# $CHF_3$ REACTIVE ION BEAM ETCHING OF Si AND $SiO_2$: CONTRIBUTION OF BOTH ACTIVE NEUTRALS AND COMPENSATION ELECTRONS

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**ABSTRACT :** Reactive ion beam etching is obtained from an Electrostatic Reflex Ion Source operated with $CHF_3$. The dependence of the $SiO_2$ and Si etch rates on the pressure is reported for a variation range $3x10^{-3}$-$3x10^{-4}$ mbar within the source chamber, the pressure is an order of magnitude smaller in the interaction chamber and the neutral flow/ion flow ratio varies in the range 10/1. It is then shown and explained that the compensating electron density has a negligible influence on both the $SiO_2$ and Si etch rates. Conversely these latter increase as far as the target temperature is decreased (-75°C) whereas the $SiO_2$/Si selectivity decreases. It is concluded that the etching behavior for room temperature exposure is determined by the ion beam characteristics, in particular its composition which effects are emphasized.

## 1 - INTRODUCTION :

Reactive Ion Beam Etching (RIBE) from sources operated either with $CF_4$ or $CHF_3$ provides a very convenient process for selective etching of $SiO_2$ over Si, a basic problem in semiconductor technology /1,2/. Furthermore ion beam experiments provide a good simulation of the mechanisms which govern the behavior of reactive ion etching (RIE) in a plasma environment. It is known that the selective etching of $SiO_2$ over Si is achieved because of the growth of a carbonaceous overlayer the thickness of which entails the slow-down of the Si etch rate /1-5/.The aims of the present work were to determine the respective contribution of the active neutral species and the compensation electrons on the kinetics and mechanism of the fluorocarbon overlayer formation during etching of Si simultaneously bombarded by fluorocarbon ions.

In this paper only the information obtained from etch rate measurements and on-line variations of $SiF_4$ partial pressure are emphazised. This latter will be hereafter refered to as ES (Etch Signal).

## 2 - EXPERIMENTAL SET-UP :

The experimental set-up has been described elsewhere /1/.A specific ion gun is used, the Electrostatic Reflex Ion Source (Maxi-ERIS) /6,7/. The samples to be exposed to the ion beam were stuck on the water-cooled substrate holder driven by a motorized load-lock system. A small Faraday cup is included in the sample holder to measure the irradiation current density. Masked samples were used for etch rate measurements. Thermal silicon dioxide grown on silicon and Si single-crystal were used for the present results. For the analysis of the etching interaction kinetics and mechanisms, unmasked samples were considered. The Si substrates were n-type, (100)-oriented crystals (0.4 and 0.6 Ωcm). The active species effuse out the gun-ionization chamber through the ion beam formation grids. The pressure in the interaction chamber ($p_i$) is in the range $10^{-5}$-$10^{-4}$ mbar and the neutral flow/ion flow ratio of the heavy particles which impinge on the samples is in the range 1-10, i.e. a much smaller value than that encountered in a plasma environment. The pressure ($p_S$) within the source chamber is recorded by a capacitance manometer and is an order of magnitude higher than $p_i$. Pure $CHF_3$ neutrals are

injected into the gun-ionization chamber; they are fragmented via electron collisions (100-120 eV); the variation of the injected gas flow entails the modification of the mass spectrum of both the ion beam and the neutral flow. They are on-line recorded respectively by a magnetic mass separator (MMS) and a quadrupolar mass filter (QMS), in particular the $SiF_4$ partial pressure.

## 3 - EXPERIMENTAL RESULTS :

### 3.1 - Etch rates and $SiO_2$/Si selectivity *versus* ion source pressure :

The dependence of $SiO_2$ and Si etch rates and resulting $SiO_2$/Si selectivity for a 500 eV ion beam at normal incidence *versus* $p_S$ is shown in Fig.1. For these data the ion current density is maintained at a constant value $j^+=0.25$ mAcm$^{-2}$ (or $\phi^+=1.55\text{x}10^{15}$ ions/cm$^2$/s) with a proper variation of the discharge current and voltage. From the highest to lowest values in Fig.1, these latter were respectively 3.2 A, 95 V and 4 A, 130 V. The etch rates have been normalized to a 1 mAcm$^{-2}$ current density in order to make easier the comparison between various RIBE data /1/. The source pressure decrease entails both the decrease of the flux $\phi^*$ of the effusing neutral species and the variation of the composition of the ion and neutral flows. These features are the consequences of the modifications of both electron energy distributions and chemical reaction rates in gas phase. As far as the ion beam is concerned, three mass spectra are shown in Fig.2, corresponding to three typical pressure values $p_S=3\text{x}10^{-3}$ mbar (high pressure HP); $p_S=8\text{x}10^{-4}$ mbar, the optimum pressure (OP) which maximizes the selectivity and $p_S=3\text{x}10^{-4}$ mbar (low pressure LP). It must be mentionned that the mass 21 peak corresponds to fluorine ions $F^+$ which have collided with $CHF_3$ neutrals all along their path in the downstream chamber (about 80 cm) to give $FH^+$ having the $F^+$ velocity and thus being mass analyzed with an apparent mass 21. As already known the high selectivity value which might be achieved from RIBE process with fluorocarbon ions is due to the preferential growth of a carbonaceous blocking-overlayer on the silicon surface /1/. On $SiO_2$, the oxygen prevents - or as will be seen later on reduces the growth of the carbonaceous overlayer. The respective behaviors of either $SiO_2$ and Si ES are illustrated in Fig.3 where the ES of a 100nm $SiO_2$ layer over Si and of a virgin Si are shown. The samples have the same dimensions (10x20mm$^2$) so that the ES amplitudes might be compared. The $SiO_2$ to Si transition is clearly seen. At this energy (500 eV) and pressure (HP), a net signal increase is achieved as far as the thickness of the remaining $SiO_2$ allows the bombarding ions to reach the underneath silicon. As far as no more oxygen is left (etching end point) the carbonaceous overlayer grows and the signal now decreases from its maximum value $R_0$ down to a constant value $R_S$, corresponding to the steady state thickness of the overlayer. A few comments can be made about these graphs for a thin $SiO_2$ layer over Si : the steady state signal $R_S$ is the same for both samples whereas the maximum $R_0$ of the virgin Si is slightly higher than that recorded for the $SiO_2$/Si transition. $R_S/R_0$ is the attenuation factor of the chemical etching of the silicon once the blocking overlayer has grown up. The time or ion dose which is required in order to achieve the steady state of the overlayer is the same as that for a virgin silicon. (Interface enlarging through ion-mixing is negligible). The origin of the time scale for the silicon (introduction into the ion beam) has been shifted in order to obtain the same position for both the maximum of the Si signal etching without attenuation and the maximum of the $SiO_2$ to Si transition.

The samples exposed to the ion beam are submitted to the synergetic effects of three kinds of particles : the energetic ions (density $j^+=e\phi^+$, energy $W^+$, incidence q); the compensating electrons ($j_e=j^+$ for a standard current compensation) and the neutral species including stable molecules and radicals (density $\phi^*$). What about the contribution of both neutral species and compensation electrons in the actual RIBE data, in particular on the overlayer thickness and on the resulting etching of the underneath substrate? A series of experiments was performed, attempting to answer this question. In the following results, we have limited the analyze to the case of a single source pressure, OP= $8\text{x}10^{-4}$ mbar maximizing the selectivity for 500 eV ions, for discharge parameters giving an ion flow $j^+=0.75$ mAcm$^{-2}$ on the target ($\phi^+=4.7\text{x}10^{15}$ ions/cm$^2$/s). The gas flow rate is then 3 sccm. The QMS mass spectrum of the stable neutral phase is shown in Fig.4. As a crude and fast estimation we have neglected this

composition for the estimation of the flow density of the neutrals which impinge on the substrate after effusing downstream the three grid apertures. It has been estimated to be $\phi^*=1.7x10^{16}$ part/$cm^2$/s, i.e. a neutral/ion flow ratio=3.6/1

**3.2 - Downstream exposure of Si samples :**

For ion energy smaller than 150 eV at OP, the gun is not able to deliver a collimated beam without forced-injection of electrons in order to insure the neutralization of the local space charge. Therefore in order to analyze the effects of the active neutrals simultaneously assisted either by electrons or low energy ions, the setup is now used as a "remote plasma" exposure process. Neutrals effuse downstream the plasma through the grid apertures. As concerns the charged particles, a convenient biasing of the various available electrodes of the gun permits the selection of either electrons or ions to impinge on the target. Their current density is recorded from the target probe and their energy is estimated from the imposed potential differences. Ions are issued from the plasma which potential is close to that of the discharge anode. The more energetic electrons are issued from the discharge hot cathode, negatively biased at -120V with reference to the anode. Two kinds of complementary measurements are then used to characterize the samples having undergone such a "downstream exposure", refered hereafter to as pre-treatment. Someones are taken out the reactor for surface analysis whereas others are introduced back into the ion beam for a standard RIBE exposure, the ES being recorded (XPS data have been reported elsewhere /3/). ES are given in Fig.5 corresponding to various pre-treatments which effects will be discussed now.

**Without pre-treatment** : for time and signal references, the ES for the first introduction of a virgin Si (with its native oxide) and for all further consecutive introductions are shown in Fig.5-a. As far as the overlayer has reached its steady state, the silicon is partially "passivated" and the overlayer is stable if the sample is kept out of the beam whatever is the duration of its stay. The steady state value is not affected. The characteristic time of the vacuum equipment is about 2 seconds; it affects the signal increase which would be very sharp in the limit of a vanishing characteristic time. The time origin corresponds to the penetration into the beam which of course has not a sharp edge, although homogeneous over a large plateau.

**Electron-assisted pre-treatment** : the electron bombardment results in the growth of a polymer film both on Si and $SiO_2$ with a constant rate which has been estimated to be 5nm/min from profilometer or ellipsometer data, the electron current density being 0.5 $mAcm^{-2}$. The film growth is also detected from the delay for the Si to be etched when introduced into the beam. In Fig.6, the delay time is plotted *versus* the pre-treatment time. The effect of a smaller electron density (0.1 $mAcm^{-2}$) is also shown which demonstrates a saturation of the assistance by the electron flow, the growth rate being then governed by the reactive species flow rate. For a 50 nm thickness the delay time is 34 seconds which corresponds to a 90 nm/min rate for the etching of the polymer under the fluorocarbon 500 eV ion beam i.e. about 20 times the deposition rate.

**Ion-assisted pre-treatment** : the lowest energy that has been available for ion bombardment without electrons was 80 eV. The ion current density was then $3x10^{-2}$ $mAcm^{-2}$. As shown both in Fig.5-b and Fig.6 such a pre-treatment entails a film growth with a constant rate of about 1 nm/min. It is interesting to compare this value to the arrival rate of carbon atoms transported by the $CF_x^+$ ion flow i.e. 1.1 nm/min with a 2 $gcm^{-3}$ density corresponding to graphite. It may then be concluded that the C matter carried on by ions is sufficient to justify quantitatively the film deposition rate without neutral species assisted chemistry, the deposition effect of which may eventually been balanced. The samples in Fig.5 have been previously passivated before the pre-treatment which thus does not affect the thickness of the existing overlayer. Now, as far as the ion energy is increased, the film growth rate decreases and vanishes at about 140 eV. The evolution of the signal shape in Fig.5-c for a 3 min pre-treatment with increasing energy, demonstrates that an increasing fraction of the blocking overlayer is consumed before the thickness of growing film has reached the value which prevents its etching. The increasing etching yield of the incoming ions counterbalances their deposition ability. A 150 eV energy is required for the pre-treatment in order to obtain an introduction signal which shape is the closest to that of a virgin Si sample. For the present parameters the current density was 0.2 $mAcm^{-2}$ and time necessary to "clean" the 500 eV blocking overlayer is 3 min. For longer exposures, the same signal is observed. It corresponds to a thinner steady-state blocking overlayer which results from a 150 eV ion beam exposure. This particular value of the ion

energy (150 eV) is named "in-situ cleaning energy" $W^+$. It depends on the source pressure (and injected neutrals). Standard RIBE exposures of samples give about the same value for the energy which insures the deposition/etching balance.

### 3.3 - Influence of the compensating electrons :

The influence of the compensation electrons has been analyzed from both ES and ellipsometry which sensitivity has been shown to detect surface modifications /1/. The electron current density $j_e$ has been modified in the range $j^+$ - $2j^+$ for $SiO_2$ samples which require a local current compensation on the insulating target for a well defined energy of the impinging ions, and in the range 0 - $2j^+$ for Si. For this latter however, at either a low energy or a low pressure for which the beam self-neutralization of the local space charge (creation of electrons through ion-neutral collision ) become less efficient, it has not been possible to explore the no-compensated limit, because of the slight but significative modification of the beam shape as the sample-holder is either introduced-in or driven-out the beam. This study has shown that if the ion energy is slightly higher than the cleaning energy $Wc^+$ which has been defined in the previous section, the electron current density has a negligible effect on the etching signal for both Si and $SiO_2$ and on the Si blocking overlayer thickness (negligible means smaller than experimental uncertainties) and this for all the pressure range ($3x10^{-4}$-$3x10^{-3}$ mbar). The influence of the electron energy, fixed by the auxiliary source biasing, has also been examined but unsuccessfully. However this result may be easily explain if one now considers the large ratio between the polymer etching rate by the ion beam and the electron-assisted deposition rate of this polymer. At OP, the increase of $j_e$ from $j^+$ (standard compensation) to $2j^+$ (over-compensation) entails a slight shift of $Wc^+$ towards higher energy by about 10-15 eV, the differential increase of the etching efficiency balancing the extra-deposition rate. The extra-deposition is also detected if the ion energy is smaller than the etching/deposition balance energy : for a 10 min. exposure at OP and 100 eV ion beam (0.5 $mAcm^{-2}$), the thickness of the deposited film for a 10 min. exposure increases from 80 nm for a standard compensation to 90 nm for an over-compensation.

### 3.4 - Influence of the substrate temperature :

The cooling of the substrate holder with a circulation of cold vaporized nitrogen pumped from liquid nitrogen - instead of the standard water-cooling - has permited to obtain preliminary results in the range +15°C; -75°C for the target temperature. No regulation was provided. In Fig.7 are shown the ES of a 600 nm $SiO_2$ layer over silicon at +15°C and -75°C; only the sample introduction and $SiO_2$ to Si transition periods are drawn on these graphs, and the 15°C transition time has been shifted in order to emphazise the signal evolution. The following comments may be pointed out. The temperature decrease entails the increase of the $SiO_2$ etch rate by a factor 1.15 - 1.20 which is smaller than that of silicon (factor 2), the corresponding attenuation factor $R_S/R_0$ increasing from 0.2 to 0.4 ($SiF_3^+$ ES and step data are in fair agreement). As concerns Si, the enhanced etching may be imputed to a smaller thickness of the blocking overlayer because of the increase of the sputtering rate as a result of a higher surface coverage with high F/C ratio reactive species. This assertion is in agreement with the observed increase of the time which is required to reach the overlayer steady-state : 60 seconds at +15°C and 90 seconds at -75°C, although in the latter case the thickness is supposed to be thinner than in the former. The deposition/etching balance which insures a constant thickness of the carbonaceous overlayer is really modified, involving a less protecting effect of the underneath silicon against the incoming fluorine atoms. A further confirmation of the carbon removal increase is shown from the observed shift towards lower values of the ion energy which insures the balance between either a carbon film deposition (smaller range) or the Si etching : for a standard compensated beam, at OP, the values of these energies are respectively : 150 and 120 eV for Si and 125 - 100 eV for $SiO_2$. The influence of the ion energy on the ES of $SiO_2$ at -55°C is shown in Fig.8. The development of a blocking overlayer of finite thickness is seen at 120 eV. At 100 eV a film growth is achieved which impedes the Si etching after a 40 seconds exposure.

## 4 - DISCUSSION :

From the above reported results about $CHF_3$ RIBE, the following features may be pointed out :

i) A carbonaceous blocking overlayer is known to develop on Si and thus to reduce the etching rate ($R_S/R_0$). It has been shown that a similar overlayer may also develop on $SiO_2$ if the exposure conditions allow the carbon deposition rate to overcome against the C removal rate, this latter being effectively higher for $SiO_2$ than for Si (see Fig.8, as the ion energy is decreased for constant flux and composition conditions).

ii) The effect of the active neutrals entails an increase of the C removal rate and thus a decrease of blocking overlayer thickness, in particular if the substrate temperature is decreased below 0°C. This feature is justified by the following facts :

- Except the low ion energies, the electronic impact assisted polymerization rate which has been clearly pointed out is very inferior to the effective removal rate of such a polymer when submited to the ion beam + neutral bombardment.
- Impact of ions alone on these same reactive species does not seem to contribute to the deposition of a polymer the growth rate of which, only observed for low ion energies, is completely consistent with the carbon contribution of ions alone. The reactive species - classic precursors of polymerization - as CF and $CF_2$ do not seem to be sensitive to ion impact to generate a polymer, as they are under electron impact; this phenomenon is well known by electronic microscopists /8/ and we have pointed it out too in the case of the present discharge DC plasma for a tenth times higher neutral flow.

iii) The substrate temperature decrease entails an enhanced efficiency of the etch rate of the carbonaceous overlayer which can be imputed to the increase of the coverage rate of highly fluorinated radicals ($CF_3$), known for their very weak sticking coefficient at room temperature /9/, in the opposite to the polymerization precursors which stick very easily at room temperature but are very sensitive to temperature increase (negligible sticking coefficient above 70°C) /10/. Temperature decrease has a less sensitive effect on $SiO_2$ and on the initial attack ($R_0$) of non-passivated silicon than on the passivated silicon etching. This effect can be interpreted by the blocking overlayer thickness modification which determines the silicon etching attenuation and all things considered, the selectivity. So, the temperature decrease is not propitious to the improvement of the etching selectivity $SiO_2$/Si under fluorocarbonated ions and neutrals. In a recent paper /11/, we have demonstrated that the temperature increase above 15°C of a Si substrate does not appreciably affect its etch rate when a fluorocarbonated blocking overlayer developed under ions+neutrals is established ($R_S$=constant). One can then think that at room temperature, radicals with strong etch rate, the effect of which appears for decreasing temperatures have a negligible influence. Consequently it seems reasonable to admit that for the flow conditions of Fig.2, the results obtained for samples at room temperature, represent effects that are essentially associated to the mass composition of incident ion beam well characterized by the F/C ratio concept /12/. Ion provided carbon is in competition with erosion terms (cinematic mechanisms and physico-chemical reactions) to determine the blocking overlayer thickness. To confirm this assertion, it is seen that ion energy which insures the C-deposition/Si etching transition through a limited thickness layer is in good agreement with the values found by Tachi et al. for bombardment of Si by $CF_x^+$ ions /13/.

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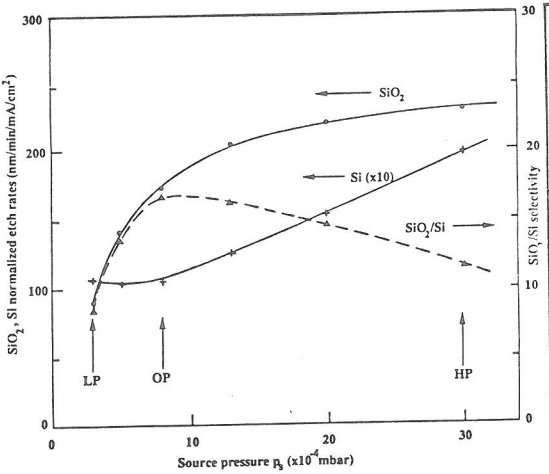


Fig.1 - Etch rates and selectivity versus source pressure ($p_S$) : Energy $W^+$ = 500 eV; incidence $\theta = 0°$; $j^+ = 0.25$ mAcm$^{-2}$.

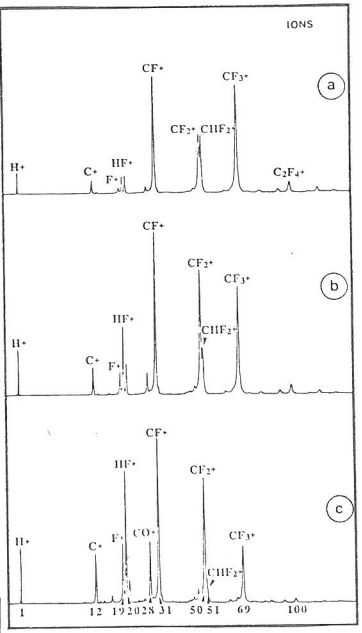


Fig.2 - Ion beam mass spectra for three values of the source pressure : (a) $3x10^{-3}$ mbar (HP); (b) $8x10^{-4}$ mbar (OP); (c) $3x10^{-4}$ mbar (LP).

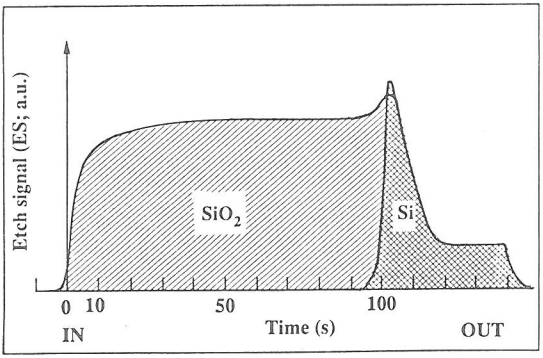


Fig.3 - Etch signatures ($SiF_3^+$ QMS peak height) : of a 100 nm $SiO_2$ layer over Si and a virgin Si; $W^+$ = 500 eV; $\theta = 0°$; $j^+ = 0.25$ mAcm$^{-2}$; $p_S = 30x10^{-4}$ mbar.

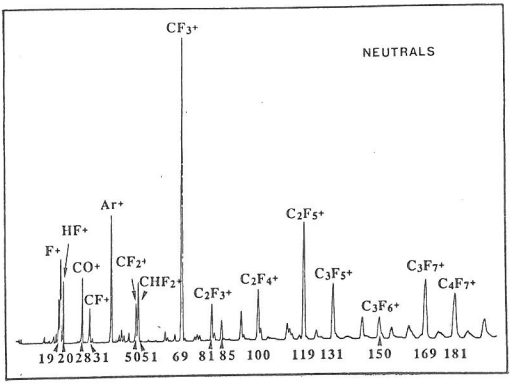


Fig.4 - QMS mass spectra of the stable neutral phase: OP : $8x10^{-4}$ mbar cf. (b) in Fig.2; $I_D$ = 2.3 A; $V_D$ = 120 V.

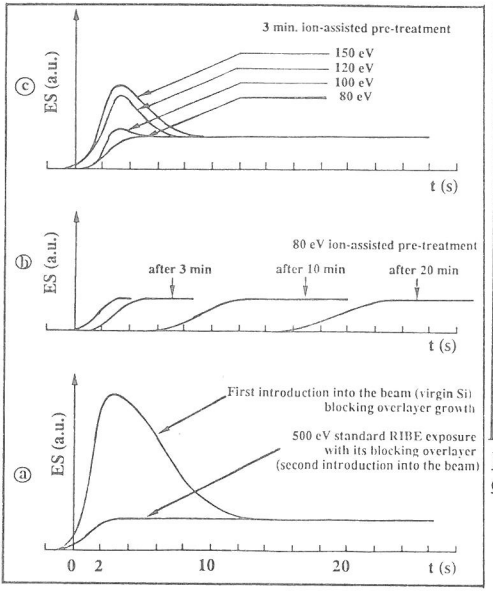


Fig.5 - Etch signatures of Si after pre-treatment exposures.

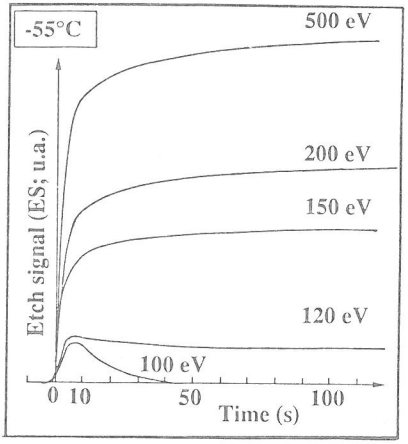


Fig.8 - Etch signature of $SiO_2$ *versus* ion energy at a target temperature of -55°C.

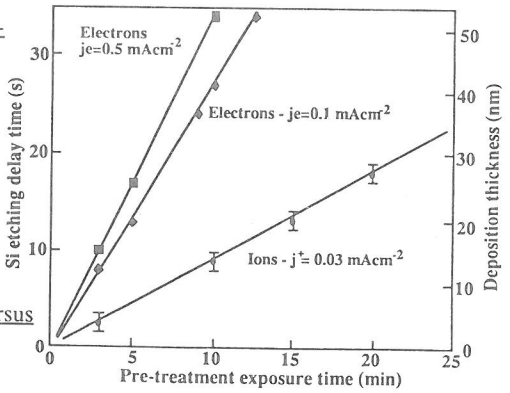


Fig.6 - Etch delay time (500 eV) versus pre-treatment exposure time.

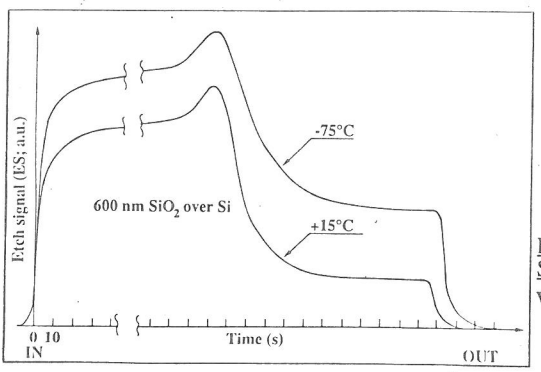


Fig.7 - Etch signatures of a 600 nm $SiO_2$ over Si at +15°C and -75°C :
$W^+$ = 500 eV; $\theta = 0°$; $j^+ = 0.4$ mAcm$^{-2}$; $p_S = 8 \times 10^{-4}$ mbar.