Towards the understanding of CH_3F/O_2 chemistry

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A high selective nitride spacer etching chemistry has been studied in order to have some insights on the etching mechanism. The CH_3F/O_2 chemistry builds up a thicker polymer layer on SiO_2 than on Si3N4 surface. According to some Energy Filter TEM analysis using the N, C, O, Si, F elements mapping on a crossected sample, this polymer layer is rich on oxygen.

Introduction

Silicon nitride (Si_3N_4) films are widely used as poly gate spacers in today's devices. Usually the spacer formation requires a thin oxide layer as etch-stop of the nitride spacer etch, in order to prevent active area etch. An spacer etch usually consist of two steps: the main step in which most of the nitride is removed anisotropically and the etch is end-pointed with moderate selectivity to oxide; the overetch (OE), which is the more interesting step, should have high selectivity to oxide and can be slightly isotropic for short OE times. One of the standard processes to etch Si_3N_4 selective to silicon oxide (SiO_2) and silicon, which has produced good results, is based on CH_3F/O_2 chemistry. According to literature, silicon etch rate decreases with increasing etch time due to polymer buildup. The nitride to oxide selectivity increases very quickly as the O_2/CH_3F ratio increases [1] nevertheless, the mechanism involved is not known with certainty. On this line, the aim of this paper is to provide some valuable experimental results that can help to clarify the mechanism involved on the OE step.

Experimental

All dry etch processes were carried out in a Lam research Versys 2300 etch chamber on 200 mm wafers. This particular etch reactor uses a transformer coupled plasma (TCP™) that allows plasma power and substrate bias (or bottom electrode power) to be controlled separately. The experiments over blanket wafers were carried out under controled source power, pressure and bias at 60ºC and the gas flows ratio O_2:CH_xF_y was 1:1.4. The experiments over device wafers were crossected and inspected by Transmission Electron Microscopy (TEM). Beside TEM, Energy Filter TEM (EFTEM) analysis was used to explore the chemical composition.

Results and discussion

The cross sectional TEM images after spacer etching without oxide liner revealed a ~2nm polymer layer on top and side of the nitride, and on the pad area (silicon surface oxide rich) the polymer layer of 5nm is formed blocking the etching (Figs. not showed). This suggests that the polymer deposition is higher on the oxide than on the nitride surface in agreement with literature [1]. According to our TEM micrographs, the CH_3F/O_2 chemistry builds up a polymer easily on SiO_2 than on nitride (Fig.1a). With the aim to have some insights about this polymer layer, we performed supplementary Energy Filter TEM analysis using the N, C, O, Si, F elements mapping on the crossected sample on spacers over oxide liner. The more interesting finding is that the polymer layer is rich on oxygen (Fig.1b). This valuable information can help to understand the mechanism involved in the Si_3N_4 etching selective to SiO_2 with CH_3F/O_2 chemistry.

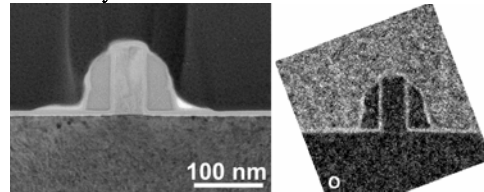


Fig.1. a) The TEM inspections of nitride spacer on SiO_2 surface revealed a polymer layer on top and side of the spacer as well on the pad area. b) EFTEM oxygen element mapping clearly revealed a rich oxygen polymer layer.

Some extra experiments were carried out on blanket wafers with three different gases which have C, H and F atoms.

Nitride blanket wafers: The etch rate (ER) between the two first gases is quite similar and increases significantly with the CHF_3 gas (Table 1). This is quite logical since, it is commonly accepted that F• radicals are active etchant of nitride, participate on Si etching and hardly etch SiO_2 [2]. In Fig.2, the Optical

Emission Spectroscopy (OES) measurements clarify the F• effect on the ER. The F• radicals are highly produced on CHF_3 which is logical from a stoichiometric point of view. The CH_3F and CH_2F_2 gases produced F• radicals at the same extent, this can explain why the nitride etch rate is almost similar for these two gases. Compared to the other gases, the main differences observed on the OES while etching with CH_3F/O_2 are: more abundant H, CO_2, CO, CN and N_2 species while the •OH radicals are 12 and 4 times higher (Fig.2). The more remarkable observation is that carbon containing species participate more in the nitride etching with the CH_3F/O_2 chemistry, producing more CN.

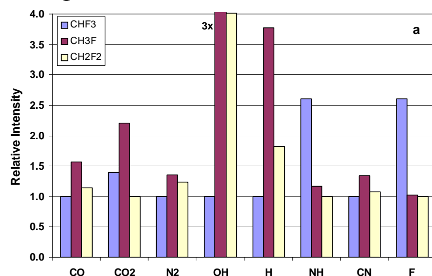


Fig. 2. OES intensities on SiO_2 blanket wafers.

SiO_2 blanket wafers: the ER is almost negligible for the CH_3F while increases as the F/C ratio increases. In Fig.3, the F• radicals are more abundant for the CHF_3 chemistry compared to the same gas on nitride blanket wafers. This suggest, that F• radicals are less consumed during the SiO_2 etching; this is in agreement with literature [2]. According to the OES, the OH species are more abundant on SiO_2 than on nitride blanket wafers when the CH_3F chemistry is used, suggesting a more abundant H• that dilutes the O• radicals.

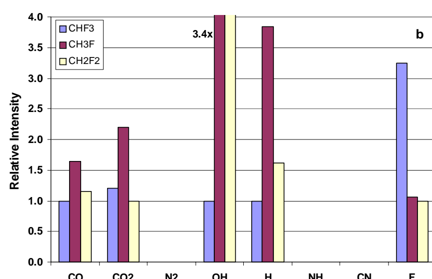
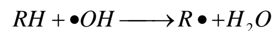
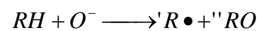


Fig. 3. OES intensities on Si_3N_4 blanket wafers.

According to our TEM, the CH_3F/O_2 chemistry forms more polymer on the SiO_2 than on the Si_3N_4 surface. The CH_3F molecule dissociates easily on $\cdot CH_x$ and F• + H•. The sputter ions can break the Si-O bonds but CF_x radicals are needed to produce volatile species, therefore, the reaction of $\cdot CH_x$ and $^-$O-Si- can easily occur, because the C-H bond energy is smaller than C-O bond (exothermic) and the formation of a polymer film of –Si-O-CH_x (R-H) could occurs, this is quite possible since EFTEM mapping did not detect F atoms on the poly layer. So, how to explain the abundance of oxygen on that poly layer? According to the oxygen plasma for etching carbon base materials, one of the possible path which involves •OH radicals and O- ions is the abstraction mechanisms [3]:



$$RH + \bullet OH \longrightarrow R\bullet + H_2O$$



$$RH + O^- \longrightarrow 'R\bullet + ''RO$$

The poly radical site formation can easily combine with $\cdot CH_x$ radicals and form a polymer layer mainly composed by C, H and O.

The possible reason because the polymer layer is less thick on the nitride, could be related to the strength bond of Si-N which is weaker compared to Si-O, making the etching more dynamic on the nitride surface. Also, the $\cdot CH_x$ radicals can easily combine with the -Si-N due to the exothermic nature of this reaction producing C-N + •H. According to the OES the CN is more produced on the CH_3F/O_2 chemistry than on the other two chemistries.

Conclusions

In the overetch step on the spacer etch, the CH_3F/O_2 chemistry buildups a polymer layer (constituted mainly of C, H and O) more easily on the SiO_2 surface rather than on the Si_3N_4 surface. This can be explained on terms of surface reaction dynamics: the polymer deposition is slow on the Si_3N_4 because there are F• radical, the $\cdot CH_x$ can combine with N and produce CN; while on SiO_2 surface, the reactants for etch this material are scarce and the polymer layer buildups faster than the scavenger process.

References

[1] J.M. Regis *et al.*, Adv. Semiconductor Manufacturing Conference 252 (1977).

[2] T. Sugano *et al.*, Applications of Plasma Processes to VLSI Tech. NY (1985) P36.

[3] F.D. Egitto, Pure & Appl. Chem. **62** 1699 (1990).

	Etch Rate (nm/min)			Selectivity		Uniformity (%)		
	Si_3N_4	SiO_2	Si	Si_3N_4/SiO_2	Si_3N_4/Si	Si_3N_4	SiO_2	Si
CH_3F	26	1	2	26	13	1.5	1.1	0.42
CH_2F_2	28	16	8	1.8	3.5	0.43	0.3	0.1
CHF_3	145	55	61	2.6	2.3	7.5	0.5	0.1

Table 1. Etch rate, selectivity ratios and uniformity measured on blanked wafers. O_2 flow was constant.