

Tungsten metal gate etching in Cl_2/O_2 inductively coupled high density plasmas

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Plasma etching of W in a poly-Si/TiN/W/HfO₂ gate stack is investigated in Cl_2/O_2 based plasmas. Preliminary studies have illustrated the issues induced with the introduction of a metal layer in the gate stack. Based on scanning electron microscopy observations, the authors first show that a mixture of Cl_2 , O_2 , and NF_3 is required to successfully pattern the W layer without damaging the HfO₂, poly-Si, and TiN profiles. For a better understanding of etch mechanisms, W etching is studied on blanket wafers and etch rates are presented and discussed with respect to the plasma parameters. The evolution of the etch rates as a function of O_2 ratio in Cl_2/O_2 and $\text{Cl}_2/\text{O}_2/\text{NF}_3$ plasmas is interpreted. X-ray photoelectron spectroscopy analyses demonstrate that the introduction of O_2 in Cl_2 leads to the creation of a thick WOCl_x deposit on the gate sidewalls. However, the WOCl deposition can be controlled and eliminated by adding fluorine in the plasma during W etching. © 2008 American Vacuum Society. [DOI: 10.1116/1.3002392]

I. INTRODUCTION

With the reduction in the complementary metal-oxide-semiconductor (CMOS) device dimensions on standard polysilicon gates, the polydepletion effect¹ has a significant impact on the transistor performances. Indeed, it is becoming a major problem to achieve low equivalent oxide thickness in order to get acceptable currents. Inserting a well chosen metal layer between the polysilicon and the dielectric is one of the solutions² that transforms a pure silicon gate into a metal gate. The metal work function of the metal layer is a key factor in the selection of metal gate materials for device integration because it directly affects the threshold voltage and performance of a transistor.² Appropriate materials have to be chosen so that the threshold voltages for *n*- and *p*-channel transistors are complementary and sufficiently small to achieve high transistor drive currents for a given supply voltage. One promising solution consists in introducing two metals, one with a *n*⁺ poly-Si-like work function for *n*-channel transistors and another with a *p*⁺ poly-Si-like work function for *p*-channel transistors. This work reports on the successful integration of thin tungsten layers (10-nm) as a *p*-type metal on 300 mm diameter wafers. W integration into the gate stack (poly-Si/TiN/W/HfO₂) requires new dry etch approaches. TiN is also introduced in the gate stack to avoid any silicidation of tungsten during polysilicon deposition. Some studies have already been performed on W alloy etching^{3–12} but, to our knowledge, this type of complex gate stack structure has never been explored before.

The process development of the metal gate stack requires the investigation of new etching chemistries and plasma op-

erating conditions. In particular, it is necessary to find plasma chemistries leading to the formation of volatile etch products with the metal to prevent their redeposition on the gate sidewalls and chamber walls. One of the main issues for W integration in CMOS devices is to generate vertical profiles in the W layer while maintaining those in poly-Si and TiN. The second key challenge is to generate a process presenting a high selectivity with respect to the HfO₂ layer in order to preserve the high-*k* and silicon substrate from plasma-induced damage.

Starting with blanket tungsten wafers, we have studied the impact of several elementary chemistries on the etch rate of W. By using various diagnostic tools, we have investigated the Cl_2/O_2 chemistry in terms of etch rate, selectivity over HfO₂, and profile control. Thanks to the experiments on patterned wafers, we have finally developed a $\text{Cl}_2/\text{O}_2/\text{NF}_3$ process that controls the metal gate profile.

II. EXPERIMENTAL SETUP

The etching of patterned wafers and all etch rate measurements have been carried out on 300 mm wafers in a high density inductively coupled plasma (ICP) etching reactor (LAM Versys Kiyō) manufactured by LAM Research. One of the particularities of this ICP reactor is the potential use to control directly the rf bias voltage at the chuck by using a closed-loop control system based on a voltage sensor.¹³ By this way, we control independently the ion energy and the ion flux. The scheme of the basic configuration system is given elsewhere.¹³ In this study, tungsten layers of 10 nm and thin HfO₂ films of 2.5 nm have been deposited by metal-

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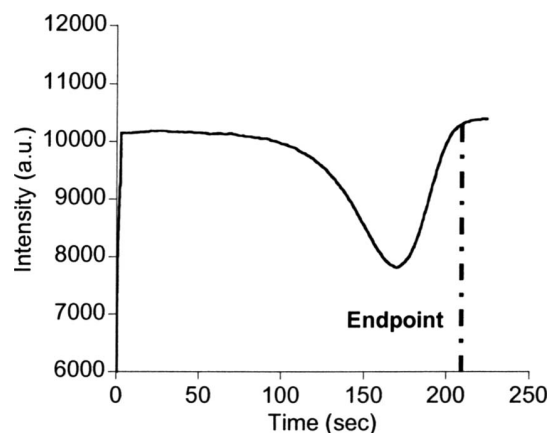


FIG. 1. End point detection from the interferometric trace recorded at 230 nm while etching a 40 nm thick W layer deposited on 2.5 nm of HfO_2 in a Cl_2/O_2 plasma.

organic chemical vapor deposition. Thickness measurements of W and HfO_2 have been performed by x-ray reflectometry before etching. Etch rates of W and HfO_2 are measured by *in situ* optical emission spectroscopy and *in situ* interferometry. For example, Fig. 1 displays the interferometric signal recorded at 230 nm while etching a tungsten layer in a Cl_2/O_2 plasma. The end point is followed by a plateau which indicates that the W layer has been completely removed. Both optical emission and interferometry signals can be collected and observed simultaneously in a wavelength range between 200 and 900 nm with an optical resolution of 0.4 nm. To determine the relative F atom concentration in CF_4 , NF_3 , and SF_6 plasmas, an optical emission spectroscopy (actinometry technique^{14,15}) was employed. The actinometry technique is widely employed to determine the relative F atom concentration in CF_4 ,¹⁶ NF_3 ,¹⁷ and SF_6 (Ref. 18) plasmas. A 5% concentration of argon added to the gas flow served as an actinometer for the study of relative variation in F concentrations in the different plasmas investigated. For actinometry purposes, the 703.7 nm F line and the 750.4 nm Ar line were used.^{14,19} Comparing the intensities of these two lines, the relative atomic fluorine density in the plasma can be monitored. However, several assumptions have to be made for the actinometry technique. Two primary assumptions are that the excitation cross sections of both Ar and F show the same energy dependence and that excited F^* radicals only originate from direct excitation from the ground state. With respect to the first assumption, the two transition lines employed in the present experiments (703.7 nm for F and 750.4 nm for Ar) are chosen to have a small difference in the excitation threshold energies (14.74 eV for F and 13.5 eV for Ar).¹⁹ The second assumption is valuable if the production of F^* by dissociative excitation (i.e., $\text{CF}_4 + e \rightarrow \text{CF}_3 + \text{F}^* + e$) is negligible.¹⁹ In our work, we assume that relative F atoms concentration in CF_4 , NF_3 , and SF_6 gases can be compared even if such dissociative excitation mechanisms are possible.

In order to study the integration of W as a metal gate, W etching has been performed on patterned wafers using the

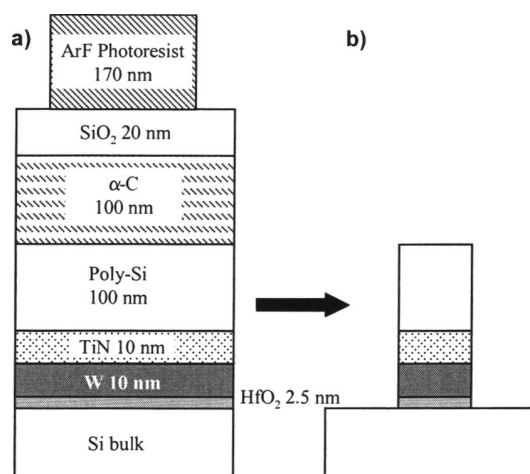


FIG. 2. Scheme of the metal gate stack: (a) before etching and (b) after etching.

following metal gate stack: HfO_2 (2.5 nm), W (10 nm), TiN (10 nm), undoped poly-Si (100 nm), amorphous carbon (100 nm), SiO_2 (20 nm used as capping layer), and 170 nm thick JSR1682 ArF photoresist. A scheme of the metal gate stack is given in Fig. 2. After plasma etching, the metal gate profile has been investigated by scanning electron microscopy (SEM).

Quasi-*in situ* x-ray photoelectron spectroscopy (XPS) measurements have been performed on a customized 220I system from VG Scientific²⁰ directly connected under vacuum to an etching tool [decoupled plasma source (DPS) from Applied Materials, described in detail elsewhere²¹] accepting 200 mm diameter wafers. To manage *in situ* XPS analyses on tungsten after etching, pieces of 300 mm tungsten wafer have been fixed on a 200 mm wafer of amorphous carbon with KaptonTM. After etching in the DPS reactor, the wafer is transferred under vacuum to the XPS tool through a cooldown chamber. A nonmonochromatized x-ray source ($\text{Mg K}\alpha$ at 1253.6 eV) is used at a dwelling time of 100 ms and at a pass energy of 20 eV for the core level spectra. Chemical compositions are extracted from the areas of the different XPS core level spectra: Si 2p (99.3 eV), F 1s (688.5 eV), C 1s (285 eV), O 1s (530 eV), Hf 4f (14.4 eV), Cl 2p (199.8 eV), Al 2p (72.9 eV), and W 4f (31.4 eV). Using a numerical fitting procedure, spectral deconvolution is performed to extract the peak contributions in the acquired energy regions. Individual line shapes are simulated with a combination of Lorentzian and Gaussian functions. The background subtraction is performed using a Shirley function calculated from a numerical iterative method. After XPS analysis, the integrated intensities are divided by the theoretical Scofield cross section (Si 2p: 0.87; F 1s: 4.26; C 1s: 1.0; O 1s: 2.85; Hf 4f: 7.95; Cl 2p: 2.36; Al 2p: 0.57; W 4f: 10.27). The sum of the concentration of the different elements present on the analyzed surfaces is equal to 100%. For the W layer, the W 4f core level spectra are fitted with an energy shift of 2.18 eV and an intensity ratio of 0.72 for the spin orbit components W 4f 7/2 and W 4f 5/2.²² For the

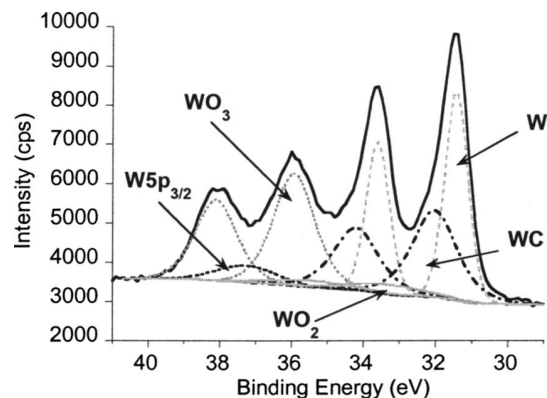


FIG. 3. W 4f XPS spectrum of as-deposited W material.

as-deposited 10 nm thick W film, the W 4f core level spectrum shows the presence of four contributions (see Fig. 3). The main peak located at 31.4 eV is assigned to W–W bonds and the contribution at 32 eV can be attributed to W in WC environment since W is deposited using a tungsten carbonyl precursor [W(CO)₆]. The presence of peaks located at 33.3 and 35.9 eV can be attributed to the native oxide (WO₂ and WO₃, respectively) on top of the tungsten layer.

To get a better understanding of the evolution of the metal etch profiles using different chemistries, we have also used a new technique²³ based on XPS to monitor the surface modification of an electrically floating sample exposed to the etch by-products generated during metal etching. This floating sample of Al₂O₃ is fixed on a W wafer with an air gap between the sample and the W wafer in order to prevent rf biasing, i.e., the floating sample is bombarded by ions at the floating potential. Thus, after plasma etching, the coatings formed on the floating Al₂O₃ sample are representative of the coatings deposited on the chamber walls²³ and on the side-walls of the poly-Si/TiN/W gate stack. Indeed, using a low pressure process, the sheath is collisionless, so we assume that the ion bombardment on the gate sidewalls is negligible. As the sample is physically clamped on the wafer, it can be transferred under vacuum to the XPS chamber, allowing quasi-*in situ* analyses of the deposited layers. Due to the insulating behavior of the floating sample, charging occurs and the spectra are recorded after stabilization of the XPS peak position. To take into account the energy shift due to this charging phenomenon, the XPS spectra are calibrated in energy by applying an energy correction of the Al 2p peak with respect to its original position at 74.5 eV (Ref. 23) (referring to the Al₂O₃ sample).

III. RESULTS AND DISCUSSION

A. Impact of plasma chemistries on W etch rate and profile control

1. W etch rate versus plasma chemistries

First, we have investigated a wide variety of basic etch chemistries on blanket wafer of tungsten in order to select the most appropriate chemistry. For this study, the pressure, source power, chuck temperature, and gas flow rate have

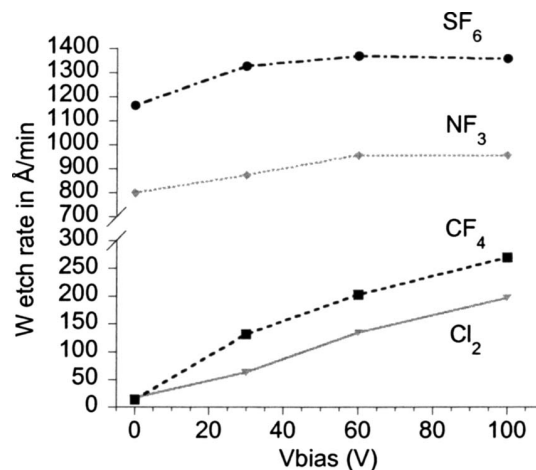


FIG. 4. Etch rate of W as a function of bias voltage for different elementary chemistries. Plasma conditions are 50 SCCM gas flow, 10 mTorr pressure, 500 W source power, and 60 °C chuck temperature.

been set at 10 mTorr, 500 W, 60 °C, and 50 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. Figure 4 summarizes the different experiments and shows the W etch rate as a function of the bias voltage which controls the ion energy. First, we can notice that the tungsten etch rate is higher in fluorine containing chemistries. This result is in good agreement with the high product volatility formed between W and fluorine (see Table I which shows the melting points and boiling points of W compounds related to the gases used in these experiments^{4,5}). Moreover, the etch rate in SF₆ and NF₃ chemistries is almost independent of the bias voltage variation, indicating that the W etch mechanism is rather chemical in fluorine based chemistries. For the CF₄ case, the etch mechanisms are quite different since there is a competition between fluorocarbon deposition and W etching by free fluorine. The balance between fluorocarbon deposition and etching has been widely studied on other materials such as silicon.²⁴ On the other hand, in Cl₂ plasmas, the etch

TABLE I. Boiling and melting points of the compounds formed during etching of poly-Si, Ti, and W by fluorine and chloride based plasmas (from Refs. 3 and 4).

Compound	Boiling point (°C)	Melting point (°C)
SiF ₄	−86	−90
SiCl ₄	58	−69
SiO ₂	2590	1710
TiF ₄	284	...
TiCl ₄	58	...
WF ₄	...	800
WF ₆	17	2
WOF ₄	186	108
WO ₂	1730	1500
WO ₃	1837	1470
WOCl ₄	227	211
WCl ₅	275	248
WCl ₆	347	275

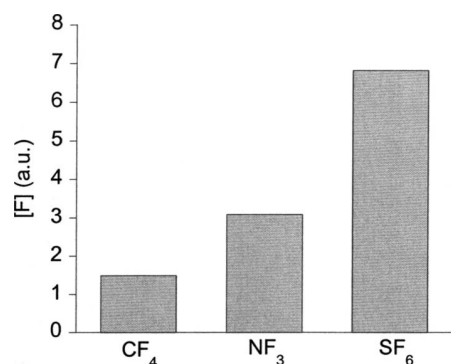


FIG. 5. Relative fluorine concentration determined by actinometry in CF₄, NF₃, and SF₆ plasmas. Plasma conditions are 50 SCCM gas flow, 10 mTorr pressure, 500 W source power, 60 °C chuck temperature, and no bias voltage.

rate of W linearly increases as a function of bias voltage, i.e., the ion energy, showing that the etch mechanism is strongly assisted by the ion bombardment. Finally, since W etching is strongly driven by chemical etching reactions, the differences in etch rates measured between CF₄, NF₃, and SF₆ should be largely attributed to the differences in F atom concentration in the plasma gas phase. To determine the relative F atom concentration in CF₄, NF₃, and SF₆ plasmas, we have used the actinometry technique as described in the experimental setup. We have monitored successively CF₄, NF₃, and SF₆ plasmas with the same previous experimental conditions without applying any bias voltage and without any wafer. Ar gas (5%) has been added to the gas phase chemistry for the actinometry measurements. Figure 5 shows that the atomic fluorine density in SF₆ plasma is almost twice that obtained in NF₃ plasma, which is itself about twice that in CF₄ chemistry. These results show that W etch rate is very sensitive to the F atom concentration in the plasma gas phase and confirm the chemical nature of W etch rate. In CF₄ chemistry, without V_{bias} , the fluorocarbon deposition is predominant and the W etch rate is close to zero.

2. Limitation of standard chemistries for profile control

First, a typical process has been used to etch the metal gate stack from the SiO₂ capping layer down to the TiN layer including an amorphous carbon mask trimming step. The metal gate etch strategy developed in this study is based on a “layer by layer” strategy in which each layer is etched selectively with respect to the underlayer. This type of strategy allows a better control of the etching uniformity and micro-loading effects. Details of the etching parameters are given in Table II. After resist trimming and mask layer opening using typical processes developed in the ICP source, the poly-Si layer has been etched in three different steps. The main etch (ME) step is performed in a SF₆/CH₂F₂/He/N₂ chemistry and generates a fluorocarbon based passivation layer on the poly-Si sidewalls. The soft landing (SL) step is performed in a HBr/He/Cl₂/O₂ chemistry and allows the etching of the last 25 nm of poly-Si selectively with respect to TiN. Finally,

TABLE II. Details of the plasma chemistry used in the different steps involved in mask layers and poly-Si layer etching.

	Chemistry	Step type
Cure	HBr	Timed
Trim	HBr/O ₂ /CHF ₃	Timed
HM	CH ₂ F ₂ /CF ₄ /He	End pointed
APF	HBr/O ₂	End pointed
ME Si	SF ₆ /CH ₂ F ₂ /HeN ₂	Timed
SL	Cl ₂ /HBr/He/O ₂	End pointed
OE	HBr/He	Timed

the overetch (OE) step is performed using a HBr/He chemistry to remove any silicon residues prior metal layer etching.

Preliminary experiments have been performed on patterned wafers using aggressive chlorine and fluorine containing chemistries in order to etch the W and TiN layers. On one hand, straight profiles in the metal layers but with severe sidewall attack of the poly-Si layer are obtained in Cl₂/NF₃ based chemistries [Fig. 6(a)] whereas perfectly straight polysilicon sidewalls were obtained before metal etching (not shown here). It shows that Cl and F radicals produced by the discharge during metal etching generate a strong profile distortion at the foot of the polysilicon layer where the passivation layer is the thinnest [see Fig. 6(a)]. On the other hand, the use of a polymerizing chemistry to avoid any notch in poly-Si generates a sloped profile in the W layer [Fig. 6(b)].

In fluorine based chemistries, silicon etch by-products are more volatile than WF_x etch by-products as shown in Table I. By adding a fluorocarbon gas such as CH₂F₂ or CF₄ during W etching, a thin fluorocarbon based layer is formed on the silicon sidewalls, which preserve them from the chemical etching by fluorine radicals. However, the CF_x species formed in the gas phase are also deposited on tungsten surfaces during the etch process. This reduces the W lateral etch rate and thus results in sloped profiles [Fig. 6(b)]. Increasing the ion bombardment (pictures not shown here) can enhance the etching anisotropy and thus improve the metal layer profile. However, in this case, the etch selectivity to HfO₂ is badly impacted and a degradation in the thin HfO₂ layer is generated. Consequently a trade-off must be found between the metal profile, the poly-Si profile, and the selectivity over high-*k* gate oxide. The process window with fluorine chemistries being too narrow, we have to use a chemistry that forms anisotropic etching profiles in the metal layers without inducing any degradation in the polysilicon layer. In the first approach using chlorine chemistries, the tungsten layer has been etched in a Cl₂ based plasma [Fig. 6(c)]. After polysilicon and TiN etching (stopping the etch in the W layer) in chlorine chemistries, anisotropic etching profiles are obtained both in the polysilicon and TiN layers (pictures not shown here) demonstrating that chlorine based chemistries can generate anisotropic etching profiles in TiN while keeping intact the polysilicon etch profile. However, after W etching with the same chemistry, the W profile is straight but the TiN layer has been laterally eroded [Fig. 6(c)] since highly volatile TiCl_x by-products can be formed (see Table I).

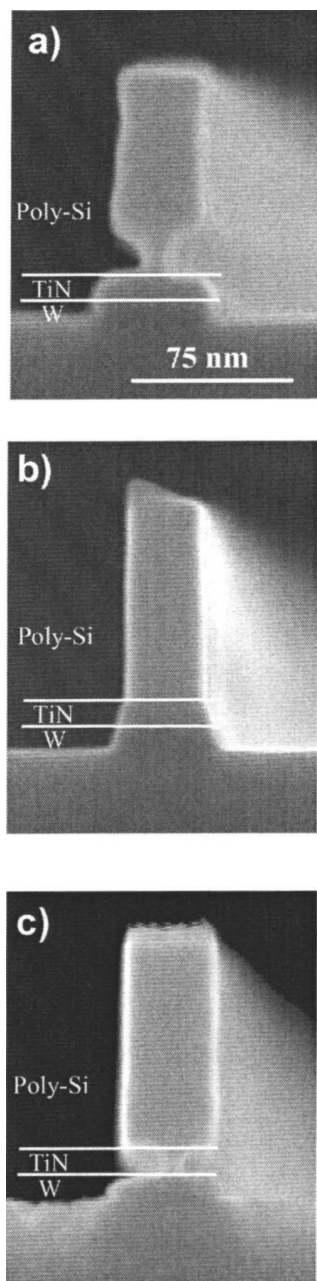


FIG. 6. Cross-sectional SEM observations of metal gate stacks when the TiN and W metal layers are etched in (a) Cl_2/NF_3 plasma, (b) $\text{SF}_6/\text{CH}_2\text{F}_2$, and (c) Cl_2 based plasma.

3. Improvement in metal gate profile control in Cl_2/O_2 based chemistry

Several papers in the literature^{4,5} demonstrate that high W etch rates can be obtained in Cl_2/O_2 based chemistries. Furthermore, this plasma chemistry can preserve the passivation layers formed on the polysilicon sidewalls during the $\text{SF}_6/\text{CH}_2\text{F}_2$ polysilicon etching step. It is therefore possible to determine the appropriate mixture of Cl_2/O_2 that will etch W anisotropically with a high selectivity with respect to the thin HfO_2 layer without inducing any damage on the poly-Si/TiN etch profiles. In this new approach, before etch-

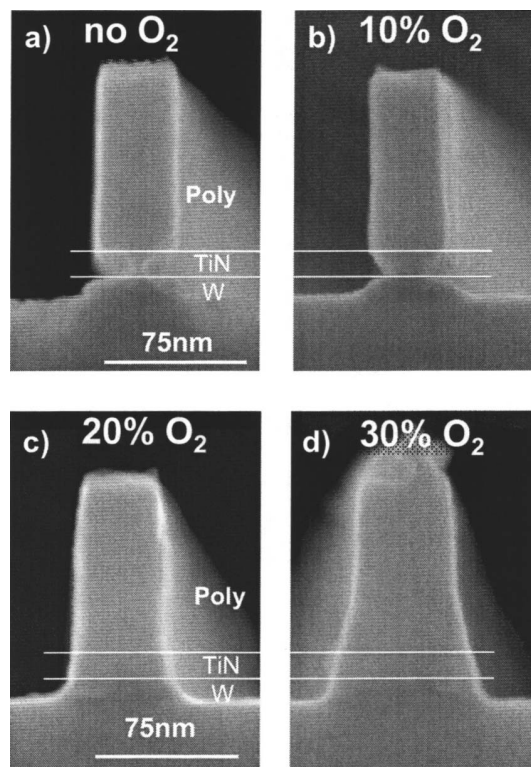


FIG. 7. Cross-sectional SEM pictures of four metal gate stacks obtained after etching the W layer in Cl_2/O_2 chemistry: (a) pure Cl_2 , (b) Cl_2/O_2 10%, (c) Cl_2/O_2 20%, and (d) Cl_2/O_2 30%.

ing the W layer, the TiN layer has been etched in a Cl_2/HBr based chemistry which generates straight profiles in the TiN layer without impacting the poly-Si profile.²⁵ The following experimental conditions are used for W etching: chamber pressure of 5 mTorr, chuck temperature of 50 °C, 450 W source power, 30 V bias voltage, and a total gas flow rate of 80 SCCM. In the first set of experiments, the ratio of O_2 in Cl_2/O_2 is varied. During W etching in pure Cl_2 plasma, Fig. 7(a) shows that TiN is laterally eroded. O_2 addition in Cl_2 decreases the lateral etch rate of TiN by inducing a sidewall oxidation of TiN and by reducing the etch time of the W etch step (i.e., by increasing the W etch rate). When we keep increasing the O_2 concentration in the feed stock gas, lateral etching of TiN is eliminated while a thick deposition is formed on the gate sidewalls [Figs. 7(b)–7(d)]. By adding a controlled amount of fluorine into the Cl_2/O_2 gas mixture the amount of deposition on the sidewalls can be controlled since fluorine helps in forming volatile etch products.

Figure 8 shows that fluorine addition to the gas phase is well adapted to drive the poly-Si/TiN/W gate etch profile. By varying NF_3 gas flow in the mixture, W etch profile varies from a slight slope [7 SCCM NF_3 , Fig. 8(b)] to a slight notch [11 SCCM NF_3 , Fig. 8(c)]. However, higher NF_3 flows may generate lateral etching in poly-Si and W [Fig. 8(d)]. In conclusion, using appropriate concentrations of Cl_2 , O_2 , and NF_3 in the gas mixture, anisotropic gate etch profiles can be obtained with a good selectivity to the HfO_2 under-layer.

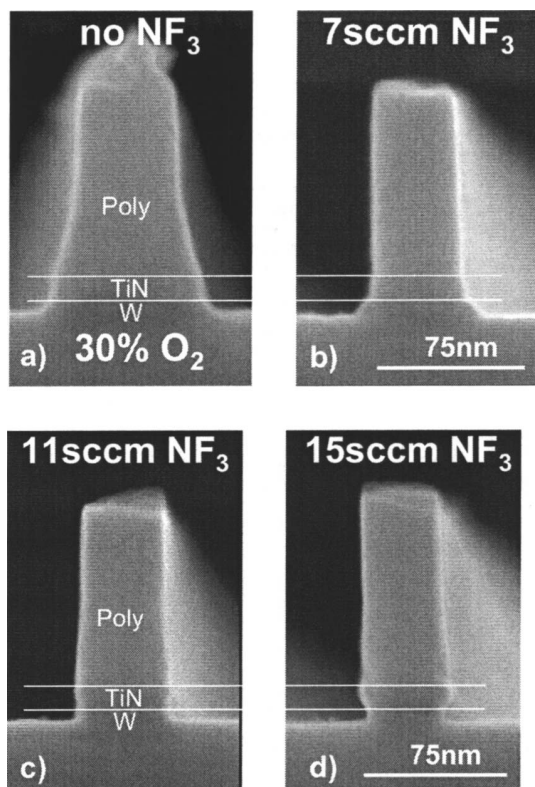


FIG. 8. Cross-sectional SEM pictures of four metal gate stacks obtained after etching the W layer in (a) Cl_2/O_2 30% chemistry and with (b) 7 SCCM NF_3 , (c) 11 SCCM NF_3 , and (d) 15 SCCM NF_3 .

B. Chemical characterization by *in situ* XPS of Cl_2/O_2 based W etch chemistry

1. Correlation between etch rates and reactive layer formation

Tungsten and HfO_2 etch rates are plotted in Fig. 9 as function of the O_2 content of the Cl_2/O_2 chemistry. In this study, the pressure, source power, self-bias voltage, chuck temperature, and total gas flow rate have been set at 5 mTorr, 450 W, 30 V, 50 °C, and 80 SCCM, respectively. Based on these experimental data on HfO_2 and W etch rates,

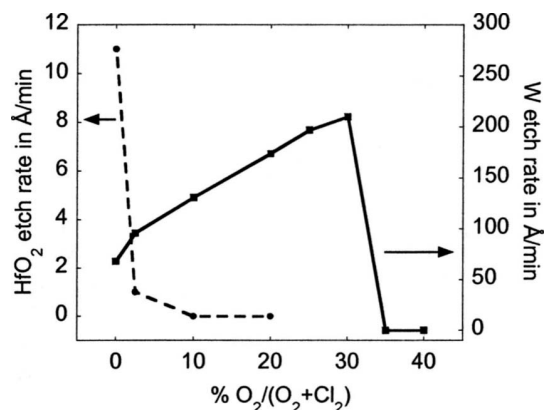


FIG. 9. HfO_2 and W etch rates as a function of the O_2 ratio in Cl_2/O_2 plasmas.

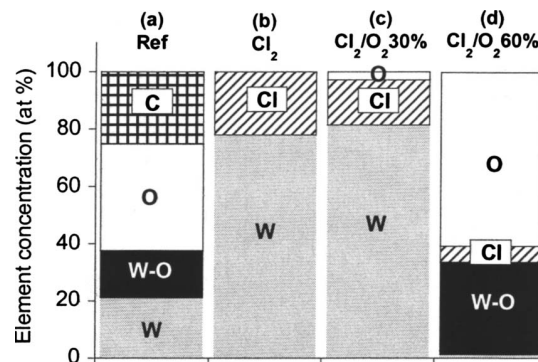


FIG. 10. Surface composition (determined by XPS) of the W layer (a) before exposure to the plasma, and after partial etching by (b) pure Cl_2 , (c) Cl_2/O_2 30%, and (d) Cl_2/O_2 60% plasmas.

Fig. 9 shows that O_2 addition to Cl_2 leads to a shutdown of the HfO_2 etch rate, demonstrating that the etch selectivity between W and HfO_2 can be infinite. A finite selectivity (6:1) between W and HfO_2 is observed in pure chlorine plasma. Figure 9 also shows that for O_2 concentration in the gas phase comprised between 0% and 30%, W etch rate increases with the O_2 concentration. Above 30% of O_2 in the gas phase, W is not etched in these conditions.

The increase in W etch rate by a factor of 3 when O_2 concentration in the gas phase increases from 0% to 30% is attributed to the increase in volatility of WOCl_x etch by-products (Table I). However, above 30% of O_2 concentration, the W surface is strongly oxidized, leading to an etch stop phenomenon.

To get a better understanding of the etching mechanisms, XPS analyses have been performed on a 40 nm thick W layer after a 25 s long Cl_2/O_2 plasma exposure. Figures 10(a)–10(d) represent the XPS quantifications of (a) the as-deposited W layer, (b) the W surface after exposure to pure Cl_2 plasma, (c) the W surface after Cl_2/O_2 30% plasma exposure, and (d) finally the W layer after Cl_2/O_2 60% plasma exposure. Figures 10(b) and 10(c) show that the thin reactive layers formed on the W surface are quite similar when the oxygen concentration in Cl_2/O_2 does not exceed 30% and is essentially a Cl-rich W layer. In the etch stop regime [Fig. 10(d)], the depth probed by XPS (~ 10 nm) shows W bonded to O (and O), demonstrating that the W surface is fully oxidized.

Figure 11 shows the W and HfO_2 etch rate evolution as a function of the Cl_2/O_2 ratio injected in the plasma when 15 SCCM of NF_3 are added to the gas mixture. The chamber pressure, bias voltage, source power, and temperature have been set at 5 mTorr, 30 V, 450 W, and 50 °C, respectively. In this case, the HfO_2 etch rate remains almost constant as a function of the O_2 ratio in the mixture and is very low compared to the W etch rate. The selectivity between W and HfO_2 remains greater than 30:1 due to the large increase in W etch rate with NF_3 present in the gas mixture. For optimized processing conditions (i.e., 56 SCCM of Cl_2 , 24 SCCM of O_2 , and 7 SCCM of NF_3), the selectivity between W and HfO_2 reaches more than 70:1.

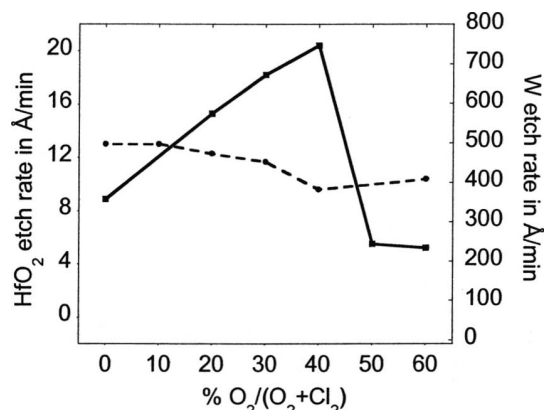


FIG. 11. HfO₂ and W etch rates as a function of the O₂ ratio in Cl₂/O₂/NF₃ plasmas (15 SCCM NF₃).

Figure 11 (15 SCCM NF₃ in the Cl₂/O₂ gas mixture) shows that the W etch rate presents the same behavior than previously observed in Fig. 9 (no NF₃ in the gas mixture) even though the W etch rate is much higher and the O₂ ratio for which W oxidation occurs is higher. With fluorine addition into the plasma, the W etch rate increases by a factor of 3 since very volatile WF₆ or WO_xF_y etch by-products can be formed (see Table I). Above 40% of O₂, a sharp decrease in the etch rate is observed. However, the etch stop regime (i.e., WO_x compound formation) is not reached, thus showing that fluorine addition in the plasma gas phase decreases the W oxidation rate, thanks to the formation of volatile WO_xF_y etch by-products. This is confirmed by XPS analyses which reveal the formation of a WO_xF_y layer at the W surface after partial etching in Cl₂/O₂ 60% plasma with additional fluorine (see Fig. 12). The peak at 36.4 eV is attributed to O_x-W-F_y bonds⁶ and is the main contribution at the W layer surface.

2. By-product deposition analysis during W etch in Cl₂/O₂ based chemistry

We have used the technique which consists in positioning a piece of Al₂O₃ floating on top of the wafer as described in

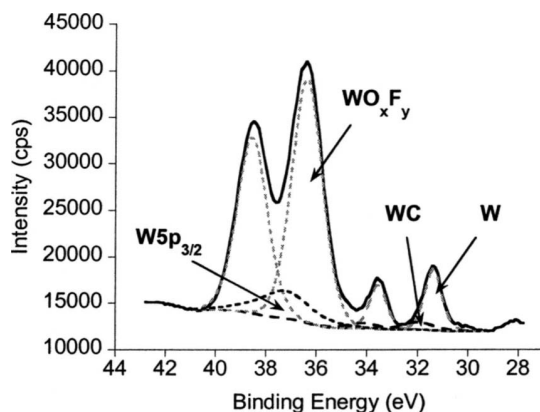


FIG. 12. W 4f XPS spectrum obtained after partial etching of W in Cl₂/O₂ 60% with fluorine addition.

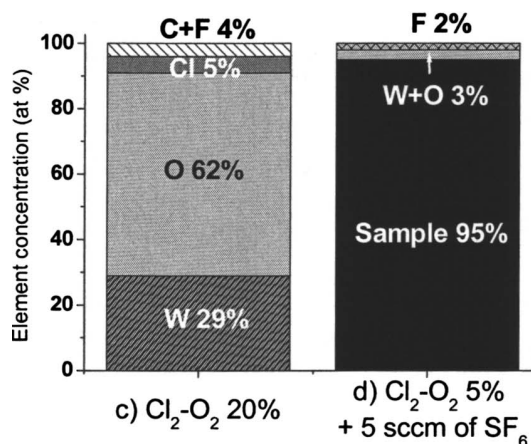
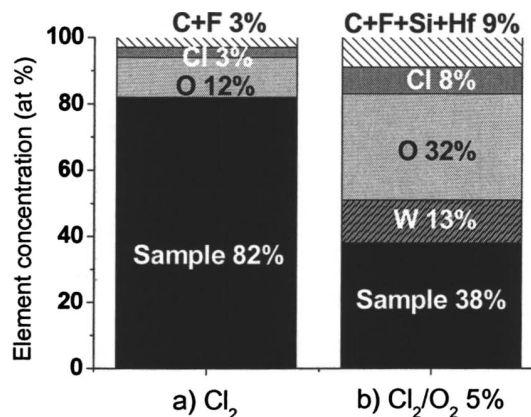


FIG. 13. Chemical composition of the volume probed by XPS (XPS analyses of Al₂O₃ floating samples) after W etching by (a) Cl₂, (b) Cl₂/O₂ 5%, (c) Cl₂/O₂ 20%, and (d) Cl₂/O₂ 5% + 5 SCCM of SF₆ plasmas.

Sec. II in order to monitor the coatings formed on the W surface during the etching process. To perform this experiment, pieces of W have been fixed on a 200 mm wafer covered with amorphous carbon in order to be as close as possible to the real situation in which poly-Si/TiN/W metal gates are patterned with amorphous carbon hard masks. Furthermore, a small piece of alumina sample has been fixed on the 200 mm diameter wafer. Thanks to Kapton rolls, a 4 mm air gap is generated between the wafer and the floating piece of Al₂O₃, limiting the ion bombardment energy to eVp (the energy acquired by the ions at the plasma potential in the plasma).

After etching the 10 nm W layer, the wafer is transferred into the XPS analysis chamber. Figures 13(a)–13(d) summarize the evolution of the layer deposited on Al₂O₃ sample after plasma etching in Cl₂, Cl₂/O₂ 5%, Cl₂/O₂ 20%, and Cl₂/O₂ 5% with 5 SCCM of SF₆, respectively.

Figures 13(a) and 13(b) illustrate a clear change in material composition coated on Al₂O₃ floating sample when going from pure Cl₂ plasmas to Cl₂/O₂ plasmas, demonstrating unambiguously that the etch by-product formation is drastically different when O₂ is added to the gas mixture. In the absence of O₂ in the gas mixture, no clear coating is formed

on the chamber walls since WCl_x etch by-products are very volatile. With O₂ addition (5% and 20%) in the gas mixture, O atoms play a major role as they generate an oxidation of WCl_x and WOCl_x etch products directly on the chamber walls. When the O flow increases, a larger percentage of WCl_x and WOCl_x species redeposited on the reactor walls is oxidized and the deposit thickness increases [Fig. 13(c)]. Since the etch by-products that are deposited and oxidized on the chamber walls and on the feature sidewalls are close in composition, we expect a strong correlation between the coatings formed on the Al₂O₃ sample and the etched profiles depicted in Figs. 7 and 8. The formation of a WOCl_x layer with Cl₂/O₂ (5 and 20%) plasmas is associated with strong profile deformations while fluorine addition to Cl₂/O₂ lead to the recycling by F atoms of the WOCl_x layer by creating volatile products such as WOF₄ and WF₆ [Fig. 13(d)]. These results show that well controlled poly-Si/TiN/W gate etch profiles can be obtained by adjusting the amount of O₂ and NF₃ added to Cl₂ in the plasma. O₂ addition will tend to generate a WOCl_x layer while NF₃ addition will tend to form more volatile WF₆ and WOF₄ products. The appropriate ratio will lead, as shown in Fig. 8, to anisotropic gate etch profiles.

IV. CONCLUSION

In this article, we have studied the etch mechanisms of tungsten embedded in poly-Si/TiN/W/HfO₂ metal gate structure. The introduction of W in the gate stack requires new dry etch approaches. Preliminary studies in fluorine based chemistries have shown the complexity to etch the metal layer while preserving the poly-Si etching profile anisotropy. We have determined that Cl₂/O₂ chemistries tend to generate the formation of more volatile etch products such as WOCl_x but the oxidation by O atoms of WCl_x leads to the creation of a tungsten oxychloride film on the gate sidewalls. NF₃ addition is the best solution to control the gate etch profiles since F radicals tend to form volatile products with W, limiting the oxidized WOCl_x layer growth. This study shows that the addition of one or two metal layers to the gate

stack increases the complexity of gate etch processes. More generally, this article shows that the compatibility between etch chemistries is the key parameter for advanced poly Si/metal gate etch processes.

- ¹K. Chen, M. Chan, P. K. Ko, C. Hu, and J. H. Huang, *Solid-State Electron.* **38**, 1975 (1995).
- ²Y. C. Yeo, *Thin Solid Films* **462–463**, 34 (2004).
- ³R. C. Betanzo, S. A. Moshkalyov, A. C. Ramos, J. A. Diniz, and J. W. Swart, *J. Electrochem. Soc.* **149**, G179 (2002).
- ⁴H. W. Kim, *J. Korean Phys. Soc.* **43**, 526 (2003).
- ⁵S. D. Park, Y. J. Lee, N. G. Cho, S. G. Kim, H. H. Choe, M. P. Hong, and G. Y. Yeom, *Thin Solid Films* **447–448**, 586 (2004).
- ⁶M. C. Peignon, Ch. Cardinaud, and G. Turban, *J. Appl. Phys.* **70**, 3314 (1991).
- ⁷X. Li, H. Zhou, C. D. W. Wilkinson, and I. G. Thayne, *J. Vac. Sci. Technol. B* **45**, 8364 (2006).
- ⁸G. Larrieu and E. Dubois, *J. Vac. Sci. Technol. B* **23**, 2046 (2005).
- ⁹S. K. Kwon, K. N. Kim, C. W. Nam, and S. I. Woo, *J. Vac. Sci. Technol. B* **13**, 914 (1995).
- ¹⁰X. Li, X. Cao, H. Zhou, C. D. W. Wilkinson, S. Thoms, D. Macintyre, M. Holland, and I. G. Thayne, *Microelectron. Eng.* **83**, 1152 (2006).
- ¹¹N. Mutsukura and G. Turban, *J. Electrochem. Soc.* **137**, 225 (1990).
- ¹²T. R. Fullowan, S. J. Pearton, F. Ren, G. E. Mahoney, and R. L. Kostelak, *Semicond. Sci. Technol.* **7**, 1489 (1992).
- ¹³R. Patrick, S. Baldwin, and N. Williams, *Solid State Technol.* **43** (2000).
- ¹⁴J. W. Coburn and M. Chen, *J. Appl. Phys.* **51**, 3134 (1980).
- ¹⁵M. Kogelschatz, G. Cunge, and N. Sadeghi, *Eur. Phys. J.: Appl. Phys.* **33**, 205 (2006).
- ¹⁶J. S. Jenq, J. Ding, J. W. Taylor, and N. Hershkowitz, *Plasma Sources Sci. Technol.* **3**, 154 (1994).
- ¹⁷V. M. Donnelly, D. L. Flamm, W. C. Dautremont-Smith, and D. J. Werder, *J. Appl. Phys.* **55**, 242 (1984).
- ¹⁸M. C. Peignon, C. Cardinaud, and G. Turban, *J. Appl. Phys.* **70**, 3314 (1991).
- ¹⁹J. S. Jenq, J. Ding, J. W. Taylor, and N. Hershkowitz, *Plasma Sources Sci. Technol.* **3**, 154 (1994).
- ²⁰F. H. Bell, O. Joubert, and L. Vallier, *J. Vac. Sci. Technol. B* **14**, 1796 (1996).
- ²¹S. Ma, M. Jain, and J. D. Chinn, *J. Vac. Sci. Technol. A* **16**, 1440 (1998).
- ²²J. F. Moulder, W. F. Stickle, and P. E. Sobol, *Handbook of X-ray Photoelectron Spectroscopy*, edited by J. Chastain (Perkin-Elmer, Eden Prairie, 1992).
- ²³O. Joubert, G. Cunge, B. Pelissier, L. Vallier, M. Kogelschatz, and E. Pargon, *J. Vac. Sci. Technol. A* **22**, 553 (2004).
- ²⁴G. S. Oehrlein and H. L. Williams, *J. Appl. Phys.* **62**, 662 (1987).
- ²⁵A. Le Gouil, O. Joubert, G. Cunge, T. Chevolleau, L. Vallier, B. Chenevier, and I. Matko, *J. Vac. Sci. Technol. B* **25**, 767 (2007).