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Citation for published version (APA):

DOI:
10.1116/1.580205

Document status and date:
Published: 01/01/1996

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Ion-assisted Si/XeF$_2$ etching: Temperature dependence in the range 100–1000 K

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(Received 14 November 1995; accepted 14 June 1996)

The Ar$^+$-ion enhanced Si(100)/XeF$_2$ reaction is studied in a multiple beam setup for silicon temperatures from 100 K up to 1000 K. The XeF$_2$ flux is 2.7 monolayers/s and the Ar$^+$ flux 0.033 monolayers/s at an energy of 1000 eV. Both the XeF$_2$ consumption and the SiF$_x$ production are measured by mass spectrometry. The enhancement of the etch rate peaks around 250 K as is observed in both the XeF$_2$ and SiF$_x$ signals. The gradual decline above 250 K is attributed to a diminished surface fluorination and XeF$_2$ precursor concentration. The dropoff below 250 K is presumably caused by sputtering of the XeF$_2$ precursor, as is concluded from the temperature dependence of the XeF$_2$/XeF$_2$ signal ratio. Around 175 K this decrease is so strong that the ions seem to no longer enhance, but rather reduce, the etch rate. Below 150 K the ions are driving the etch process. In this range the spontaneous process is blocked by XeF$_2$ condensation, but the ion-assisted process continues due to sputtering or dissociation of the condensate. © 1996 American Vacuum Society.

I. INTRODUCTION

Ion-assisted etching is considered to be the leading mechanism in plasma etching for microelectronic device fabrication. Therefore a lot of surface science studies have been devoted to this subject. In these studies the complexity of the plasma environment was avoided by using separately controllable beams of ions and reactive neutrals in an ultrahigh vacuum (UHV) setup. Coburn and Winters were the first to apply this approach. In their experiment XeF$_2$ was used as the reactive neutral, because the XeF$_2$ molecule is a convenient source of F atoms, which are the main etchant in many plasmas. The ion beam consisted of Ar$^+$ ions in order to exclude any chemical effects of the ions. They discovered a large synergetic effect: the silicon etch rate obtained with both beams simultaneously was much higher than the sum of the etch rates with each beam separately. From all the subsequent studies that were performed, it can be concluded that there are basically two mechanisms that contribute to the observed enhancement: physical sputtering (the direct release of surface species upon ion impact) and chemical sputtering (the production of weakly bound species by ion bombardment followed by desorption).

Recently there has been increasing interest in low temperature plasma etching. It was found that lower substrate temperatures can lead to an increase in anisotropy and a decrease in substrate damage. This motivated a beam study on the influence of sample temperature in ion-assisted processes. Very few studies have been done on this subject. Sanders et al. studied the product and energy distribution for the Si/Cl$_2$/Ar$^+$ system in the temperature range from 300 K up to 1000 K. McNevin and Becker studied the GaAs/Cl$_2$/Ar$^+$ system in the narrow temperature range of 300–500 K. Studies below room temperature were performed by Oostra et al. for Si/ SF$_6$/Ar$^+$ etching at temperatures from 20 K up to 100 K, and very recently by Mullins and Coburn for the Si/F/Ar$^+$ system in the temperature range 77–300 K. For the Si/XeF$_2$/Ar$^+$ system only some early work by Balooch et al. in the high temperature range (300–1300 K) is known to the authors.

Apart from this lack of data, another motivation for the present work is found in the remarkable effects that were observed in the temperature dependence of spontaneous Si/ XeF$_2$ etching: the spontaneous reaction can be enhanced enormously by decreasing the sample temperature, up to an efficiency of near 100% at 150 K. However, below this temperature the spontaneous etching stops due to XeF$_2$ condensation.

In this article quantitative data will be presented on the temperature dependence of Si/XeF$_2$/Ar$^+$ etching for temperatures ranging from 100 K up to 1000 K. In Section II we will give a short description of the experimental setup. Subsequently we will present the results on the XeF$_2$ reaction and SiF$_x$ production in Sections III and IV, and discuss them in Section V. In Section VI we will summarize our conclusions.

II. EXPERIMENTAL SETUP

A short description of the features used in this study will now be given. For a detailed description of the total multiple beam setup, we refer to a previous article.

The silicon sample [Si(100), n type, phosphorus, 2–3 ω cm] is clamped to a nickel sample holder, positioned in a UHV chamber (<10$^{-8}$ Torr) at the intersection of the XeF$_2$ and the Ar$^+$ beam. Heating of sample and holder is achieved by means of a coaxial heating wire, and cooling by a liquid nitrogen vessel. The temperature is measured by a thermocouple in the holder, just below the silicon sample. To be able to derive the ion flux from the sample current, the samples are biased at +100 V to prevent secondary electron emission.
The XeF$_2$ gas is supplied by means of a multicapillary effusive gas source. The XeF$_2$ flux can be varied from 0.06 monolayer (ML) s$^{-1}$ up to 3.6 ML s$^{-1}$, on the 3-mm-diam detection area of the sample. The unit ML, i.e., monolayer, is defined as the surface density of the sample studied [Si(100): 1 ML = 6.86 x 10$^{18}$ m$^{-2}$].

The Ar$^+$ ions are produced in a Kratos WG 537 macrobeam ion gun. The beam is carefully positioned by means of two deflection plates and the shape can be described as a Gaussian envelope with a full width at half-maximum (FWHM) of 5 mm. The ion energy can be varied from 0.2 up to 2.5 keV, and fluxes up to 0.1 ML s$^{-1}$ on the 3 mm detection area can be reached. The ion beam was switched on and off by switching the acceleration voltage for easy comparison with spontaneous etching.

The mass spectrometer is positioned along the surface normal in a separate UHV chamber (< 10$^{-9}$ Torr). Due to two differential pumping stages, only a small fraction of the species desorbing from the sample reaches the detector. However, this assures that 85% of the detection signal is caused by species that desorb directly from the detection area of the sample and without wall collisions.

For the experiments described in this article an ion energy of 1.0 keV was used and an Ar$^+$ flux of 3.3 x 10$^{-2}$ ML s$^{-1}$. The XeF$_2$ flux was 2.7 ML s$^{-1}$, which implies an ion over neutral flux ratio $R$ of 0.012. From a previous study on the flux dependence we conclude that for this ratio the etch rate is limited by the ion flux.19 The sample temperature was varied from 100 K up to 1000 K.

The experimental procedure was identical to the one used in previous work.19 Before mounting, the silicon sample was cleaned with HF to remove native oxide. Then the SiF$_3^+$, SiF$_4^+$, XeF$_2^+$ and XeF$^+$ mass spectrometer signals were monitored during steady state spontaneous etching (only XeF$_2$) and steady state ion-assisted etching (XeF$_2$ + Ar$^+$). In the spontaneous etching period the inert nickel sample holder was occasionally shifted into the detection area for a few minutes to calibrate the detection signals.18 All signals were corrected for background influences and the temperature dependence of the detection probability.18 During this study several silicon samples were used and each sample was used for several experiments.

III. REACTION OF XeF$_2$

The reaction of XeF$_2$ was monitored by the XeF$^+$ and XeF$_2^+$ mass spectrometer signals. In previous studies by our group,17,18,20 it was found that for spontaneous etching the ratio of these signals is independent of etching parameters like the XeF$_2$ flux or the sample temperature. Therefore it was concluded that both signals originate from the XeF$_2$ molecule and that there is no XeF desorption or fractional usage of XeF$_2$. However, in ion-assisted etching experiments at room temperature,19 it was found that the $I$(XeF$^+/I$(XeF$_2^+$) signal ratio increases from 2.0 during spontaneous etching up to 2.6 for an ion/neutral flux ratio of $R$ = 0.15. This led to the conclusion that a significant XeF flux leaves the surface. We explain this effect as sputtering or dissociation of the XeF$_2$-precursor by the ions.

In the present work we used a constant ion to neutral flux ratio ($R$ = 0.012) and varied the sample temperature. The effect on the XeF$^+$ to XeF$_2^+$ signal ratio is shown in Fig. 1. We find that for high sample temperatures the signal ratio approaches the value for spontaneous etching, as was observed previously.21 However, for lower temperatures the signal ratio increases exponentially. This confirms the hypothesis that this effect is related to sputtering or dissociation of the XeF$_2$ precursor, since the precursor concentration was also shown to increase exponentially below 300 K.17 As is shown in Fig. 1, the temperature dependence of the signal ratio is described quite well by an Arrhenius curve with an activation energy of 94 meV. This is more than the activation energy of 32 meV, which was found for the low temperature increase of the spontaneous etch rate.17 We suspect that this rise in the apparent activation energy is caused by a reduction in surface roughness due to ion bombardment. For temperatures of 150 K and below the signal ratio decreases again. This may not be surprising, since this is the range in which XeF$_2$ condensation becomes significant and new effects, like sputtering of condensed species, might occur.

We express the reaction of XeF$_2$ in the reaction coefficient $\epsilon$, which is defined in agreement with our previous work as

$$\epsilon = \frac{\Phi_s(XeF_2) - \Phi(XeF_2)}{\Phi_s(XeF_2)}.$$  

Here, $\Phi_s(XeF_2)$ is the incident flux of XeF$_2$ molecules and $\Phi(XeF_2)$ the flux of XeF$_2$ desorbing from the sample. We measure the reaction coefficient by comparing the XeF$_2$ signals from the silicon sample to the signals from an inert nickel reference surface.18 Since the two XeF$_2$ ionic frag-
ments are no longer proportional during ion-assisted etching, this results in two different reaction coefficients $\epsilon_X$ and $\epsilon_Y$. Due to the ion-induced dissociation of XeF$_2$, as discussed above, $\epsilon_X$ is larger than $\epsilon_Y$, but the difference was always less than 12%. In this article we will approximate $\epsilon_X$ by $\epsilon_Y$, since $\epsilon_X$ is the largest, and presumably the more relevant, signal.

In the upper panel of Fig. 2 the reaction coefficients for spontaneous and ion-assisted etching are plotted as a function of sample temperature. The behavior that was observed for steady state spontaneous etching (after Ref. 17) is shown by the dashed curve for comparison. When we compare the data, we find that most of the present spontaneous reaction coefficients, measured in between the periods with ion bombardment, are significantly lower than those obtained previously for continuous spontaneous etching. This was noticed before for the room temperature ion-assisted experiments. We use this approximation because we know the calibration factors $C_{SiF_4}$ for the detection of SiF$_4$, and $C_{SiF_2}$ for the detection of SiF$_2$ as SiF$^+$. These calibration factors can be determined from a simple F-atom mass balance for spontaneous etching, where the product distribution is known quite well. At the end of this section we will discuss to what extent this approximation is valid.

We will first analyze the SiF$_3$ signal. In Fig. 3 we have plotted the behavior of the raw SiF$_3$ signals for sample temperatures of 300 K, 200 K, and 175 K. The SiF$_3$ production is measured by the SiF$^+$ and SiF$_2$ mass spectrometer signals. We will use the approximation that the SiF$_3$ signal originates from thermally desorbing SiF$_4$ and the SiF$^+$ signal (after correction for the SiF$_4$ contribution) from thermally desorbing SiF$_2$. This is the same approach as was used for the room temperature ion-assisted experiments. We use this approximation because we know the calibration factors $C_{SiF_4}$ for the detection of SiF$_4$, and $C_{SiF_2}$ for the detection of SiF$_2$ as SiF$^+$. These calibration factors can be determined from a simple F-atom mass balance for spontaneous etching, where the product distribution is known quite well. At the end of this section we will discuss to what extent this approximation is valid.

**IV. PRODUCTION OF SiFx**

The SiF$_x$ production is measured by the SiF$^+$ and SiF$_2$ mass spectrometer signals. We will use the approximation that the SiF$_3$ signal originates from thermally desorbing SiF$_4$ and the SiF$^+$ signal (after correction for the SiF$_4$ contribution) from thermally desorbing SiF$_2$. This is the same approach as was used for the room temperature ion-assisted experiments. We use this approximation because we know the calibration factors $C_{SiF_4}$ for the detection of SiF$_4$, and $C_{SiF_2}$ for the detection of SiF$_2$ as SiF$^+$. These calibration factors can be determined from a simple F-atom mass balance for spontaneous etching, where the product distribution is known quite well. At the end of this section we will discuss to what extent this approximation is valid.

We will first analyze the SiF$_3$ signal. In Fig. 3 we have plotted the behavior of the raw SiF$_3$ signals for temperatures of 300 K, 200 K and 175 K. For 300 K we observe the familiar behavior: When the ion beam is switched on during steady state spontaneous etching conditions, we first observe a transient and subsequently the signal reaches a higher steady state level. This behavior was also observed for all SiF$_3$ signals above room temperature and for the SiF$^+$ signal over the whole temperature range. However, when the sample temperature is decreased, the behavior of SiF$_3$ changes significantly. The spontaneous and ion-assisted signals are both seen to grow at lower temperature, but the increase in the spontaneous signal is much stronger. The result is that, at 200 K, the enhancement has disappeared and, at 175 K, the SiF$_3$ signal is even reduced by the ion bombardment. Fur-
thermore, we find that after the ion beam is switched off it takes a while before the SiF\textsubscript{3}\textsuperscript{+} has returned to the original spontaneous etching level.

Let us now compare the temperature dependence of this SiF\textsubscript{3}\textsuperscript{+} signal to that of the SiF\textsuperscript{+} signal. The ratio of these signals is shown in Fig. 4. For spontaneous etching the temperature dependence of the signal ratio is similar to what was observed previously.\textsuperscript{17} Below 600 K the signals are largely attributed to SiF\textsubscript{2} production. The maximum around 300 K is explained by a maximum in the Si\textsubscript{2}F\textsubscript{6} contribution (<10%). Above 600 K the signal ratio increases due to the production of SiF\textsubscript{2}.\textsuperscript{22}

For ion-assisted etching the signal ratio is found to be larger than for spontaneous etching at temperatures below 700 K. This implies the production of SiF\textsubscript{3}, radical species, presumably by physical sputtering processes. Above 700 K the signal ratios for spontaneous and ion-assisted etching become quite comparable, which could indicate that the product distribution is similar. A special situation occurs below 150 K: no SiF\textsubscript{2} signals are detected during spontaneous etching due to XeF\textsubscript{2} condensation. By contrast, for ion-assisted etching these signals remain nonzero, their low ratio indicating mainly SiF\textsubscript{4} production.

In order to obtain quantitative information on the formation on the production of SiF\textsubscript{4} and SiF\textsubscript{2} we introduce the production coefficients \(\delta_4\) and \(\delta_2\). Analogous to the reaction coefficient \(\delta_3\), this production coefficient \(\delta_2\) is defined as the fraction of the incident fluorine flux that leaves the sample as an SiF\textsubscript{2} product:

\[
\delta_2 = \frac{\Phi_{\text{SiF}_2}}{\Phi_{\text{XeF}_2}} = \frac{I(\text{SiF}_2^+)}{I(\text{SiF}_4^+)} C(\text{SiF}_4^+;\text{SiF}_2^+) / C(\text{SiF}_4^+;\text{XeF}_2^+).
\]  

For the present experiments the calibration coefficient was found to be \(C(\text{SiF}_4^+;\text{SiF}_2^+) = 4.0 \times 10^{-4} \text{ ML count}^{-1}\). This led to the production coefficients displayed in Fig. 6; again the difference between the ion-assisted and spontaneous production coefficients is plotted in the lower panel of the figure.

Now we return to the assumptions made at the beginning of this section, i.e., that the SiF\textsubscript{3}\textsuperscript{+}-signal can be attributed to thermally desorbing SiF\textsubscript{4} and the SiF\textsuperscript{+} signal to thermally desorbing SiF\textsubscript{2}. If these assumptions are correct, the reaction coefficient \(\epsilon\) should equal the sum of the production coefficients \(\delta_4\) and \(\delta_2\), as a consequence of F-atom conservation. As can be seen from Fig. 7, this is clearly not the case. The difference between the reaction and the total production coefficient changes depend on the sample temperature. At 300 K the data are in agreement with previous observations.\textsuperscript{19} There, it was argued that the difference \((\epsilon - \delta_4 - \delta_2)\) may only be partially explained by other reactions, while the larger part was attributed to SiF\textsubscript{3} radicals desorbing with
superthermal energies, as observed by Haring et al. These superthermal radicals have a reduced detection probability and therefore the real production coefficient is higher. For the temperature range covered in this study, however, the difference between reaction and production coefficients can become rather large and can have either sign. Especially below 200 K the value of \( \epsilon - \delta_4 - \delta_2 \) increases dramatically.

In this regime the explanation is that XeF\(_2\) condensation becomes important, which means that not all of the consumed XeF\(_2\) is used for SiF\(_x\) production. It is clear that a simple description, with thermal SiF\(_4\) species and superthermal SiF\(_2\) species, offers only a crude approximation of the complex product distribution during ion-assisted etching. To achieve a better insight in the temperature dependence of this product distribution more information is required, e.g., the energy distribution of the desorbing species. Even so, the present data allow one to draw a few interesting conclusions.

V. DISCUSSION

Our previous room temperature experiments\(^1^9\) were found to be rather well described by a four-step mechanism consisting of surface fluorination, spontaneous etching, physical sputtering and chemical sputtering. For the temperature range studied here, such a simplified model cannot be used, since it was shown above that a production described on the basis of SiF\(_4\) and SiF\(_2\) alone is not adequate. Therefore we are limited to a rather qualitative description.

Obviously, the effect of the ions on the etching process can be inferred from the reaction coefficient \( \epsilon \) as well as from the production coefficients \( \delta_4 \) and \( \delta_2 \). Let us first consider the behavior of \( \epsilon \).

From the bottom panel of Fig. 2 we observe a maximum enhancement around 250 K. The smaller enhancement above this temperature may be explained by the decrease in the XeF\(_2\) precursor concentration at higher temperature. In addition a diminished surface fluorination may play a role: We expect the thickness of the SiF\(_x\) reaction layer to decrease at higher temperatures, because SiF\(_x\) radical species like SiF\(_2\) become volatile at these temperatures. This will reduce the probability of both physical and chemical sputtering processes and thus the ion enhancement.

For temperatures below 250 K the enhancement in \( \epsilon \) by the ions is also reduced. The likely explanation is that the ions sputter away part of the XeF\(_2\) precursors which were seen to promote the etching process (see upper panel of Fig. 2). Furthermore, processes that do not involve the XeF\(_2\) precursor, like physical sputtering, make a significant temperature independent contribution to the ion-assisted etch rate. Both effects contribute to a decrease in ion enhancement below 250 K.

For temperatures of 175 K and less the XeF\(_2\) reaction coefficient \( \epsilon \) is seen to decrease by ion bombardment rather than to increase. This is a result of the definition (Eq. (1)). In this temperature range XeF\(_2\) condensation takes place and in the absence of ion bombardment the reaction coefficient becomes unity by definition, but loses its significance. By contrast, the ion-assisted reaction coefficient does not reach unity, since we still measure some XeF\(_2\) signal due to sputtering of the condensate.

The production coefficient \( \delta_4 \) is affected by the ions in much the same way as the reaction coefficient, also showing a peak enhancement around 250 K (see bottom panel of Fig. 5). Again, the smaller enhancement below 250 K is attributed to XeF\(_2\) precursor sputtering. Below 150 K, however, a
new effect is visible. At this point the spontaneous etching process has stopped due to the blocking effect of the XeF₂ condensate (see upper panel of Fig. 5), but there is still SiF₄ production during ion bombardment. This means the ions are now driving the etch process. Probably, the ions sputter condensed XeF₂ and enable the etching process to continue. The reduction in the production coefficient as compared to temperatures above 150 K indicates that the flux ratio \( \frac{R_{\text{e}}(\text{Ar}^+)}{R_{\text{e}}(\text{XeF}_2)} = 0.012 \) used in the present study is too small to completely prevent XeF₂ condensation.

Finally, we turn to \( \delta_2 \) (Fig. 6). The maximum enhancement of this coefficient seems to be located at 200 K, at a slightly lower temperature than for \( \epsilon \) and \( \delta_4 \). But in contrast to \( \epsilon \) and \( \delta_4 \), the dropoff of \( \delta_2 \) below 200 K is now related to an absolute decrease in the SiF⁺ signal and not to a relative decrease of the ion-assisted contribution with respect to the spontaneous contribution; the latter is absent. We expect that here the increased coverage of the silicon surface with XeF₂ precursor species (XeF₂ condensate, below 150 K) inhibits physical sputtering of SiF₂ species, which is thought to be the main source of the SiF⁺ signal.

Summarizing, from the measurements presented in this article we conclude that the influence of ions on the Si/XeF₂ reaction is quite different in three temperature regimes.

1. For temperatures above 250 K the ions enhance the etch reaction. This is the most common behavior that has been observed for many other systems, and it is attributed to a combination of physical and chemical sputtering mechanisms. In this regime the enhancement decreases with increasing temperature, which was also observed by Balooch et al.\textsuperscript{10} We attribute this to a decrease in the surface fluorination and the XeF₂ precursor concentration.

2. If the temperature decreases from 250 K down to 150 K, the ion enhancement is reduced. This is attributed primarily to sputtering of the XeF₂ precursor. A reduction of the etch rate by ion bombardment has been observed before for other systems like Al(100)/Cl₂/Ar⁺ and Cu/Cl₂/Ar⁺.\textsuperscript{23} The occurrence of both ion enhancement and ion reduction in a single system has only been observed for Nb/XeF₂/Ar⁺. The NbF⁺ signal was found to be reduced by ion bombardment at a low XeF₂ flux, whereas a slight enhancement was observed for a high XeF₂ flux.\textsuperscript{23}

3. In the temperature regime below 150 K, the spontaneous etching process ceases, whereas the ion-assisted etching continues. We suspect that the ion bombardment prevents the XeF₂ from forming a blocking overlayer. Another possibility is that the ions actually induce a reaction between the XeF₂ condensate and the silicon. In that case, similar effects occur as were observed by Oostra et al.\textsuperscript{14} They found that Ar⁺ bombardment of a SF₆ condensate layer on silicon led to SiF₄ production.

Our observations are very similar to the recent work by Mullins and Coburn.\textsuperscript{15} In their experiments on the SiF/Ar⁺ system, the spontaneous etch rate stopped around 77 K by Si₂F₆ condensation, while etching continued during ion bombardment. Except for the condensation temperature, the main difference between both systems is that the spontaneous Si/F reaction decreases gradually with decreasing temperature, while the Si/XeF₂ reaction increases sharply and then ceases quite abruptly by the XeF₂ condensation.

We expect that in the complex environment of plasma-etching processes, precursor mediated reactions will also be significant. Therefore the influence of ions may not be limited to an enhancement of the etching process by physical or chemical sputtering processes. In some circumstances, especially at low sample temperatures, the ions might actually reduce the etch rate by sputtering of precursor species. Furthermore, at temperatures where plasma elements condense on the sample surface, sputtering of condensed species or ion-induced dissociation reactions become important. These effects are probably the explanation for the high anisotropy obtained in cryogenic etching.\textsuperscript{7,10,11}

VI. CONCLUSIONS

We found that the enhancement of the XeF₂ consumption by Ar⁺ ion bombardment reaches a maximum at a silicon temperature of 250 K. The decreased enhancement for temperatures below 250 K is accompanied by sputtering of the XeF₂ precursor. A similar temperature dependence was observed for the enhancement in SiF₄ production. The SiF₄ production is actually reduced by ion bombardment below 200 K. While the spontaneous etching process ceases for temperatures of 150 K and below, it was found that the etching continued during ion bombardment. This seems to offer an attractive method to achieve highly anisotropic etching in this system. A simple interpretation of the SiF⁺ and SiF₂ mass spectrometer signals in terms of SiF₂ and SiF₄ products was not possible. The product distribution was found to be complex and temperature dependent.

The measurements demonstrate that, apart from physical and chemical sputtering mechanisms, sputtering and dissociation of adsorbed precursors or condensed species can also be significant effects in ion-assisted processes.