Surface processes in SF_6/O_2 reactive ion etching of CVD tungsten.

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Abstract

The reactive ion etching of CVD (Chemical Vapor Deposition) tungsten in SF_6/O_2 rf plasma has been studied by means of optical emission spectroscopy, mass spectrometry and in-situ X-ray photoelectron spectroscopy (XPS). Two etch products are detected : WF_6 and WOF_4. A correlation is found between their concentration in the gas phase and the amount of atomic fluorine and oxygen, as measured by actinometry. After etching, the tungsten surface contains three chemical elements : sulfur, oxygen and fluorine. Their role during the etching process of tungsten is discussed.

INTRODUCTION

It recently appeared that the role of the plasma active species, particularly atomic fluorine and oxygen, could be different for tungsten and silicon etching [1] [2]. With silicon, the main etch product is found to be SiF_4. In the case of tungsten, etching with CF_4/O_2 and SF_6/O_2 results in two direct gas products : WF_6 and WOF_4 which prevails in F-rich plasmas and in O-rich halogenated plasmas respectively. The optimum etch rate for tungsten is achieved with plasmas containing more oxygen than in the case of silicon. These results lead to the conclusion that atomic oxygen has an active role during etching of tungsten [1].

The aim of the present study is to improve the knowledge of the plasma-surface interaction in the case of an SF_6/O_2 gas mixture and a tungsten surface. In particular, we have to address the effect of sulfur.

EXPERIMENTAL

The apparatus used in this work has been described previously [3]. The plasma is excited with a 13.56 MHz rf generator. The applied power is 50 W. The total pressure is maintained at 13.3 Pa (100 mtorr) with a gas flow rate of 30 sccm.

The reactor is equipped with three diagnostic systems : a quadrupolar mass spectrometer (QMG 511 Balzers), an optical emission spectrometer (Jobin-Yvon monochromator HR 640 and E.G.G. O.M.A. III), an in-situ X-ray photoelectron spectroscopy using a MgKα source.

The CVD tungsten samples are etched for 2 minutes in SF_6/O_2 plasmas and then are transferred under vacuum into the surface analysis system.

RESULTS.

A - Optical emission spectroscopy.

The argon optical signal (750.4 nm) is used to normalize the fluorine (703.7 nm) and the oxygen (844.6 nm) optical emission signals [4] [5]. In Fig. 1, the ratios I(703.7)/I(750.4) (a) and I(844.6)/I(750.4) (b) are shown versus the amount of oxygen fed to the discharge.

The effect of a consumable cathode (e.g. silicon) is to decrease the concentration of atomic fluorine. This so-called loading effect is less effective in an oxygen-rich plasma. When compared to the presence of an aluminum cathode, the use of a silicon wafer also causes the atomic oxygen concentration to decrease, but to a less extent than for fluorine. Another effect of the silicon wafer is to enhance considerably the emission intensity of the two band spectra in the 250-320 nm range : one due to S_2 molecules ($B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ transitions) and the other, to SO molecules ($A^3\Pi \rightarrow X^3\Sigma^-$) as recently reported [6].

B - Mass spectrometry of neutral species.

The neutral etched products, WF_6 and WOF_4, are detected by means of in-line mass spectrometry, as in our previous studies [1]. These molecules are detected by measuring the signal intensity of peaks m/e = 281 a.m.u. (WF_5^+) and m/e = 255 a.m.u. (WOF_3^+) respectively. Several other molecules are detected in the SF_6/O_2 discharge : SOF_2, SOF_4, SO_2F_2, SO_2, SF_4 SF_2, S_2F_2, S_2F and S_2 as previously reported [7]. Small signals are detected at m/e = 271 - 275 a.m.u. and assigned to WSF_3^+ or $WO_2F_3^+$ ions formed from the corresponding neutral compounds.

In Fig. 2 the evolution of the WF_5^+ and WOF_3^+ intensities in the SF_6/O_2 plasma is shown. The SiF_4 molecule, formed by etching of the silicon wafer is not represented on Fig. 2. The results in Fig. 2 show the existence of two regimes of SF_6/O_2 plasmas. In *SF_6-rich plasmas* (gas mixture containing less than 40% O_2), the main etch product is WF_6. Its concentration is correlated with the amount of fluorine in the gas phase depending on the cathode material. When using an aluminum cathode, an important amount of WOF_4 is observed in a SF_6-rich plasma whereas it is not the case for a silicon cathode. This result is probably related to the wet aluminum oxide which is always present on an aluminum surface. WOF_4 could result from the hydrolysis of the abundant WF_6. Another source of WOF_4 may also be the reaction of WF_n radicals with Al_2O_3. In *O_2-rich plasmas* (gas mixture containing more than 40% O_2), WOF_4 appears in large concentration with the silicon cathode. It is considered as a direct etch product of tungsten resulting from the simultaneous action of fluorine and oxygen atoms. Even with a SF_6/O_2 (20/80) mixture the formation of WF_6 is not negligible, this fact suggesting a competition mechanism for the formation of the two etch products. With an aluminum cathode, the oxygen rich plasma contains a large concentration of atomic fluorine (see Fig. 1), and we observe a larger concentration of WF_6 than with a silicon cathode. The excess of F in the gas phase enhances the formation of WF_6 to the detriment of WOF_4.

C - In-situ XPS analysis of the etched tungsten surfaces.

The surface layer on the etched tungsten samples has been analyzed by in-situ XPS. The thickness increases monotonically from 0.7 - 0.8 nm for pure SF_6 plasma up to 1.8 - 2.2 nm for an SF_6/O_2 (20/80) plasma. The surface contains three elements : sulfur, oxygen and fluorine.

C-1- W 4f Spectra.

Fig. 3 shows tungsten W 4f photoemission spectra obtained for samples that have been etched for 2 minutes. For comparison the W 4f distribution corresponding to an unetched sample is also shown. The contributions located at 31.5 eV (W $4f_{7/2}$) and 33.7 eV (W $4f_{5/2}$) are due to bulk tungsten (W− W bonds), whereas the native oxide on the surface is responsible for the doublet located at 36.0 eV (W $4f_{7/2}$) and 38.0 eV (W $4f_{5/2}$) which is assigned to WO_3 species. For W samples etched in a pure SF_6 plasma, no $W-F_n$ bonds are observed. Tungsten W 4f spectra obtained for surfaces after etching in a SF_6/O_2 (20/80) plasma show evidence of a weak doublet at 36.7 eV (W $4f_{7/2}$) and 38.7 eV (W $4f_{5/2}$). For each cathode, its intensity follows the same evolution than the WOF_4 concentration as measured by mass spectrometry. Therefore we assign this 36.7 eV doublet to O_x-W-F_y species which would be the precursors of the WOF_4 etch product. As WOF_4 is known to have a low volatility at room temperature (bp = 187.5 °C), WOF_4 species in a condensed phase (mp = 110 °C) could be themselves at the origin of the W 4f doublet at 36.7 eV and 38.7 eV.

C-2- O 1s Spectra.

Fig. 4 shows an oxygen O 1s distribution obtained after etching in a SF_6/O_2 (40/60) plasma. The O 1s spectra can be decomposed into two peaks. A first component situated at a binding energy of 531 eV is assigned to O−W bonds. This component shows a behaviour similar to the W 4f doublet located at 36.7 eV and 38.7 eV and attributed to WO_xF_y (C-1). In this view, the peak located at 531 eV is due to O−W bonds in WO_xF_y species. The peak located at 533 eV increases as a function of the oxygen content in the SF_6/O_2 mixture. A small shift of -0.2 to -0.4 eV is observed for the latter when etching in a SF_6/O_2 (20/80) plasma. We assign this component to O−S bonds in O_x-S-F_y species.

C-3- F 1s Spectra.

Fig. 5 shows a typical fluorine F 1s distribution. The F 1s spectra were fitted with three components giving binding energies of 684.5 eV, 686.4 eV and 687.7 eV. The peak located at 686.4 eV increases proportionaly with O_2 in the gas mixture. We assign this component to F− S bonds in O_x-S-F_y species. Following the literature data which report F 1s (F−W) at various binding energies according to the mode of adsorption of the WF_n species on the surface, we assign the 684.5 eV component to F−W bonds characteristic of chemisorbed WF_n (or WO_xF_y) species, whereas the 687.7 eV contribution corresponds to physisorbed tungsten fluorides such as WF_6 and WOF_4 condensed on the surface. The contribution located at 684.5 eV has a higher intensity for W samples etched on an aluminum cathode than for those treated with a silicon cathode. This result correlates the fluorine concentration in the plasma as measured with optical spectroscopy. The oxygen addition to the plasma gives a slight chemical shift of +0.5 eV. This value (685 eV) corresponds to F−W bonds in an oxidized environment.

C-4- S 2p Spectra.

Typical sulfur S 2p spectra corresponding to pure SF_6 and SF_6/O_2 (40/60) etching conditions are shown in Fig. 6. Two components can be observed. The first is located at a binding energy of 162 eV and is assigned to S−W bonds in WS_2 type compounds. The WS_2, as obtained from the 162 eV peak, decreases as the proportion of O_2 increases. Its intensity is greater with a silicon cathode, this result is correlated to the presence of S_2 in the plasma [6]. The sulfide WS_2 which is formed on the surface is a solid compound at room temperature and will play an inhibitor role in the etching process. The present

XPS study clearly shows that the sulfur generated in a SF_6 discharge is not inactive during the plasma/surface interaction.

The component located at binding energy of 170 eV follows a similar evolution with the two cathodes. A chemical shift of -0.8 eV is observed on the S 2p spectrum for samples etched in an oxygen-rich plasma (80% O_2). As this peak follows the same trend as the O 1s (533 eV) component and the F 1s (686.4 eV) component, we attribute this contribution to S− O and S− F bonds in O_x-S-F_y groups. Two origins can explain the formation of SO_xF_y groups in the surface layer on the etched tungsten : one is the direct reaction on tungsten of F, O and S atoms coming from the SF_6/O_2 plasma, and the other is the adsorption of SO_xF_y radicals formed in the gas phase.

SUMMARY AND CONCLUSION.

Reactive ion etching of tungsten in SF_6/O_2 plasmas has been studied by means of optical spectrometry, mass spectrometry of the gas phase and in-situ XPS of the etched surfaces.

The cathode material strongly influences the generation of the etched products of tungsten : WF_6 and WOF_4. With an aluminum cathode, WF_6 concentration remains superior to that of WOF_4 for the entire range of O_2 in SF_6/O_2 ; whereas the consumption of fluorine by the silicon cathode promotes the formation of WOF_4 in O_2-rich plasmas. This result proves the competitive role of oxygen and fluorine during etching.

The study of the surface chemistry of the etched tungsten shows that the reactive layer contains three elements besides tungsten : sulfur, oxygen, fluorine. WS_2, WF_n, WO_xF_y, and SO_xF_y species have been identified on the surface by using in-situ XPS. In a pure SF_6 plasma, sulfur plays a passivation role. Atomic oxygen contributes to the elimination of sulfur and tungsten by the formation of oxyfluoride compounds : SO_xF_y, WOF_4. Fluorine is adsorbed on tungsten in three ways giving birth to : chemisorbed F−W species at a F 1s binding energy of 684.5 eV, physisorbed F−W species at a F 1s binding energy of 687.7 eV and physisorbed O_xSF_y at a F 1s binding energy of 686.4 eV. These groups are the precursors of the etch products.

Acknowledgments.

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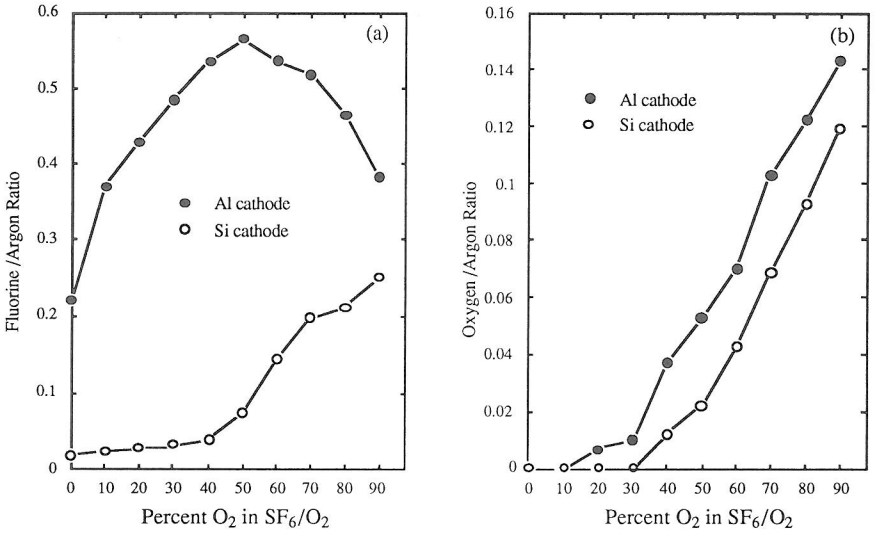

Fig. 1. Relative optical emission intensities of F (a) and O (b) versus oxygen percentage in SF_6/O_2 RIE.

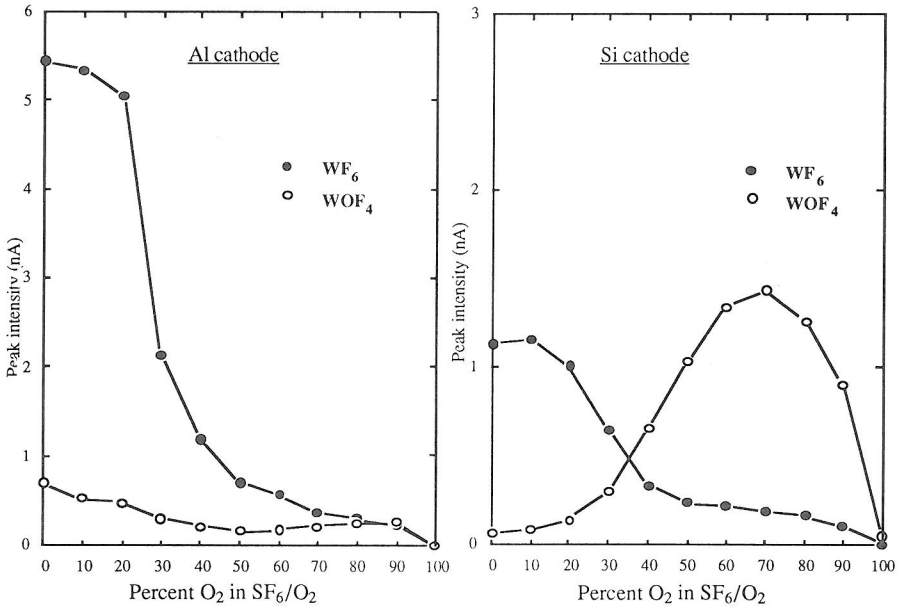

Fig. 2. Intensities of WF_5^+ (WF_6) and WOF_3^+ (WOF_4) detected in SF_6/O_2 rf plasmas with a 29 cm^2 tungsten sample.

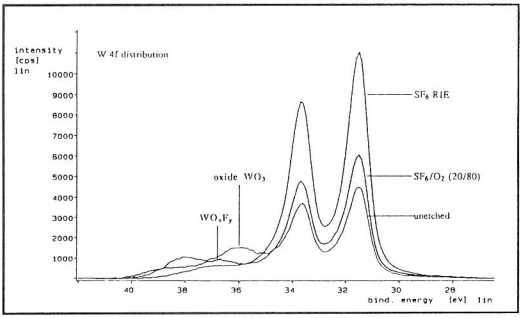

Fig. 3. Tungsten W 4f photoemission spectra with samples etched for 2 min with a silicon cathode.

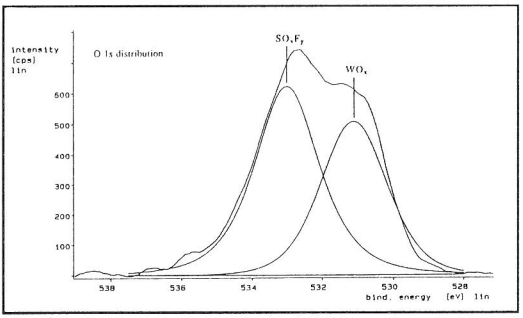

Fig. 4. Oxygen O 1s spectrum for tungsten films after SF_6/O_2 (40/60) RIE with a silicon cathode.

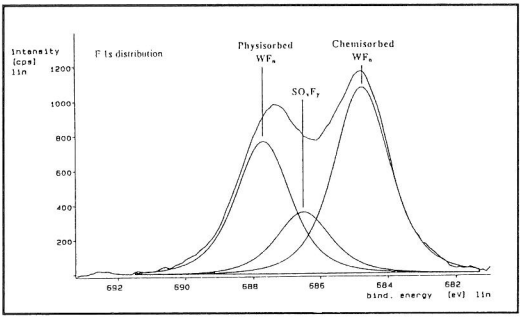

Fig. 5. Fluorine F 1s spectrum of etched tungsten in SF_6/O_2 (80/40) plasma with an aluminum cathode.

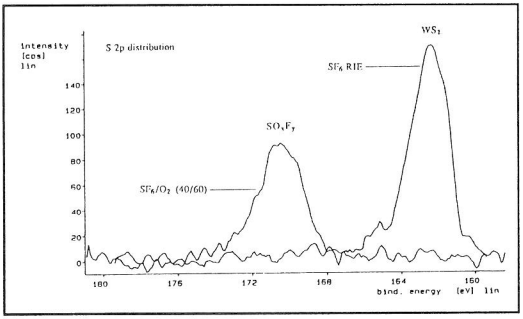

Fig. 6. Sulfur S 2p spectra for tungsten films after pure SF_6 and SF_6/O_2 (40/60) RIE with a silicon cathode.