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PLASMA ETCHING OF REFRACTORY METALS (W, Mo, Ta) IN SF_6 AND $SF_6 - O_2$

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ABSTRACT

The etching rates and reaction products of refractory metals (W, Mo and Ta) and silicon have been studied in a $SF_6 - O_2$ r.f. plasma at 0.2 torr. The relative concentrations of WF_6 and WOF_4 and the intensities of the WF_n^+ (n = 3-5), WOF_m^+ (m = 1-3), MoF_n^+ and MoF_m^+ ions have been measured by mass spectrometry. A comparison with the results obtained for silicon show that at least two species are involved for W and Mo etching : fluorine and oxygen species.

1. INTRODUCTION

The refractory metals (Mo, W, Ta) and metal silicides ($MoSi_2$, WSi_2, $TaSi_2$) are increasingly used in integrated circuit technology due to the emergence of VLSI (very large scale integration). Because of their low resistivity and their thermal properties they are a promising alternative to polycristalline silicon for application as self-aligned gate electrodes and interconnections in M.O.S. (metal oxide semiconductor) technology.

Many papers dealing with the dry etching of these materials in fluorinated or chlorinated plasmas have recently been published (1) (2). In order to obtain a good control of the etching processes and to select the appropriate gas mixture, a better understanding of the mechanisms involved in the plasma-material interaction is needed.

The basic reactions involved in the plasma etching of refractory metals have not been studied as so extensively as those of silicon etching. The comparison of the vapour pressures of SiF_4 and refractory metal fluorides (WF_6, MoF_6, TaF_5) clearly shows that these later are far less volatile and thus uneasily detected. Until now, no direct detection of these gas halides during plasma etching has been published. The only evidence of MoF_6 in a fluorocarbon plasma was furnished by J. Coburn (3) who made use of a molybdenum cathode.

This communication aims to expose the results obtained from a mass spectrometric analysis of the reaction products of SF_6 and $SF_6 - O_2$ plasmas interacting with the refractory metals W, Mo and Ta. In order to emphasize the different mechanisms, a comparison is made with silicon. The tight correlation existing between the gas products and the etching rates permits the proposal of a reaction scheme.

2. EXPERIMENTAL APPARATUS

The apparatus has been previously described (4). The reactor consists of two electrodes in aluminum with an area of 71 cm^2 put in alumina tube of 7.5 cm in diameter. The samples to be etched are placed on the lower electrode which may be either the cathode or the grounded electrode (anode).

The reactor parameters are the following : p = 200 mtorr, P = 50 W (0.7 W/cm^2), Q = 40 sccm, f = 13.56 MHz. The gases used are SF_6 (99.85 % purity) and O_2 (99.995 % purity). The results given here deal with the reactive ion etching mode.

The silicon samples consisted in 0.58 mm thich monocrystalline wafers (n type, (100), 3-5 Ω.cm). The tungsten and molybdenum samples are 0.15 mm thick foils (Goodfellow Metals ; W purity : 99.95 % ; Mo purity : 99.9 %). The etching rates are determined by weighing the samples before and after given etching periods.

The mass spectrometer is that previously described (4). The concentration of neutral molecules in the plasma is obtained by using a calibration method previously described for the study of C_2F_6 and CHF_3 plasmas (5). This calibration takes into account the mass interferences between ions coming from different parent molecules and the mass dependence of the mass spectrometry apparatus.

3. EXPERIMENTAL RESULTS

3.1. Etching rates

Figure 1 gives the evolution of the etching rates of W, Mo and Ta in an R.I.E. mode as a function of the $SF_6 - O_2$ mixture composition. The maximum etching rate of both W and Mo is obtained for a (30 : 70) $SF_6 - O_2$ mixture whereas the tantalum etching rate, as to that of silicon, is optimum for 10 – 30 % O_2 in SF_6.

3.2. Products of the etching of tungsten

As shown in Figure 2 two neutral molecules WF_6 and WOF_4 have been detected during etching of W in an $SF_6 - O_2$ plasma. The concentration of these products is given in arbitrary units because their electron impact ionization cross-sections are unknown. It is to be noted that WF_6 concentration is maximum for a SF_6 predominant gas mixture, whereas WOF_4 is maximum for a O_2 predominant mixture.

The positive ions issued from the plasma, WF_n^+ (n = 2 - 5) and WOF_m^+ (m = 1 - 3) have also been detected. These species are supplied by the dissociative ionization of neutral molecules WF_6 and WOF_4. There exists a good correlation between the ion intensities and the etching rate of tungsten.

The WF_5 ion has been used as a detection of the end-point in etching of W Si_2 film in a W Si_2 – Si polycide, in a $SF_6 - O_2$ plasma.

3.3. Products of the etching of molybdenum and tantalum

The neutral molecules resulting from the etching of molybdenum in the $SF_6 - O_2$ plasma have not been directly detected. Two reasons can be put forward :

(i) The MoF_6 and MoF_5 vapor pressures are lower than that of WF_6 (2).

(ii) MoF_6, like $MoCl_5$, tends to be hydrolyzed in presence of small quantities of water vapor. Similarly, Kurogi and Kamimura (6) reported having fail to detect $MoCl_5$ and $MoOCl_4$ by mass spectrometry during etching of Mo in a $CCl_4 - O_2$ plasma.

Positive ions issued from the $SF_6 - O_2$ plasma and containing molybdenum atoms, MoF_n^+ (n = 3 - 5) and $MoOF_m^+$ (m = 1 - 3), have been detected.

During the plasma etching of tantalum, traces of TaF_4^+ and TaF_3^+ have been detected but no indication of $TaOF_n^+$ have been found.

3.4. Variations in the neutral composition of the plasma during etching

Many secondary reactions between atoms, radicals and molecules take place in the $SF_6 - O_2$ plasma. This results in the formation of secondary neutral products such as SF_4, SO_2, SOF_2, SOF_4, SO_2F_2 and F_2 (4,7,8). The molar fractions M of these molecules have been measured in four different experimental conditions : without sample, with Si, W and Mo samples.

The etch process of these samples consumes preferentially atomic reactive species such as F or O. Therefore some variations in the production rates of secondary molecules would be induced by these etching reactions. Such variations in molar fraction have effectively been determined by mass spectrometry.

Figure 3 shows the evolution of the quantity ΔM for etching of W. Similar results have been obtained with Mo. A comparison with the results obtained for Si suggests different mechanisms : contrary to Si, during Mo or W etching the molar fractions of SO_2F_2 and F_2 decrease whereas that of SO_2 increases.

4. DISCUSSION

The results of etching rate for W and the detection of the neutral products WF_6 and WOF_4 allow several hypothesis to be put forward. WOF_4 may arise from gas phase oxidation of WF_n compounds ($n \leq 5$) but in this case, it is doubtful that such an oxidation would appreciably influence the etching rate and account for the observed optimum for the dominant oxygen gas mixture. It seems consistent with the reported results to consider that atomic oxygen, or oxygen ions, react with the tungsten surface and contribute to its etching. WOF_4 is thus for a part a direct etching product.

Use of thermodynamical data of Hildenbrand (9) gives the following sequence :

(i) formation of W fluorides

$$W + F \longrightarrow WF \qquad \Delta H_f = -5.64 \text{ eV}$$
$$WF + F \longrightarrow WF_2 \qquad \Delta H_f = -5.70 \text{ eV}$$
$$WF_2 + F \longrightarrow WF_3 \qquad \Delta H_f = -5.17 \text{ eV}$$
$$WF_3 + F \longrightarrow WF_4 \qquad \Delta H_f = -5.18 \text{ eV}$$

(ii) fluorination or oxidation of WF_4, stimulated by ion bombardment

$$WF_4 + F \longrightarrow WF_5 \qquad \Delta H_f = -4.58 \text{ eV}$$
$$WF_5 + F \longrightarrow WF_6 \qquad \Delta H_f = -5.45 \text{ eV}$$
$$WF_4 + O \longrightarrow WOF_4 \qquad \Delta H_f = -6.65 \text{ eV}$$

(iii) gas phase or surface reactions with secondary products

$$WF_2 + SO_2F_2 \longrightarrow WOF_4 + SO \qquad \Delta H_f = -1.63 \text{ eV}$$

followed by

$$SO + O \longrightarrow SO_2$$
$$WF_4 + SO_2F_2 \longrightarrow WOF_4 + SOF_2 \qquad \Delta H_f = -0.91 \text{ eV}.$$

These reactions are consistent with the experimental results obtained by mass spectrometry. The optimal etching rate is obtain in oxygen rich gas mixtures and bring evidence of the direct involvement of oxygen species (O, O^+, O_2^+) in the etching reaction.

The results obtained for etching of Mo and W are very similar, as well as for etching rates as for products detected by mass spectrometry. So, a reaction scheme analogous to that of W can be proposed for Mo etching.

5. CONCLUSION

The $SF_6 - O_2$ plasma has been analyzed by mass spectrometry during etching of refractory metals W, Mo and Ta. A comparison has been made with silicon. From this study the following conclusions may be drawn.

(i) These materials may be divided into two groups :

- Si and Ta which present a maximum etching rate in a dominant SF_6 gas mixture, corresponding to an optimum of atomic fluorine concentration in the plasma.
- W and Mo which present a maximum etching rate for dominant O_2 gas mixture, but zero etching rate in pure O_2 plasma.

(ii) The ion bombardment of the samples modifies not only the etching rates but also the optimal value of the $SF_6 - O_2$ mixture.

(iii) The neutral etching products of tungsten have been directly detected for the first time : that is WF_6 and WOF_4. The positive ions MoF_n^+ ($n = 3 - 5$) and $MoOF_m^+$ ($m = 1 - 3$) have been observed during the etching of Mo. A good correlation between the relative concentrations of these reaction products and the etching rates was obtained. A quantitative comparison, in the case of SiF_4, shows that a variable fraction of the etching products is redecomposed in the plasma.

(iv) Reaction schemes involving two kinds of atomic species (F and O) have been proposed and are consistent with the experimental results.

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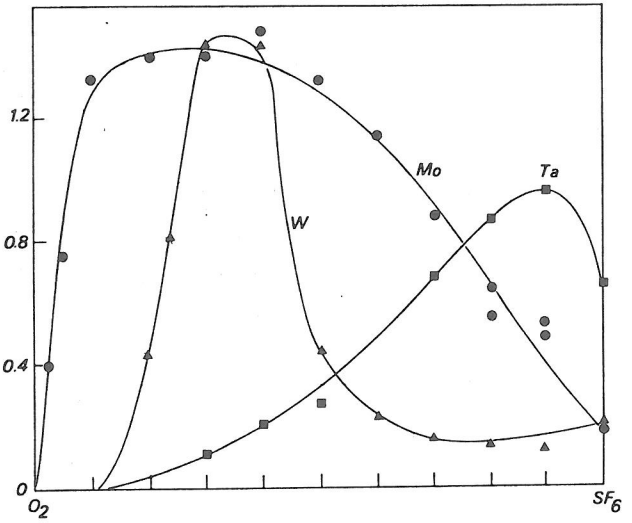

Fig. 1. Etching rates of W, Mo and Ta, for RIE mode, in a $SF_6 - O_2$ plasma (A = 12 cm^2, p = 0.2 torr, P = 50 W, Q = 40 sccm).

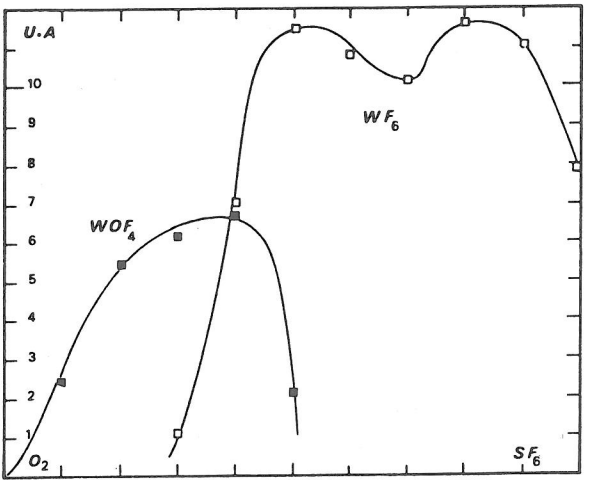

Fig. 2. Evolution of WF_6 and WOF_4 concentrations during the etching of W as a function of the starting gas composition.

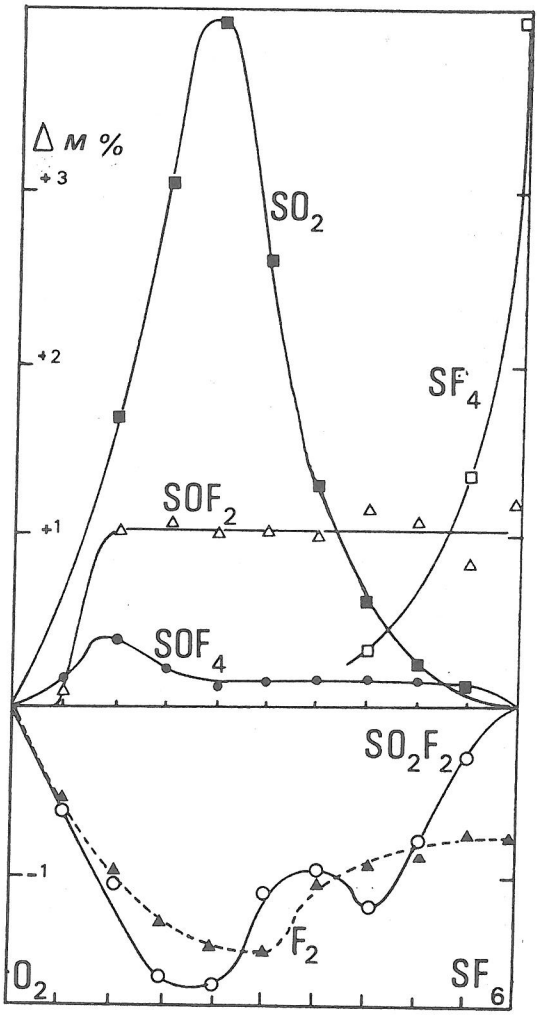

Fig. 3. Variations ΔM of the molar fractions of neutral secondary products synthetized in the $SF_6 - O_2$ plasma during the etching of tungsten.