# Plasma Etching of $Si_3N_4$ with High Selectivity Over Si and $SiO_2$

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### *Abstract*

*The results of a comparative study of etching of silicon nitride, silicon oxide and silicon in various fluorine containing gas mixtures ($CF_4/H_2$, $CF_4/O_2/N_2$, $SF_6/O_2/N_2$, $SF_6/CH_4/N_2$ and $SF_6/CH_4/N_2/O_2$) are presented. The main objective of the work is to obtain high selectivity of silicon nitride over silicon oxide and silicon. The roles of different components of the gas mixtures in the process are discussed.*

## 1. Introduction

Silicon nitride is one of the primary materials used in various microfabrication processes as a dielectric, mask material, etc. In a CMOS technology, the removal of silicon nitride film is one of the critical steps as it represents a possible source of device damage. In a technology currently under development in the CCS-UNICAMP, a 120 nm thick silicon nitride layer is deposited over a thin (with thickness of 40 nm) silicon oxide layer. Possible overetch during the nitride processing may result in damages of a thin oxide film. Furthermore, etchants can reach the underlying silicon substrate through imperfections of the oxide. Most of dry (plasma) processes currently used for nitride layer stripping have a silicon etch rate much higher than that of silicon nitride. This may cause serious damages of a silicon substrate (formation of craters) and affect the device performance. So, high selectivity of nitride etching over both silicon and silicon oxide is strongly desired.

For plasma etching of silicon nitride, usually gases containing fluorine like $CF_4$, $NF_3$, $CHF_3$ and $SF_6$ [1-8] are used, in most cases in mixtures with other gases as $O_2$, $N_2$, $H_2$, Ar and NO. Several approaches to solve the problem of $Si_3N_4/SiO_2/Si$ etch selectivity were analyzed. In particular, the use of gases which promote formation of carbonaceous (polymer) films on the surfaces was shown to be favorable for etching selectivity. In this case, the surface fluorination and subsequent material removal competes with the deposition of non-volatile fluorine-carbon species and formation of polymer film on the surface. The thickness of a steady-state polymer film was shown to depend essentially on the substrate material, so that under certain conditions it was possible to reduce considerably the etch rate or even stop completely the etching of Si [3]. With respect to silicon oxide, it is unlikely to obtain high $Si_3N_4/SiO_2$ etch selectivity using surface polymerization as it is an essential step for most known $SiO_2$ etching processes (carbon atoms act as reaction intermediates in the process of removal of oxygen from the oxide, occurring in the form of CO or $CO_2$).

In recent papers [5,6], it has been proposed to use chemical dry etching (CDE) of $Si_3N_4$, instead of more common reactive ion etching (RIE). In contrast to RIE, in the CDE method the synergistic effect of ion bombardment, which is known to enhance strongly the etch rate, is not available. Instead, material removal occurs through purely chemical interactions taking place at the processed surface. In this case, the etching selectivity may be improved considerably by a proper choice of etching gases and reaction intermediates. On the other hand, in the lack of ion bombardment, etch rates for certain materials can be suppressed as many surface reactions require high activation energy. In particular, one can expect that absence (or reduction) of ion bombardment will favor higher $Si_3N_4/SiO_2$ etch selectivity as the energy of the Si-O chemical bond (8.3 eV) is considerably higher than that for Si-N (4.6 eV). Note that the energy of the Si-F bond has an intermediate value of 5.7 eV. Therefore, ion bombardment is essential to promote $SiO_2$ etching using fluorine chemistry, while the $Si_3N_4$ etching is less sensitive to ion bombardment. It was shown that addition of $N_2$ and $O_2$ (or NO) to etching gases may improve considerably the process selectivity [5,6] as nitrogen atoms or NO molecules can accelerate the removal of nitrogen from the silicon nitride.

The objective of the present study was to optimize the conditions of silicon nitride etching using a conventional RIE etcher and different gas mixtures. Considering various gas mixtures, we were looking for the conditions, which provide not only an adequate surface chemistry but lower DC bias values as well.

## 2. Experiment

In etching experiments, a conventional parallel-plate capacitively coupled RF-driven (13.56 MHz) plasma reactor was used. RF power was applied to a smaller Al electrode (12 cm in diameter). Most experiments were performed with a Si wafer (100 mm in diameter) placed on the electrode. The wafer was used as a sample holder. Experiments were carried out with 3 kinds of samples: 1) monocrystalline Si, 2) films of $SiO_2$ (thickness of ~1μm) produced by thermal oxidation of mono-Si, and 3) films of $Si_3N_4$ (thickness of ~0.5 μm) deposited by a CVD process over thin oxide films using silicon substrates.

Samples (with areas in the range of 0.2-0.3 $cm^2$) were patterned by a AZ 5214 photoresist mask, with an open area exceeding 50%. Mixtures of gases containing $SF_6$, $CH_4$, $CF_4$, $N_2$, $H_2$ and $O_2$ in different compositions were used for etching. Experiments were carried out with gas pressures in the range of 40-150 mTorr, total gas flows of 20-100 sccm, RF power of 35-150 W, DC self-bias voltage of 40 - 750 V. In some cases, when bias values were changing significantly during the discharge, the average values were recorded (and shown hereafter). In most experiments, etching time was 10 minutes, but in some cases (for oxygen-rich plasmas) it was reduced to 1-2 minutes, to avoid a complete resist removal during the process. Etch depths were measured by a DEKTAK profiler. The accuracy of measurements was better than ±10%. To improve a reproducibility of results (which may be seriously affected by the process prehistory, especially when polymerizing gases are used), discharges in $SF_6/O_2$ were utilized after each process for the chamber cleaning. Reproducibility of etch results was usually better than ±20%.

## 3. Results and Discussion

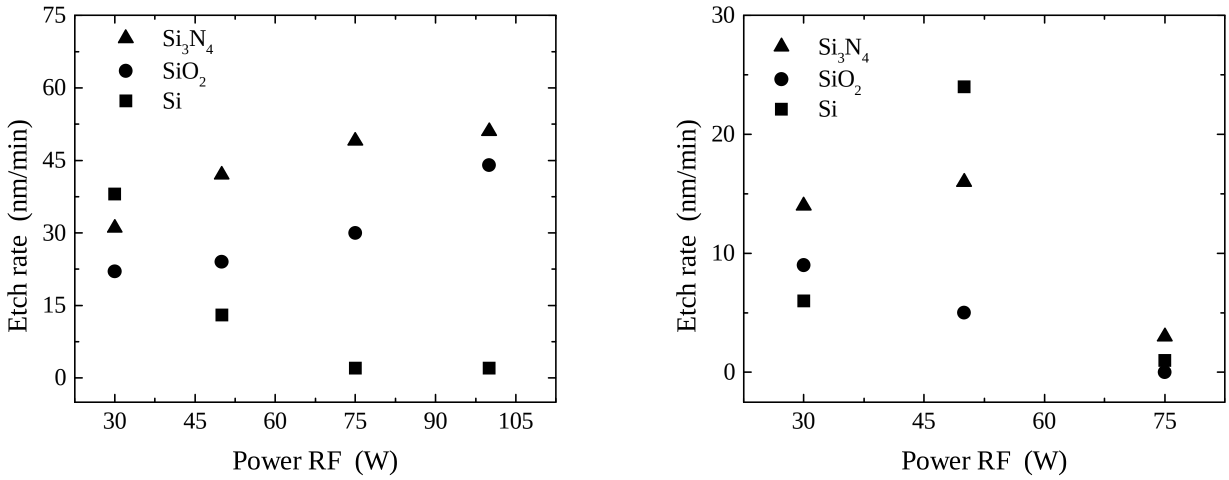
### A. Etching in $CF_4/H_2$

First series of experiments was performed with $CF_4/H_2$ gas mixtures. This chemistry was shown to provide good selectivity over Si [1]. Hydrogen is used to enhance the polymer formation on silicon surface. The main problem here is that in this case, the DC bias is relatively high, this makes it difficult to obtain high etch selectivity over $SiO_2$. The best results in terms of $Si_3N_4$ etch selectivity over both $SiO_2$ and Si (close to 2) were obtained at a high pressure (low DC bias). Power dependencies of $Si_3N_4$ and $SiO_2$ etch rates are shown in Fig. 1 for two different pressures (40 mTorr and 150 mTorr). It can be seen that polymerization which increases with power, affects etching of nitride, oxide and silicon in different ways. At higher pressure (150 mTorr) and lower DC bias, polymerization is stronger and reduces rapidly the nitride, oxide and silicon etch rates at the power level exceeding 50 W. At lower pressure (40 mTorr) and higher DC bias (i.e., higher ion bombardment), the nitride etch rate saturates as the power rises above 50 W, while for the oxide an increase on the etch rate is observed, and for the silicon the polymerization increases with power, reducing rapidly the etch rate .

| Gas flow (sccm) $CF_4/H_2$ | Power RF (W) | Pressure (mTorr) | Bias DC (V) | Etch rate (nm/min) | | | Selectivity | |
|---|---|---|---|---|---|---|---|---|
| | | | | $Si_3N_4$ | $SiO_2$ | Si | $Si_3N_4/SiO_2$ | $Si_3N_4$/Si |
| 15/5 | 75 | 40 | 625 | 65 | 41 | <10* | 1.5 | >6 |
| 15/6,6 | 75 | 40 | 612 | 45 | 35 | <10* | 1.2 | >4 |
| 15/10 | 75 | 40 | 627 | 49 | 30 | <10* | 1.6 | >5 |
| 15/15 | 75 | 40 | 637 | 40 | 47 | 31 | 0.8 | 1.2 |
| | | | | | | | | |
| 15/10 | 30 | 40 | 342 | 31 | 22 | 38 | 1.4 | 0.8 |
| 15/10 | 50 | 40 | 495 | 42 | 24 | 13 | 1.7 | 3.2 |
| 15/10 | 100 | 40 | 730 | 51 | 44 | <10* | 1.1 | >5 |
| | | | | | | | | |
| 15/10 | 75 | 60 | 615 | 15 | 39 | <10* | 0.3 | >1 |
| | | | | | | | | |
| 15/10 | 30 | 80 | 289 | 17 | 9 | 16 | 1.8 | 1.1 |
| 15/10 | 75 | 80 | 524 | 17 | 39 | 6 | 0.4 | 2.8 |
| 15/10 | 75 | 150 | 438 | 3 | <1* | 1* | >3 | 3 |
| | | | | | | | | |
| 15/5 | 30 | 150 | 227 | * | * | * | ---- | ---- |
| 15/5 | 75 | 150 | 479 | 1.3 | * | * | ---- | ---- |
| | | | | | | | | |
| 15/10 | 30 | 150 | 228 | 14 | 9 | 6 | 1.5 | 2.3 |
| 15/10 | 50 | 150 | 267 | 16 | <5* | 28 | >3.2 | 0.5 |
| 15/5 | 50 | 150 | 290 | 45 | 20 | 19 | 2.2 | 2.3 |

* Strong polymerization

**Table 1: Etching results in $CF_4/H_2$ plasmas**




**(a)**

**(b)**

**Figure 1: Etch rate vs. power RF in $CF_4/H_2$ plasma. Process conditions: 15/10 sccm, (a) 40 mTorr, DC bias varied (342→ 730 V), (b) 150 mTorr, DC bias varied (245→ 438 V)**

## B. Etching in $CF_4/O_2/N_2$

The second series was carried out with $CF_4/O_2/N_2$ gas mixtures. In Ref. [5], remote plasma processing using $O_2/N_2$ with small additions of $NF_3$ or $CF_4$ was studied. The role of NO molecule in the surface chemistry was shown to be important, promoting the enhanced removal of nitrogen atoms from the nitride. Our studies (see Table 2) have shown that under the present plasma conditions (RIE regime), with DC bias being relatively high, it is unlikely to achieve high nitride etch selectivity over both silicon and silicon oxide.

An important point is that the photoresist used is stripped by the oxygen-rich plasma in a short time (2-3 min), i.e. before the removal of the 120 nm thick silicon nitride can be complete.

| Gas flow (sccm) $CF_4/O_2/N_2$ | Power RF (W) | Pressure (mTorr) | Bias DC (V) | Etch rate (nm/min) | | | Selectivity | |
|---|---|---|---|---|---|---|---|---|
| | | | | $Si_3N_4$ | $SiO_2$ | Si | $Si_3N_4/SiO_2$ | $Si_3N_4$/Si |
| 5/20/30 | 60 | 150 | 444 | 15 | 18 | ~11 | 0.8 | 1.3 |
| 5/30/30 | 75 | 150 | 529 | 14 | 27 | ~14 | 0.5 | 1 |
| | | | | | | | | |
| 15/30/30 | 30 | 150 | 228 | 12 | * | 5 | * | 2.4 |
| 15/30/30 | 50 | 150 | 324 | 35 | 25 | 8 | 1.4 | 4.3 |

* Strong polymerization

**Table 2: Etching results in $CF_4/O_2/N_2$ plasmas**

## C. Etching in $SF_6/O_2/N_2$

The third series was carried out with $SF_6/O_2/N_2$ gas mixtures. Our previous studies have shown that the presence of $SF_6$ in the plasma reduces considerably the DC bias. This factor may favor the nitride over oxide selectivity. However, in this case it is rather difficult to keep the silicon etch rate at low level (see Table 3). Once again, selectivity over the photoresist is not satisfactory. In Fig. 2, the effect of $SF_6$ addition on the etch rates is shown. As the $SF_6$ content rises, etch rates increase fast for silicon nitride and especially for silicon, while almost no changes are observed for oxide. In Fig. 3, power dependence of etch rate is shown for the three materials, at a gas pressure of 150 mTorr. At lower powers, etching for all materials is suppressed likely due to formation of a O/N reaction layer on the surfaces [4-6].

| Gas flow (sccm) $SF_6/O_2/N_2$ | Power RF (W) | Pressure (mTorr) | Bias DC (V) | Etch rate (nm/min) | | | Selectivity | |
|---|---|---|---|---|---|---|---|---|
| | | | | $Si_3N_4$ | $SiO_2$ | Si | $Si_3N_4/SiO_2$ | $Si_3N_4$/Si |
| 3/30/30 | 75 | 150 | 257 | 14 | 16 | 8 | 0.8 | 1.7 |
| 5/30/30 | 75 | 150 | 220 | 15 | 10 | 13 | 1.5 | 1.1 |
| 7,5/30/30 | 75 | 150 | 185 | 26 | 15 | 260 | 1.7 | 0.1 |
| | | | | | | | | |
| 10/30/30 | 30 | 150 | 47 | 0 | 0 | 0 | ---- | ---- |
| 10/30/30 | 50 | 150 | 95 | 19 | 10 | 8 | 1.9 | 2.3 |
| 10/30/30 | 75 | 150 | 192 | 27 | 15 | 280 | 1.8 | 0.09 |
| | | | | | | | | |
| 5/30/60 | 75 | 150 | 241 | 17 | 16 | 10 | 1.0 | 1.7 |
| 10/30/60 | 50 | 150 | 107 | 15 | 8 | 6 | 1.8 | 2.5 |
| 10/30/60 | 75 | 150 | 192 | 25 | 18 | 13 | 1.3 | 1.9 |
| | | | | | | | | |
| 10/50/30 | 50 | 150 | 108 | 15 | 7 | 0 | 2.1 | --- |
| 10/50/30 | 75 | 150 | 200 | 20 | 14 | 8 | 1.4 | 2.5 |

**Table 3: Etching results in $SF_6/O_2/N_2$ plasmas**

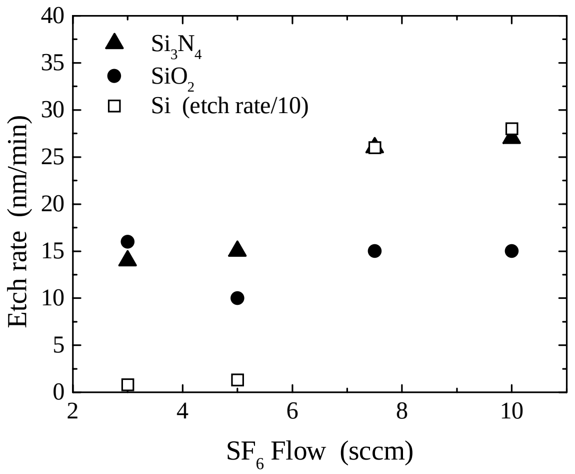



**Figure 2: Etch rate vs. $SF_6$ flow in $SF_6/O_2/N_2$ plasma. Process conditions: $O_2$ and $N_2$ flows =30 sccm, 75W, 150 mTorr, DC bias varied (192→ 257V).**

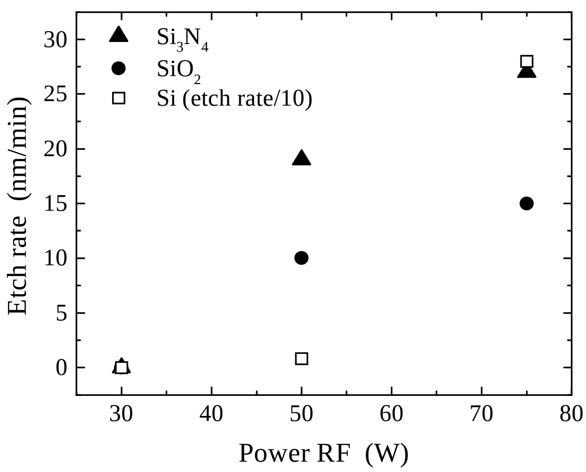



**Figure 3: Etch rate vs. power RF in $SF_6/O_2/N_2$ plasma. Process conditions: 10/30/30 sccm, 150 mTorr, DC bias varied (47→192 V).**

## D. Etching in $SF_6/CH_4/N_2$

The fourth series was carried out with $SF_6/CH_4/N_2$ gas mixtures, including methane instead of oxygen in order to: i) avoid the photoresist stripping during the process and ii) reduce the silicon etch rate by using a polymerizing gas, $CH_4$. Some experiments were performed without the Si wafer (used as a sample holder) inside the chamber. Actinometry measurements have shown that without the wafer, the fluorine radical content in the plasma is usually several times higher [9]. As a consequence, considerably higher etch rates were observed in this case, especially for silicon samples. High etch selectivity of $Si_3N_4$ over $SiO_2$ was achieved (up to 6, or even higher but at a low $Si_3N_4$ etch rate), with the $Si_3N_4$ etch rate being high enough (up to 47 nm). However, Si etch rate is still rather high in most cases. In Fig. 4, power dependence of etch rates is shown for a 100 mTorr, $SF_6/CH_4/N_2$ =5/20/20 sccm plasma (without the Si wafer). It is seen that increasing polymerization resulted in etching suppression for all the materials (all etch rates tend to zero).

| Gas flow (sccm) $SF_6/CH_4/N_2$ | Power RF (W) | Pressure (mTorr) | Bias DC (V) | Etch rate (nm/min) | | | Selectivity | |
|---|---|---|---|---|---|---|---|---|
| | | | | $Si_3N_4$ | $SiO_2$ | Si | $Si_3N_4/SiO_2$ | $Si_3N_4/Si$ |
| With Si wafer | | | | | | | | |
| 5/3/20 | 75 | 40 | 360 | 26 | 16 | 26 | 1.6 | 1 |
| 5/10/20 | 75 | 40 | 354 | 28 | 19 | 20 | 1.4 | 1.4 |
| 5/10/20 | 75 | 60 | 341 | 33 | 26 | 39 | 1.2 | 0.8 |
| | | | | | | | | |
| 10/5/20 | 50 | 40 | 242 | 31 | 23 | 37 | 1.3 | 0.8 |
| 10/5/20 | 75 | 40 | 320 | 30 | 15 | 16 | 2 | 1.8 |
| | | | | | | | | |
| 5/20/20 | 50 | 100 | 139 | 14 | ~1* | 19 | ~10 | 0.7 |
| 5/20/20 | 75 | 100 | 231 | 24 | 9 | 32 | 2.6 | 0.7 |
| Without Si wafer | | | | | | | | |
| 5/20/20 | 50 | 100 | 167 | 32 | 10 | 35 | 3.2 | 0.9 |
| 5/20/20 | 50 | 150 | 100 | 47 | 8 | 618 | 5.8 | 0.07 |
| 5/20/20 | 75 | 100 | 290 | * | * | * | ---- | ---- |
| | | | | | | | | |
| 10/5/20 | 75 | 150 | 118 | 27 | 15 | 897 | 1.8 | 0.03 |
| 5/20/20 | 35 | 100 | 86 | 12 | 10 | 149 | 1.2 | 0.08 |
| 5/20/20 | 35 | 150 | 52 | 22 | 6 | 690 | 3.6 | 0.03 |

*Strong polymerization

**Table 4. Etching results in $SF_6/CH_4/N_2$ plasmas**

## E. Etching in $SF_6/CH_4/N_2/O_2$

The fifth series was carried out with $SF_6/CH_4/N_2/O_2$ gas mixtures, using small oxygen additions in order to suppress the silicon etch rate. Results are shown in Table 5. As can be seen, by rising the oxygen content it is possible to achieve a reasonable trade-off between the $Si_3N_4$ etch rate (in the range of 30 – 40 nm/min) and the selectivity over both $SiO_2$ (between 3 and 4) and Si (close to 2). The effect of oxygen addition on etch rates is shown in Fig. 5 for mixtures with gas flows $SF_6/CH_4/N_2$ = 10/10/20 sccm (150 mTorr). As oxygen content rises, the etch rate shows the following behavior: (i) reduces gradually for nitride, (ii) drops abruptly for silicon (likely due to enhanced surface oxidation), and (iii) practically no changes are observed for oxide. For a lower $SF_6$ content, the addition of oxygen has stronger effect on the silicon etch rate (compare the results for $SF_6/CH_4/N_2$ = 5/20/20 and 10/10/20 sccm in Table 5, where the drop of the Si etch rate with oxygen addition is considerably faster for the former case).

| Gas flow (sccm) $SF_6/CH_4/N_2/O_2$ | Power RF (W) | Pressure (mTorr) | Bias DC (V) | Etch rate (nm/min) | | | Selectivity | |
|---|---|---|---|---|---|---|---|---|
| | | | | $Si_3N_4$ | $SiO_2$ | Si | $Si_3N_4/SiO_2$ | $Si_3N_4/Si$ |
| Without Si wafer | | | | | | | | |
| 5/20/20/0 | 50 | 150 | 94 | 35 | 8 | 204 | 4.3 | 0.17 |
| 5/20/20/2,8 | 50 | 150 | 104 | 30 | 8 | 27 | 3.7 | 1.1 |
| 5/20/20/5 | 50 | 150 | 110 | 28 | 9 | 14 | 3.1 | 2 |
| 5/20/20/7 | 50 | 150 | 126 | 24 | 6 | 14 | 4 | 1.7 |
| 5/20/20/9 | 50 | 150 | 116 | 25 | 6 | 9 | 4.1 | 2.7 |
| | | | | | | | | |
| 10/10/20/0 | 50 | 150 | 72 | 40 | 11 | 498 | 3.6 | 0.08 |
| 10/10/20/3 | 50 | 150 | 63 | 41 | 12 | 98 | 3.4 | 0.42 |
| 10/10/20/6 | 50 | 150 | 62 | 35 | 9 | 35 | 3.9 | 1.0 |
| 10/10/20/10 | 50 | 150 | 76 | 30 | 11 | 16 | 2.7 | 1.9 |
| | | | | | | | | |
| 10/10/5/6 | 50 | 150 | 47 | 56 | 16 | 150 | 3.5 | 0.37 |
| 10/10/10/6 | 50 | 150 | 41 | 45 | 12 | 142 | 3.75 | 0.32 |

**Table 5. Etching results in $SF_6/CH_4/N_2/O_2$ plasmas**

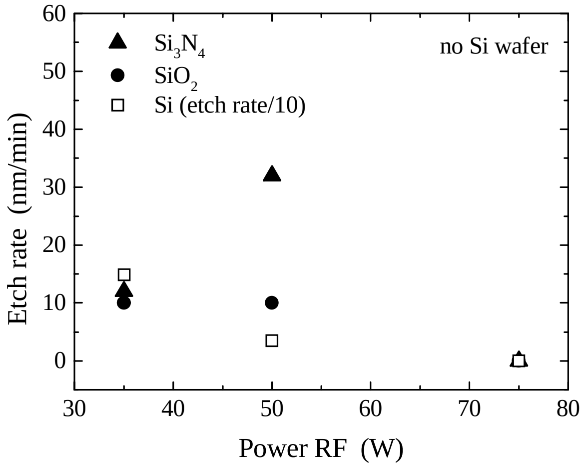



**Figure 4: Etch rate vs. power RF in $SF_6/CH_4/N_2$ plasma. Process conditions: 5/20/20 sccm, 100 mTorr, DC bias varied (86→ 290V).**

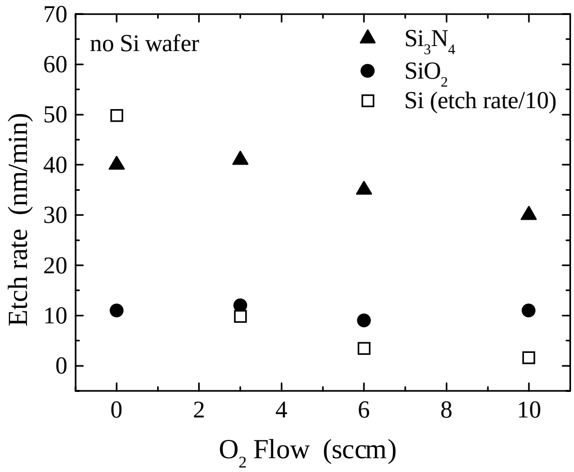



**Figure 5: Etch rate vs. $O_2$ flow in $SF_6/CH_4/N_2/O_2$ plasma. Process conditions: $SF_6$ and $CH_4$ flow =10 sccm, $N_2$ flow 20 sccm, 150 mTorr, DC bias varied (62→ 76 V).**

## 4. Conclusions

In this work, the results of a comparative study of etching of silicon nitride, silicon oxide and silicon in various fluorine-containing gas mixtures ($CF_4/H_2$, $CF_4/O_2/N_2$, $SF_6/O_2/N_2$, $SF_6/CH_4/N_2$ and $SF_6/CH_4/N_2/O_2$) are presented. The main objective of the work is to obtain high selectivity of silicon nitride over silicon oxide and silicon.

This is important for a CMOS technology currently under development in the CCS, where the process of a thin nitride layer stripping by plasma is a possible source of device damages. The roles of different components of the gas mixtures in the process are discussed. The use of multi-component gas mixtures in this case is essential as etching conditions for three different materials should be considered and optimized. The main tendency is that the etching selectivity improves with higher pressures and lower DC bias. For suppression of silicon etching, addition of gases promoting considerable oxidation and/or polymerization of the Si surface is necessary. Up to now, the best results in terms of etching selectivity and a $Si_3N_4$ etch rate have been achieved with a $SF_6/CH_4/N_2/O_2$ gas mixtures. These results, obtained with a conventional RIE reactor, are comparable with those reported in the literature for chemical dry etching (remote plasma). Further optimization of the technology is a subject of a future work.


**Acknowledgements**

Authors thank Dr. Luis da Silva Zambom (LSI-EPUSP) for providing samples of $Si_3N_4$.

The work was financially supported by CNPq and FAPESP.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