exposed to

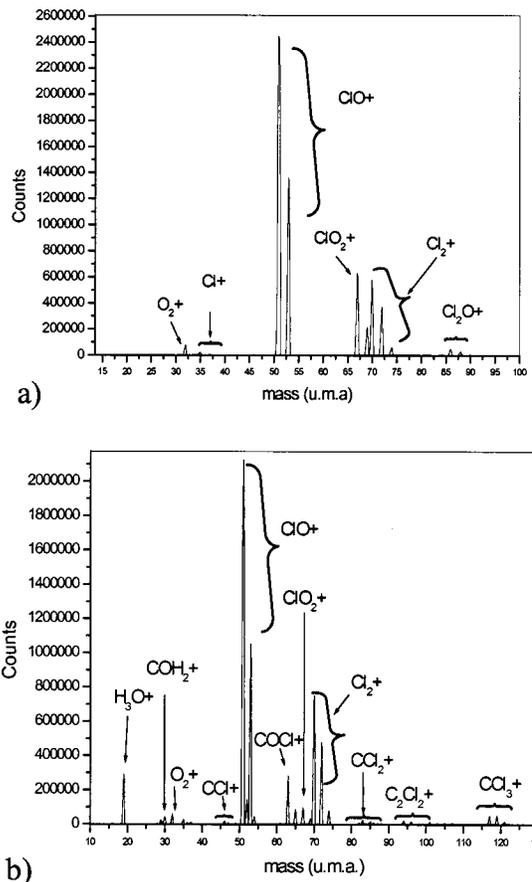


FIG. 5. Mass spectra achieved (a) on a SiO₂-blanket wafer and (b) on a resist-blanket wafer exposed to the following plasma conditions: Cl₂(70 sccm)/O₂(30 sccm)/bias(50 W)/source(500 W)/pressure(10 mT).

a chlorine plasma leads to the formation of ClO, while it is hardly etched. Some other mixed species are detected such as ClO₂⁺ and Cl₂O⁺ representative of ClO₂ and Cl₂O formed by recombination on the surfaces.

The mass spectrum achieved on resist blanket presents the same reactive species as those obtained on an oxide wafer, but shows also the appearance of new masses representative of the resist-etch-by-products. Water (represented by H₃O⁺) is formed from the hydrogen composing the resist, and the other products are formed from the carbon of the resist. These carbon-based products can be classified into three categories:

- products such as CO_xH_y which represent 11% of the total amount of carbonated resist-etch-by-products. These products are coming from the etching of the resist by atomic oxygen, as already observed in a pure oxygen plasma;
- products such as C_xH_yCl_z (45% of the total amount of the carbonated resist-etch-by-products). These products result from the etching of the resist by chlorine, and have already been obtained when the resist is exposed to a pure chlorine plasma; and
- mixed products such as COCl_x. (44% of the total amount of the carbonated resist-etch-by-products). COCl is the second resist-etch-by product after H₂O.

3. Summary

This preliminary study underlines some differences between HBr/O₂ and Cl₂/O₂ plasmas. Concerning the reactive species present in the plasma gas phase, we have seen that for both chemistries, the main oxygen-based species is not O₂ or O, but H₂O with the HBr/O₂ chemistry and ClO with Cl₂/O₂ chemistry. This draws the first difference between the two chemistries: with a HBr/O₂ chemistry, the role of the atomic oxygen is inhibited by the formation of water because of the presence of hydrogen in the gas phase (atomic bromine does not seem to play any role), whereas with a Cl₂/O₂ chemistry, atomic chlorine is the species that reacts with atomic oxygen to form ClO.

The role of chlorine is also revealed by the chemical nature of the resist-etch-by-products obtained with a Cl₂/O₂ chemistry: 45% of all the resist-etch-by-products are chlorine-rich-carbon-resist products, while with a HBr/O₂ chemistry only 22% of the resist-etch-by-products are bromine-rich-carbon-resist products. This means that with a HBr/O₂ plasma, atomic oxygen is the main etchant of the resist, while with a Cl₂/O₂ plasma, there is a competition between atomic oxygen and chlorine to react with the resist. The Cl₂/O₂ chemistry therefore leads to less volatile resist-etch-by-products than the HBr/O₂ chemistry, which mainly results in the formation of very volatile products such as CO or CO₂ (25% of the whole resist-etch-by-products). This could explain why vertical and lateral etch rates of the resist are higher with a HBr/O₂ chemistry.³

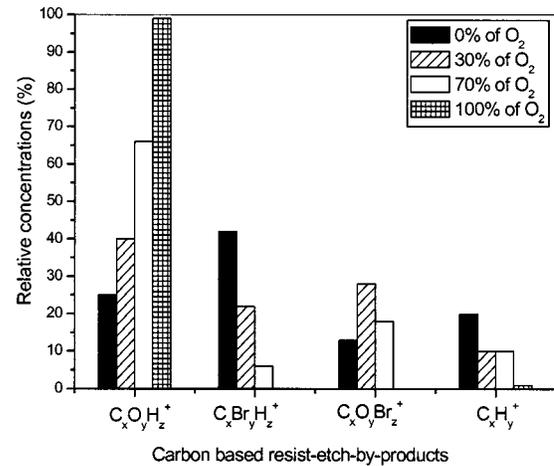
C. Study of influence of plasma parameters on chemical nature of resist-etch-by-products present in the plasma gas phase of HBr/O₂ and a Cl₂/O₂ plasmas

In this section, we have performed mass spectra on resist wafers only for both chemistries and we have calculated the relative concentrations of the resist-etch-by-products using Eq. (1). The semiquantitative calculations have only been performed on carbon-based resist-etch-by-products and we are only interested in the evolution of their concentrations with the plasma parameters. From the chemical nature of these products and their volatility, we have also explained the variation of the etch rates with the plasma parameters.

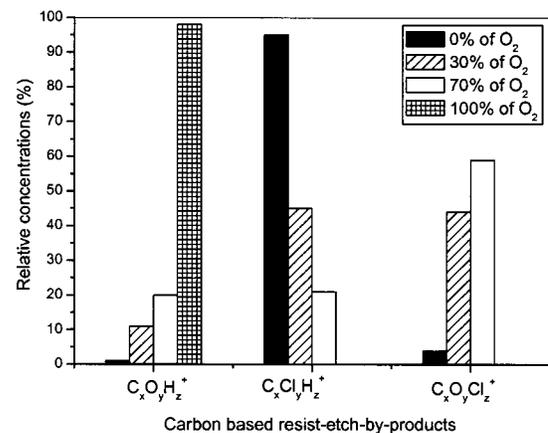
1. Influence of oxygen percentage introduced in reactor

In a previous article,³ we have shown that an increase of the oxygen concentration introduced in the plasma leads to an increase of the vertical and lateral etch rates, for both chemistries.

In this article, we have performed plasma mass spectrometry on resist wafers exposed to the following plasma conditions (HBr or Cl₂+O₂): 100 sccm/source power: 500 W/bias power: 50 W/pressure: 10 mT. The relative concentrations of the carbon-resist-etch-by-products have been calculated for four percentages of oxygen introduced in the reac-



a) HBr/O₂ plasma chemistry



b) Cl₂/O₂ plasma chemistry

FIG. 6. Evolution of the concentration of the different carbon-based resist-etch-by-products as a function of the O₂ percentage (0%, 30%, 70% and 100%) introduced in the reactor: (a) when using a HBr/O₂ trim chemistry and (b) when using a Cl₂/O₂ trim chemistry.

tor: 0%, 30%, 70%, and 100% for a HBr/O₂ chemistry [see Fig. 6(a)] and a Cl₂/O₂ chemistry [see Fig. 6(b)].

In Fig. 6(a), we can notice that increasing the O₂ percentage introduced in the reactor favors the formation of ionic species such as CO_xH_y⁺ (representative of neutral species such as CO and CO₂) rather than bromine-rich-carbon-resist-etch-by-products represented by C_xH_yBr_z⁺. Indeed, the CO_xH_y⁺ concentration varies from 10% of all the resist-etch-by-products when 0% of O₂ is introduced into the plasma, to 98% when 100% of O₂ is introduced, while the C_xH_yBr_z⁺ concentration varies from 42% to 0%.

With the Cl₂/O₂ chemistry, an increase of the O₂ percentage introduced in the plasma has the same impact on the chemical nature of the resist-etch-by-products. Figure 6(b) shows that increasing the O₂ percentage in the plasma favors the formation of products such as CO, CO₂, and mainly COCl⁺ while the concentration of chlorine-rich-carbon-resist-etch-by-products (represented by C_xH_yCl_z⁺) decreases.

In both cases, we can see that an increase in the O_2 concentration in the plasma favors the formation of very volatile species (CO , CO_2). This suggests that the attack of the resist by the oxygen is enhanced and that the etching of the resist is thus more chemical in nature resulting in higher etch rates. This result is coherent with the XPS analyses performed in Ref. 3 where we have shown that an increase in the O_2 percentage introduced in the reactor with the Cl_2/O_2 chemistry leads to a decrease of the thickness of the reactive layers formed on the resist sidewalls (when 30% of O_2 is introduced in the reactor, we found that the reactive layers formed on the resist sidewalls is 2.3 nm thick and it decreases to 1 nm when 60% of O_2 is introduced), and a decrease of the chlorine percentage in the layer (49% of chlorine is detected by XPS in the reactive layer formed on the resist sidewalls when 30% of O_2 is introduced in the reactor, while only 20% of chlorine is present when 60% of O_2 is introduced).

2. Influence of bias power

In a previous article,³ we have shown that an increase of the bias power leads to an increase of the vertical etch rates but to a decrease of the lateral etch rates, in both chemistries.

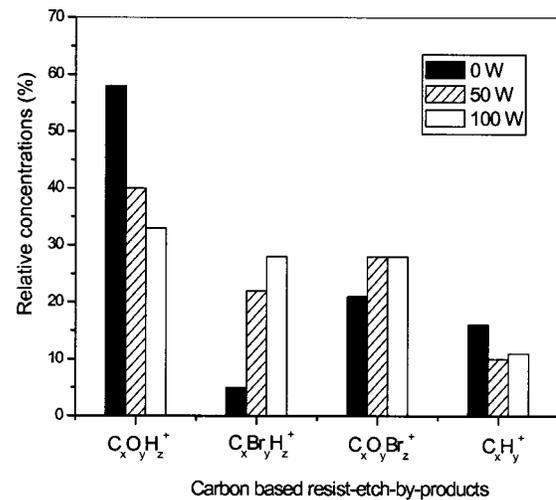
In this work, we have performed mass spectra experiments on resist wafers exposed to the following plasma conditions (HBr or Cl_2): 70 sccm/ O_2 : 30 sccm/source power: 500 W/pressure: 10 mT. The relative concentrations of the carbon-resist-etch-by-products have been calculated for three bias powers: 0, 50 and 100 W for a HBr/O_2 chemistry [see Fig. 7(a)] and a Cl_2/O_2 chemistry [see Fig. 7(b)].

In Fig. 7(a), we can notice that an increase in bias power applied to the wafer has an impact on the chemical nature of the carbon-resist-etch-by-products formed in the gas phase. By increasing the bias power from 0 to 100 W, the contribution of species such as $CO_xH_y^+$ decreases from 45% to 19%, while species such as $C_xH_yBr_z^+$ increase from 5% to 28%. This means that by increasing the bias power (resulting in an increase of the ion energy), we favor the physical sputtering of heavy and nonvolatile resist-etch-products such as $C_xH_yBr_z^+$ species.

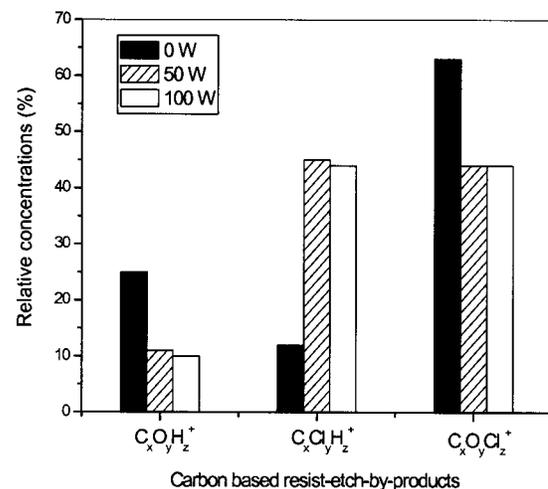
This phenomenon is also observed with the Cl_2/O_2 chemistry [see Fig. 7(b)], since an increase of the bias power enhances the formation of resist products such $C_xH_yCl_y^+$ rather than volatile resist products such as CO^+ , CO_2^+ and $COCl^+$. Moreover, $COCl$ seems to be formed quite spontaneously, since it always represents a large percentage of the resist-etch-by-products and especially, it represents 61% of the resist by-products at very low energetic bombardment (around 15 eV for a bias power fixed at 0 W).

These observations can well explain the observed etch rates. An increase in bias power logically results in an increase of the vertical etch rates, but why do we observe a decrease in lateral etch rate?

Increasing the bias power enhances the formation of halogen-based resist-etch-by-products, which are heavier and less volatile than products such as CO , CO_2 , $COCl$. These halogen-based resist by-products can thus be redeposited on



a) HBr/O_2 plasma chemistry



b) Cl_2/O_2 plasma chemistry

Fig. 7. Evolution of the concentration of the different carbon-based resist-etch-by-products as a function of the bias power applied to the wafer (0, 50 and 100 W): (a) when using a HBr/O_2 trim chemistry and (b) when using a Cl_2/O_2 trim chemistry.

the resist sidewalls, slowing down the lateral etching of the resist. This is fully consistent with the XPS analyses performed with a Cl_2/O_2 chemistry,³ which show that an increase in bias power results in an increase of the reactive layer thickness formed on the resist sidewalls (when the bias power is increased from 0 to 100 W, we have measured by XPS that the thickness of the reactive layers formed on the resist sidewalls increases from 1.6 to 4.2 nm), and also in an increase of the chlorine concentration in these layers sidewalls (when the bias power is tuned from 0 to 100 W, we have found that the chlorine concentration in the reactive layers increases from 38% to 51%).

3. Influence of source power

It has been shown³ that an increase of the source power leads to an increase of the vertical and lateral etch rates, for both chemistries.

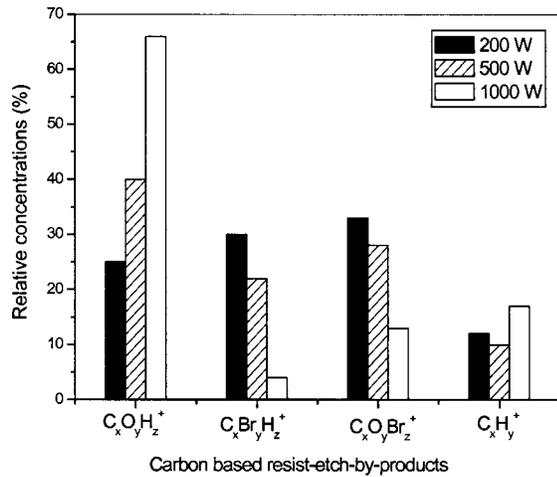
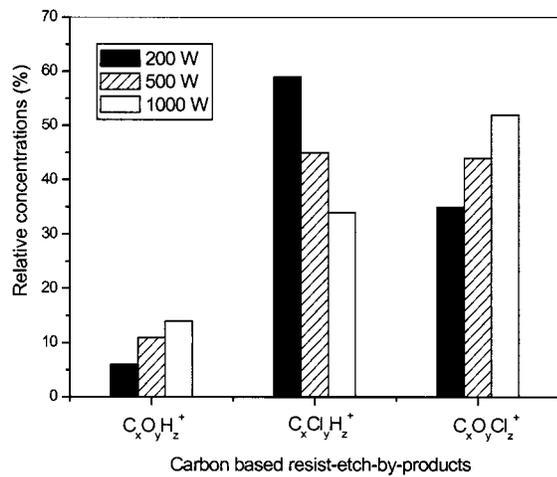
a) HBr/ O₂ plasma chemistryb) Cl₂/ O₂ plasma chemistry

FIG. 8. Evolution of the concentration of the different carbon-based resist-etch-by-products as a function of the source power applied to the wafer (200, 500, and 1000 W): (a) when using a HBr/O₂ trim chemistry and (b) when using a Cl₂/O₂ trim chemistry.

In this article, we have performed mass spectra on resist wafers exposed to the following plasma conditions (HBr or Cl₂): 70 sccm/O₂: 30 sccm/bias power: 50 W/pressure: 10 mT. The relative concentrations of the carbon-resist-etch-by-products have been calculated for three source powers: 200, 500, and 1000 W for an HBr/O₂ chemistry [see Fig. 8(a)] and a Cl₂/O₂ chemistry [see Fig. 8(b)].

For both chemistries, we can see that increasing the source power favors the formation of oxygen-based resist by-products (CO, CO₂, and COCl) and decreases the halogen-based resist-by-products formation. This means that an increase in source power injected in the plasma enhances the attack of the resist by the atomic oxygen that leads to more spontaneous etching reactions and an increase in the etch rates.

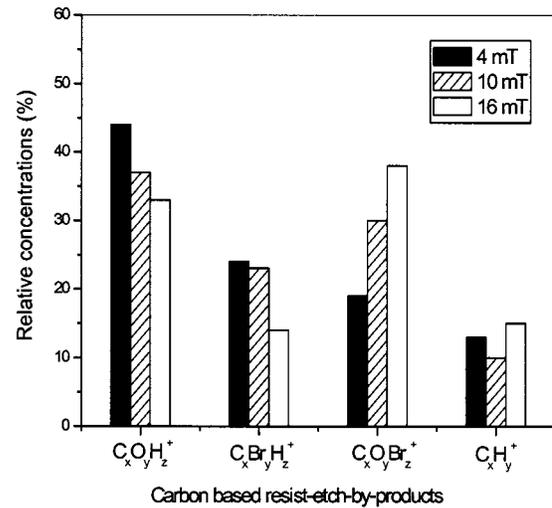
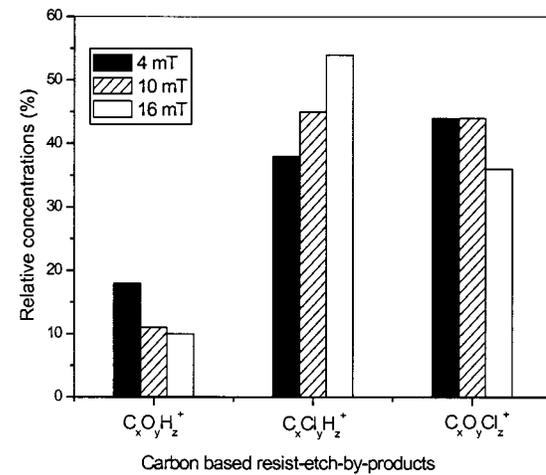
a) HBr/O₂ plasma chemistryb) Cl₂/O₂ plasma chemistry

FIG. 9. Evolution of the concentration of the different carbon-based resist-etch-by-products as a function of the pressure in the reactor (4, 10, and 16 mT): (a) when using a HBr/O₂ trim chemistry and (b) when using a Cl₂/O₂ trim chemistry

4. Influence of pressure

It has been shown³ that an increase in pressure leads to a decrease of the vertical and lateral etch rates, for both chemistries.

In this article, we have performed mass spectrometry on resist wafers exposed to the following plasma conditions (HBr or Cl₂): 70 sccm/O₂: 30 sccm/bias power: 50 W/ source power: 500 W. The relative concentrations of the carbon-resist-etch-by-products have been calculated for three pressures in the reactor: 4, 10 and 16 mT for a HBr/O₂ chemistry [see Fig. 9(a)] and a Cl₂/O₂ chemistry [see Fig. 9(b)].

There is no clear evolution of the chemical nature of the resist by-products as a function of pressure. The contribution of species such CO, CO₂, and COCl to the total concentration of resist by-products tends to decrease when increasing

pressure for both chemistries, but the tendency observed for halogen-based resist by-products is not clear. We observe a decrease of 10% of the $C_xH_yBr_z^+$ species with the HBr/O₂ chemistry when tuning the pressure from 4 to 16 mT, while the $C_xH_yCl_z^+$ increases 16% with the Cl₂/O₂ chemistry.

We cannot conclude clearly, but it seems that with the Cl₂/O₂ chemistry an increase in pressure favors the attack of the resist by atomic chlorine resulting in an increase of the contribution of chlorine-rich carbon resist by-products. This assumption is consistent with the XPS analyses of Ref. 3 that show an increase of the chlorine concentration in the reactive layers formed on the sidewalls with increasing pressure (When increasing the pressure from 4 to 16 mT, it has been found that the chlorine concentration in the reactive layers increases from 41% to 51%).

If the attack of oxygen is minimized when the pressure increases, it could explain why the etch rates are slower. Moreover, if the formation of less volatile products (such halogen-based resist by-products) is enhanced with increasing pressure, the deposition of species on the resist sidewalls is more likely. This is consistent with the XPS analyses performed with the Cl₂/O₂ chemistry which have shown that an increase in pressure leads to an increase of the thickness of the reactive layers formed on the resist sidewalls (When increasing the pressure from 4 to 16 mT, we have measured by XPS that the thickness of the reactive layers formed on the resist sidewalls increases from 1.7 to 2.7 nm).

IV. CONCLUSION

In this article, we have used mass spectrometry to get a better understanding of the mechanisms involved in resist trimming processes using either HBr/O₂ or Cl₂/O₂ chemistries.

In Secs. III A and III B, we have first shown that the etching of the resist by atomic oxygen results in the formation of volatile products such as CO and CO₂, while the attack of the resist by bromine or chlorine leads to heavy and less volatile products such as $C_xH_yBr_z$ with Br and $C_xH_yCl_z$ with Cl. Chlorine is more reactive than bromine with respect to the resist and leads to the formation of numerous chlorine-based resist by-products.

Hence, when using a Cl₂/O₂ chemistry, there is a competition between atomic oxygen and chlorine, while with the HBr/O₂ chemistry, oxygen is the main reactive species. In a way, as chlorine is less reactive than oxygen towards the resist, it slows down the attack of the atomic oxygen explaining why higher trim rates are obtained with the HBr/O₂ chemistry. In Sec. III C, we have attempted to explain the variation in etch rates with the plasma parameters by observing the evolution of the concentration of the different categories of resist by-products. For both chemistries, we have seen that plasma conditions enhancing the formation of low volatile carbon-based products such as $C_xH_yBr_z$ with Br and $C_xH_yCl_z$ with Cl are correlated with low trim rates. An explanation for that is that these products are redeposited on the resist sidewalls, slowing down the lateral etch rates. These mass spectrometry observations corroborate the XPS results obtained in Ref. 3 with the Cl₂/O₂ chemistry, since we have shown that plasma conditions leading to slower trim rates result in the formation of thicker and richer chlorine reactive layers on the resist sidewalls.

Moreover, we confirm, thanks to mass spectrometry, that the same mechanism of deposition of heavy bromine-based resist by-products on the resist sidewalls is controlling the trim rates with the HBr/O₂ trim chemistry.

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