EINDHOVEN UNIVERSITY OF TECHNOLOGY

Reaction layer dynamics in ion-assisted Si/XeF2 etching: temperature dependence

Citation for published version (APA):
Sebel, P. G. M., Hermans, L. J. F., & Beijerinck, H. C. W. (2000). Reaction layer dynamics in ion-assisted Si/XeF2 etching: temperature dependence. *Journal of Vacuum Science and Technology A*, *18*(6), 2759-2769. https://doi.org/10.1116/1.1316102

DOI:
10.1116/1.1316102

Document status and date:
Published: 01/01/2000

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:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 04. Oct. 2023

Reaction layer dynamics in ion-assisted Si/XeF_2 etching: Temperature dependence

P. G. M. Sebel, L. J. F. Hermans, and H. C. W. Beijerinck[a)]
Physics Department, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 3 February 2000; accepted 14 August 2000)

We study the dynamics of the reaction layer during Ar^+ ion-assisted Si etching by XeF_2 in the temperature range $T = 150-800$ K. Depending on temperature, the etch rate can be enhanced a factor of 8 by ion bombardment. The dynamics are studied with ion-pulse measurements on a time scale of 1–100 s in a molecular beam setup. A reaction layer with a submonolayer fluorine coverage and dangling bonds is found to be formed on the Si(100) surface during ion bombardment. The dangling bond concentration increases with ion flux and is independent of temperature in the range 150–600 K. Chemisorption on these dangling bonds results in a higher reaction probability of XeF_2. The temperature dependence of the reaction probability of XeF_2 is fully determined by the temperature dependence of the XeF_2 precursor state. A simple model gives a very good description of the reaction probability as a function of both temperature and ion flux. The model description of the behavior of the precursor concentration as a function of ion flux and temperature is confirmed by ion pulse measurements on a time scale of 1 s. Further, it is concluded that the mechanisms for enhanced SiF_4 formation during ion bombardment are the same over the temperature range studied.
© *2000 American Vacuum Society.* [S0734-2101(00)04106-3]

I. INTRODUCTION

Etching is one of the important steps in the production of semiconductor devices. The characteristics of the etching process are largely determined by the reaction layer formed on the surface. It can be defined as the surface layer consisting of intermediate reaction products and residues of the etchant. The reaction layer can influence all steps of the etching process: etchant adsorption, reaction product formation, and release of reaction products.[1] The role of the reaction layer depends on the specific etching process. In the case of Si etching with CF_x gases, the reaction layer limits the supply of reactants (step 1).[2] When Si is etched by XeF_2, Vugts *et al.* showed that it is the reaction layer's fluorine content which determines the spontaneous etch rate (step 2).[3] Finally, the condensation of Si_2F_6 at 77 K which blocks the etching process is an example of a case in which the reaction layer limits the release of reaction products (step 3).[4]

Etching of Si by XeF_2 and Ar^+ is often used as a model system to study the fundamental mechanisms behind etching.[5] However, despite its importance, little attention has been paid to the role of the reaction layer, particularly in the case of ion-assisted etching.[6–8]

The formation of a reaction layer during spontaneous etching (i.e., without ions) at ordinary temperatures can be summarized by the following steps.[3]

(i) Physisorption of XeF_2 in a precursor state.
(ii) Chemisorption of the precursors. On a clean surface, chemisorption first takes place at dangling bonds. Next, a SiF_x like monolayer coverage is formed which changes into a multilayer coverage with Si_xF_y chains on longer time scales.[9]
(iii) Desorption of chemisorbed surface species (SiF_2).
(iv) Formation of volatile reaction products (SiF_4), when physisorbed XeF_2 reacts with surface species.

The first two steps contribute to the formation of the reaction layer while the last two steps remove surface species. A steady-state reaction layer is formed when there is a balance between steps (i) and (ii) on one side and steps (iii) and (iv) on the other side. In the presence of ions, steps (iii) and (iv) are enhanced, which results in a shift of the balance. As a function of the ion flux, this was discussed in a previous article.[10]

Temperature also influences the formation of the reaction layer and will shift the equilibrium. In the case of spontaneous etching the dynamics of the reaction layer as a function of temperature were studied by Vugts *et al.*[11]

In this article we study the dynamics of the reaction layer during ion-assisted etching in the temperature range 150–800 K. The measurements were done with an ion-to-neutral flux ratio $R = 0.025$. For this flux ratio, it was concluded that the adsorption of fluorine on dangling bonds created by the ions plays an important role at room temperature.[10] The total reaction probability for this flux ratio is $\epsilon \approx 0.72$, which is near the maximum reaction probability of $\epsilon = 0.88$ in the limit of high flux ratios.

This article is organized as follows. After a brief description of the experimental setup in Sec. II, the dynamics of the reaction layer on a time scale of 100 s will be discussed in Sec. III. On this time scale, given a neutral flux of 0.55 ML/s, the reaction layer created during spontaneous etching is removed when the ions are switched on and a new steady-state situation is reached. When the ions are switched off again after 180 s, the reaction layer will reconstruct to the

[a)]Electronic mail: H.C.W.Beijerinck@phys.tue.nl

initial situation of spontaneous etching. This process is studied by looking at the response of the SiF_4 production, since this reaction product is formed within the reaction layer and thus gives information about the reaction layer. All experimental evidence leads to the conclusion that, independent of temperature, a reaction layer with a submonolayer fluorine coverage is formed in steady-state ion-assisted etching.

Based on this conclusion, a model is presented in Sec. IV to describe the steady-state values of the reaction probability of XeF_2, as a function of both temperature and ion flux. This model gives a good description of the reaction probability and indicates that the precursor concentration decreases under ion bombardment, especially at low temperatures.

In Sec. VI, the behavior of the precursor layer is studied by short-pulse measurements on a time scale of seconds. These pulse measurements confirm the model and also show that SiF_4 is formed by the same mechanisms over the whole temperature range. Finally, the conclusions are summarized in Sec. VII.

II. EXPERIMENTAL SETUP

Only the basic features of the experimental setup are described here. More details are given in a previous article.[12] The Si(100) sample (n type, 30–70 Ω cm) is placed at the intersection of the XeF_2 and Ar^+ beams in an ultrahigh vacuum (UHV) chamber (5×10^{-8} mbar). The sample is mounted on a nickel sample holder which is heated by means of a coaxial heating wire and cooled by a liquid nitrogen vessel. The temperature of the sample is measured by a thermocouple which is placed 1 mm behind the sample in the sample holder. In the experiments a XeF_2 flux $\Phi_s(XeF_2)=0.55$ ML/s and an ion flux $\Phi_s(Ar^+)=0.014$ ML/s were used. This corresponds to an ion-to-neutral flux ratio $R=0.025$. From previous measurements it is concluded that for such low flux ratios, the etch rate is already limited by the neutral flux. During the experiments several Si samples, which were cleaned by HF to remove native oxide, were used.

The etching reaction is monitored by a quadrupole mass spectrometer (QMS) positioned along the surface normal of the sample in a separate UHV chamber (1×10^{-8} mbar). The geometry of the flow resistances ensures that 85% of the mass spectrometer signal consists of species that reach the mass spectrometer directly from the sample without any wall collisions. To measure the XeF_2 flux we used the XeF^+ signal since this is the largest signal.

The reaction probability ϵ of the XeF_2 gas is measured by comparing the XeF_2 flux $\Phi(XeF_2)$ from the Si sample to the flux $\Phi_s(XeF_2)$ diffusively scattered from an inert nickel reference plate

$$\epsilon=\frac{\Phi_s(XeF_2)-\Phi(XeF_2)}{\Phi_s(XeF_2)}. \tag{1}$$

The SiF_4 signal is presented in terms of the production coefficient δ_4, defined as the probability of an incoming fluorine atom to form SiF_4, as given by

$$\delta_4=\frac{4\Phi(SiF_4)}{2\Phi_s(XeF_2)}. \tag{2}$$

The production coefficient δ_4 is calibrated from a fluorine mass balance during spontaneous etching in steady state at room temperature when SiF_4 is the only reaction product, hence

$$\epsilon_0=\delta_{4,0}. \tag{3}$$

Here, the subscript ''0'' indicates the steady-state values during spontaneous etching. For the steady-state values during ion-assisted etching, we use the subscript ''ion.''

To include the temperature-dependent detection probabilities of the QMS, all measured mass spectrometer signals $I(T)$ (both the XeF^+ and SiF_3^+) are corrected to I_{corr}, given by

$$I_{corr}=I(T)\left(0.15+0.85\sqrt{\frac{T_{room}}{T}}\right). \tag{4}$$

Here it is assumed that 85% of the signal consists of species directly leaving the surface with a velocity distribution corresponding to the surface temperature T, while the other 15% consists of species which reach the mass spectrometer after at least one wall collision and thus have a velocity distribution corresponding to the wall temperature $T=T_{room}$. For the XeF_2 signal scattered from the nickel, a different calibration curve is used, because at high temperatures nickel cannot be considered to be inert to XeF_2.[3]

Ion pulses are created by switching the acceleration voltage of the ion gun with a relay. The response time of this system is 24.8 ± 0.1 ms for 2.5 keV ions, much faster than the time scale of our measurements. In the long ion pulses, the ion beam is switched manually and the mass spectrometer signals are averaged for one second. For the short-pulse measurements, the SiF_4 and XeF_2 signals are measured with a multiscaler which has 256 channels and user-defined channel times. While counting, the multiscaler also produces user-defined pulses (5 V) to switch the ion beam. In the short-pulse experiments, channel times of 50 ms have been used and the ion beam was switched on for 75 channels and switched off for 175 channels. Before each short-pulse experiment it is ensured that a steady-state reaction layer during spontaneous etching is formed. Then the ion beam is switched on for about 120 s so a steady-state situation during ion-assisted etching is reached. Then, the response of the SiF_2 and XeF_2 signal is measured for 15 subsequent ion pulses.

III. LONG-PULSE MEASUREMENTS

A typical response of the production coefficient δ_4 to an ion pulse of 180 s at room temperature is shown in Fig. 1. In this figure, the parameters used to characterize the SiF_4 response as a function of the temperature are indicated. When the ions are switched on, a peak in SiF_4 production is observed. From the area under this transient peak, the amount of fluorine L_{loss} released from the reaction layer can be calculated. After the transient peak, a steady-state value $\delta_{4,ion}$ is

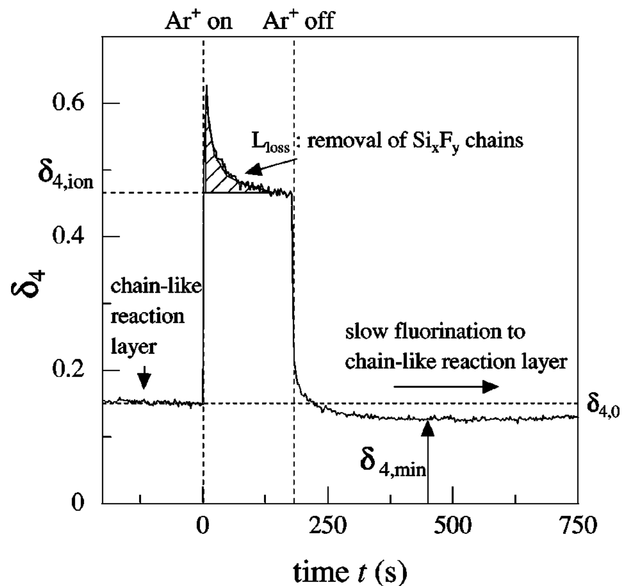

FIG. 1. Typical response of the SiF_4 production coefficient δ_4 to an ion pulse of 180 s at a sample temperature of 300 K. During the peak an amount of fluorine L_{loss} is released from the surface. Here, the chainlike reaction layer is removed and a reaction layer with a submonolayer coverage is formed. After the ion switch-off, δ_4 drops below the spontaneous value $\delta_{4,0}$ to a minimum value of $\delta_{4,min}$. On the time scale of 1000 s the chainlike reaction layer is reconstructed again.

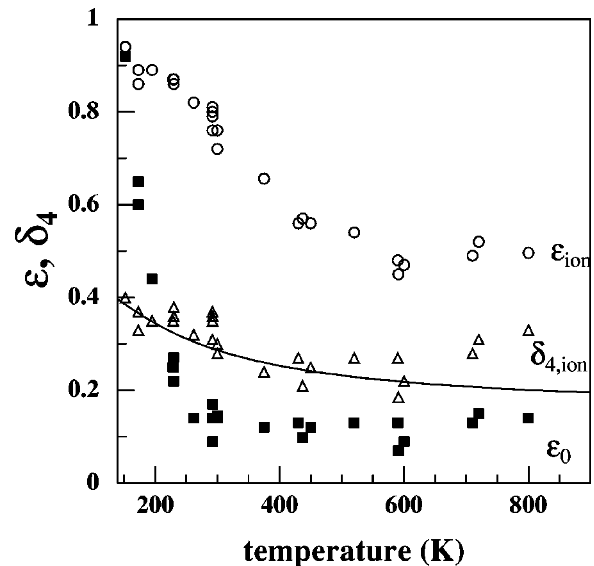

FIG. 2. Steady-state values of ϵ_0, ϵ_{ion}, and $\delta_{4,ion}$ as a function of temperature in the range $T=150-800$ K. Please note that $\epsilon_0=\delta_{4,0}$. The solid line represents the SiF_4 production coefficient, as calculated with the precursor model assuming that 40% of the reacting XeF_2 molecules form SiF_4 (Sec. V).

reached. Finally, when the ions are switched off, the production coefficient δ_4 drops below the spontaneous value $\delta_{4,0}$ and reaches a minimum value $\delta_{4,min}$ after some time. On a time scale on the order of 1000 s, the steady-state value $\delta_{4,0}$ is recovered. Because of the influence of surface roughness on the etching process as a function of temperature,[13] these parameters will only be discussed qualitatively as a function of temperature.

A. Steady-state values

The steady-state values ϵ_0, ϵ_{ion}, and $\delta_{4,ion}$ for the measured flux ratio $R=0.025$ are plotted in Fig. 2 as a function of the temperature. We see that the spontaneous SiF_4 production $\delta_{4,0}=\epsilon_0$ increases with decreasing temperature from $\delta_{4,0}=0.15$ at room temperature to $\delta_{4,0}=0.95$ at 150 K. From a comparison of $\delta_{4,0}$ with $\delta_{4,ion}$ we see that the steady-state SiF_4 production is enhanced by the ions, while for lower temperatures it is decreased by the ions. It is also seen that $\delta_{4,ion}$ increases slightly with decreasing temperature. In contrast to the production coefficient $\delta_{4,ion}$, the reaction probability ϵ_{ion} always increases under ion bombardment. The difference $\epsilon_{ion}-\delta_{4,ion}$ is due to SiF_2 production.[13]

The steady-state values during spontaneous and ion-assisted etching show the same trend as reported by Vugts *et al.*[13] In the present study higher values of $\delta_{4,ion}$ and ϵ_{ion} are measured as compared to the results of Vugts *et al.* because of the higher ion-to-neutral flux ratio by a factor of 2 ($R=0.025$ vs $R=0.012$). For a detailed discussion of the steady-state values as a function of temperature, refer to Ref. 13. In this section we focus on the dynamics of the reaction layer.

B. Transient response

In Figs. 3 and 4 the response of the production coefficient δ_4 to an ion pulse of 180 s is shown at temperatures in the range $T=150-260$ K and $T=260-800$ K, respectively. Before the ions are switched on, it is ensured that steady-state spontaneous etching has been reached.

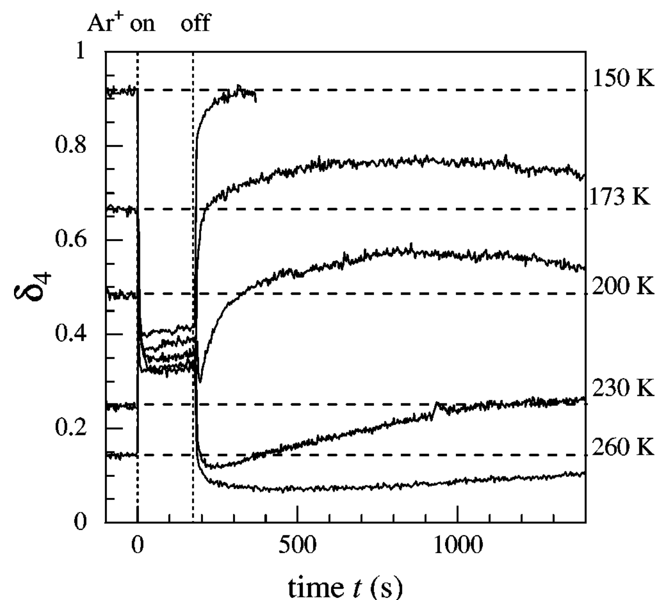

FIG. 3. Response of the SiF_4 production coefficient δ_4 to an ion pulse of 180 s for $T<300$ K. For $T<210$ K, the production coefficient δ_4 drops when the ions are switched on. The dashed lines indicate spontaneous SiF_4 production $\delta_{4,0}$ for each temperature. The steady-state value $\delta_{4,ion}$ during the ion bombardment can be found in Fig. 2.

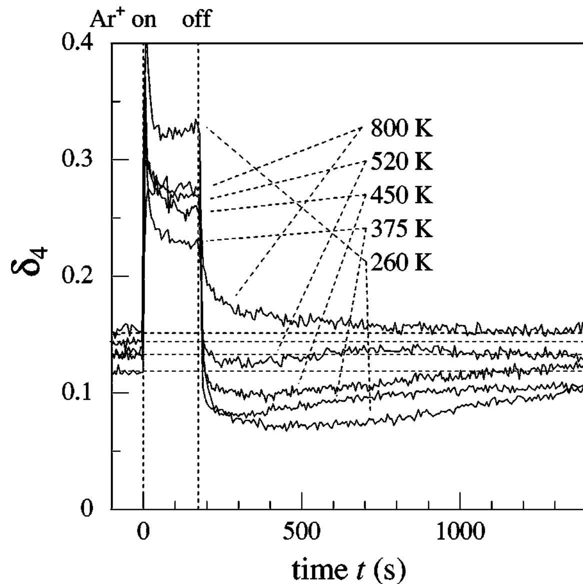

FIG. 4. Response of the SiF$_4$ production coefficient δ_4 to an ion pulse of 180 s for at $T>300$ K. At ion switch-on a transient peak is observed. At ion switch-off, it is observed that at $T>600$ K the production coefficient δ_4 does not drop below the spontaneous value $\delta_{4,0}$.

When the ions are switched on, a transient peak in the SiF$_4$ production is observed over the temperature range 260–800 K (Fig. 4). From the area under the peak, it is found that the amount of fluorine L_{loss} released from the reaction layer decreases at both higher and lower temperatures, as compared to room temperature.

When the ions are switched off, δ_4 first drops and at $T<600$ K it reaches a value $\delta_{4,\mathrm{min}}$ which is lower than the spontaneous value $\delta_{4,0}$. In the temperature range $260<T<600$ K the value $\delta_{4,\mathrm{min}}$ increases at higher temperatures (Fig. 4). Above 600 K no dip in SiF$_4$ production is observed when the ions are switched off: $\delta_{4,\mathrm{min}}=\delta_{4,0}$.

At room temperature, the spontaneous value $\delta_{4,0}$ is reached on a time scale of 1000 s after the dip. In Fig. 3, it is seen that at lower temperatures the SiF$_4$ signal reaches $\delta_{4,0}$ on a shorter time scale. However, after having reached the spontaneous value $\delta_{4,0}$ at $T<210$ K, the SiF$_4$ signal reaches a maximum after about 600 s after which it drops to reach $\delta_{4,0}$ again. At temperatures above room temperature the steady-state value is also reached on a shorter time scale as compared to room temperature.

The response of ϵ (not shown) shows no transient peak when the ions are switched on but increases monotonically until the steady-state value ϵ_{ion} is reached. When the ions are switched off, ϵ decreases on the time scale of seconds. After this fast decrease, ϵ reaches the same value as δ_4 and shows an identical response as δ_4 for the whole temperature range, including the dip.

C. Spontaneous SiF$_4$ formation

To obtain a better understanding of the spontaneous SiF$_4$ formation, first the steps for SiF$_4$ formation are discussed in some more detail. With this information the experimental results can be better understood. For the precursor concentration $[\mathrm{XeF_2}]_p$ in step i in the formation of a reaction layer, Sec. I, it is assumed that it is proportional to the incoming XeF$_2$ flux,[14]

$$[\mathrm{XeF_2}]_p = c\Phi_s(\mathrm{XeF_2}). \tag{5}$$

At lower temperatures a larger precursor concentration is formed during spontaneous etching[11,13] and thus c increases at decreasing temperatures.

At room temperature, the reaction layer consists of SiF–SiF$_2$–SiF$_3$ chains.[3,9] Gray *et al.* showed that under ion bombardment at room temperature the reaction layer consists of SiF$_2$ species.[6] Bermudez showed that at room temperature the reaction layer consists of SiF, SiF$_2$, and SiF$_3$ species and less fluorinated species become more important at higher temperature up to 550 K.[15] For the purpose of modeling we assume that the reaction layer consists of only SiF$_2$ species, independent of ion flux and temperature.[14]

The spontaneous SiF$_4$ formation and thus the desorbing flux $\Phi_{\mathrm{spon}}(\mathrm{SiF_4})$ is now proportional to the precursor concentration $[\mathrm{XeF_2}]_p$ and the SiF$_2$ concentration $[\mathrm{SiF_2}]$ with a reaction probability k_e,

$$\Phi_{\mathrm{spon}}(\mathrm{SiF_4}) = k_e[\mathrm{SiF_2}][\mathrm{XeF_2}]_p = k_e\, c[\mathrm{SiF_2}]\Phi_s(\mathrm{XeF_2}), \tag{6}$$

where $k_e c$ is the overall reaction probability (physisorption followed by chemisorption) of XeF$_2$ to form SiF$_4$ spontaneously.

The SiF$_2$ surface species can also leave the surface and contribute to etching when their thermal energy overcomes the desorption energy of 260 meV. This process is only of importance for temperatures above 600 K.[11,16]

D. Discussion of transient response

During the transient peak after the ions are switched on an amount L_{loss} of fluorine is observed to be released from the surface. The interpretation is that the chainlike reaction layer formed during spontaneous etching is removed (Fig. 1).[10] The SiF$_2$ surface concentration decreases and a reaction layer with a submonolayer fluorine coverage is formed. The lower fluorine content of this depleted layer results in a lower spontaneous SiF$_4$ production [Eq. (6)], which is reflected in the dip $\delta_{4,\mathrm{min}}$. After the dip, the chainlike reaction layer has to be rebuilt. This is a slow process,[3] which takes over 1000 s to reach the steady-state spontaneous etch rate again. Thus, the dip and the transient peak are related: a smaller peak indicates less removal of the reaction layer, which results in a smaller dip in the SiF$_4$ production when the ions are switched off again.[10]

From the behavior of the transient peak as a function of temperature (Figs. 3 and 4), it is concluded that less fluorine is removed from the reaction layer by the ions (decrease of L_{loss}), both at *increasing* and *decreasing* temperatures with respect to room temperature. Above room temperature this is confirmed by a smaller dip in the SiF$_4$ production (Fig. 4). Below room temperature, the dip cannot be measured

correctly because the SiF_4 signal increases again on a shorter time scale and coincides with the dip. This increase in SiF_4 signal is explained by a faster reconstruction of the precursor concentration at lower temperatures which occurs on a much shorter time scale than the rebuilding of a reaction layer.[13] The lower SiF_4 production under ion bombardment is explained by a lower precursor concentration [Eq. (6)]. Thus, besides the reaction layer, also the precursor concentration is removed by ion bombardment.

E. Comparison to thermal desorption measurements of spontaneous etching

When we compare the conclusions about the removal of the reaction layer by the ions to the results of a study of the spontaneous reaction layer by thermal desorption (TDS),[11] similar trends are observed. In TDS measurements, the reaction layer during spontaneous etching formed at a surface temperature T is studied by the SiF_4 flux desorbing from the sample when the sample is heated after the XeF_2 flux has been turned off. As a function of the heating temperature T_{heat} several characteristics of the reaction layer are observed. First, the removal of a precursor layer is observed as the so-called ''γ peak'' at around $T_{heat}=200$ K. The desorption of weakly-bound species is measured in an ''α peak'' in the temperature range of $T_{heat}=300-600$ K. We interpret this peak as the desorption of species from the chainlike reaction layer.[9] At $T_{heat}=600$ K the α peak stops abruptly. Finally, the desorption of tightly bound species is measured in a ''β peak'' in the range of $T_{heat}=600-900$ K. This corresponds to the desorption of fluorine from a reaction layer with a monolayer coverage.

Above a sample temperature of 600 K, no dip in spontaneous SiF_4 production was observed in our long-pulse measurements (Fig. 4). In the TDS measurements only a β peak is observed when the sample is heated, corresponding to a monolayer fluorine coverage during spontaneous etching. When the ions are switched on, still some release of fluorine was observed which corresponds to the creation of dangling bonds. We conclude that above sample temperatures of 600 K the reaction layer during ion-assisted etching consists of a submonolayer fluorine coverage. When the ions are switched off, the dangling bonds are fluorinated again: only a thin reaction layer has to be rebuilt and thus the SiF_2 concentration reaches steady state on a short time scale and no dip in the SiF_4 formation is observed. Because of spontaneous SiF_2 release at $T>600$ K, no chainlike structures can be formed on the surface.

In the sample temperature range 250–600 K, the dip decreases at higher temperatures, which corresponds to the removal of a thinner chainlike reaction layer. From TDS measurements it is concluded that the chainlike reaction layer has a maximum fluorine content around room temperature. Thus, the fluorine removed by the ion bombardment shows the same trend as observed by TDS measurements. We already know that the reaction layer during ion-assisted etching consists of a submonolayer fluorine coverage and dangling bonds.[10] The correspondence between the TDS measurements and the long pulse measurements now indicates that a reaction layer with a similar structure is formed in the temperature range 250–600 K.

Finally, at sample temperatures below 250 K, it is concluded from our long pulse measurements that the amount of fluorine released from the reaction layer decreases at lower temperatures. The TDS measurements show that the fluorine content of the Si_xF_y chains decreases and a reaction layer with a monolayer coverage during spontaneous etching is formed at lower temperatures. No multilayer coverage can be formed at these low temperatures because of the large SiF_4 production. During spontaneous etching, the thick reaction layer is replaced by a thick precursor concentration,[13] as observed in a γ peak in the TDS measurements.

From this, we conclude that the reaction layer below room temperature also consists of a submonolayer fluorine coverage under ion bombardment.

F. Temperature-independent reaction layer

For the ion-to-neutral flux ratio $R=0.025$ it was concluded that a reaction layer with a submonolayer fluorine coverage and dangling bonds is formed during ion-assisted etching at room temperature.[10] From a comparison between TDS measurements and the response of the SiF_4 signal upon ion bombardment, we now propose that, *independent of temperature*, such a reaction layer is formed. This suggests that dangling bonds are mainly created by ion impact. From previous measurements it was concluded that besides the reaction layer also the precursor layer is removed by ion bombardment.[13] Thus, in contrast to the reaction layer, the precursor concentration is a function of both temperature and ion flux.

IV. MODEL FOR REACTION PROBABILITY

In this section a model will be presented to describe the temperature dependence of ion-assisted etching based on the suggestions from the previous sections that:

(1) independent of temperature a reaction layer with a submonolayer coverage of SiF_2 and dangling bonds is formed during ion bombardment; and
(2) the precursor concentration depends both on the ion flux and the temperature.

Before the model is presented, first the steady-state reaction probability at room temperature is discussed.

A. Steady-state reaction probability

At room temperature the steady-state reaction probability ϵ_0 during spontaneous etching is limited by the reaction probability k_e to form SiF_4 [Eqs. (2), (3), and (6)]

$$\epsilon_0=2ck_e\approx 0.15. \tag{7}$$

Here, a totally fluorinated surface ($[SiF_2]=1$) is assumed. During ion-assisted etching, ϵ_{ion} is limited by the much higher reaction probability k_f to fluorinate dangling bonds

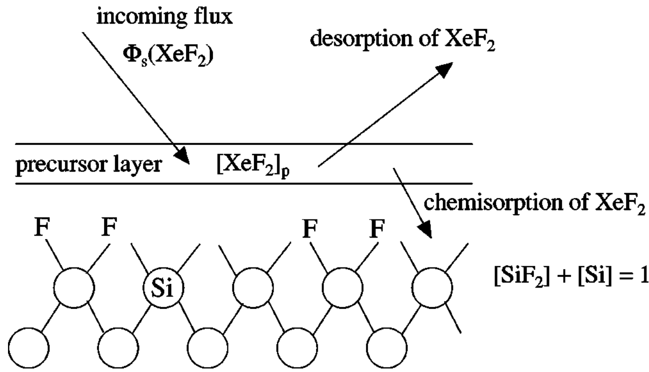

FIG. 5. Schematic representation of the reaction layer during ion-assisted etching as used in the model to describe the precursor concentration $[XeF_2]_p$. The precursor concentration increases due to the incoming XeF_2 flux $\Phi_s(XeF_2)$ and decreases due to desorption and chemisorption onto dangling bonds. The reaction layer on the silicon is represented by a surface consisting of fluorinated sites and dangling bonds.

$$\epsilon_{ion}=ck_f\left(1+\frac{\mathcal{P}}{1+\mathcal{P}}\right)=ck\approx 0.88, \tag{8}$$

with $\mathcal{P}=p_c/p_p$ the ratio of the probabilities for chemical and physical sputtering for the ion-induced formation of SiF_4 and SiF_2, respectively.[14] The reaction constant k can be considered as the effective reaction probability to fluorinate dangling bonds, which includes the ion-induced reaction of XeF_2 with fluorinated sites which results in the enhanced SiF_4 formation.

In Eqs. (7) and (8) it is assumed that c is independent of the ion flux. The precursor concentration c is already known as a function of temperature in the case of spontaneous etching.[11] However, it was shown that c is a function of the ion flux. On the other hand, we have experimental evidence in this article that the reaction layer and dangling bond concentration during ion-assisted etching is independent of temperature. Thus, to capture the temperature dependence of the etching process, we describe the precursor concentration $[XeF_2]_p$ as a function of temperature and ion flux.

B. Precursor concentration

The precursor concentration $[XeF_2]_p$ is described by the rate equation

$$\frac{\partial[XeF_2]_p}{\partial t}=\Phi_s(XeF_2)-\frac{[XeF_2]_p}{\tau}-k[XeF_2]_p[Si]. \tag{9}$$

Similar to the reaction layer (Sec. I), the steady-state precursor concentration $[XeF_2]_p$ results from a balance between several mechanisms (Fig. 5). In more detail, the *increase* by the incoming XeF_2 flux $\Phi_s(XeF_2)$ [first term on the right-hand side of Eq. (9)] is balanced by the decrease by thermal desorption and chemisorption (second and third term on the right-hand side). Here, only precursor-mediated chemisorption of fluorine is assumed. We assume that the thermal desorption of the precursor is the only *temperature dependent* process, as described by the residence time τ of XeF_2 in the precursor state

$$\tau=\tau_0\exp(E_d/k_BT), \tag{10}$$

with $E_d=32$ meV the desorption energy of XeF_2 from the precursor state.[11]

For chemisorption [third term on the right-hand side of Eq. (9)], the effective fluorination probability k of dangling bonds is included. It is assumed that the activation energy for chemisorption is much smaller than the desorption energy and thus k is considered to be independent of temperature. The chemisorption on fluorinated SiF_2 sites is neglected. This implies that the thermal desorption is the most important loss mechanism for XeF_2 from the physisorbed state during spontaneous etching.

In a steady-state situation Eq. (9) results in

$$[XeF_2]_p=\frac{\tau_0}{e^{\frac{-E_d}{k_BT}}+\tau_0k[Si]}\Phi_s(XeF_2)=c(R,T)\Phi_s(XeF_2), \tag{11}$$

which should be compared to Eq. (5) during spontaneous etching. We thus expressed the factor $c(R,T)$ as a function of ion flux and temperature. Equation (11) is similar to the sticking probability as predicted by the standard model for precursor-mediated chemisorption.[17] However, in these models the usual assumption is that thermal desorption is much more important than chemisorption,[18] comparable to spontaneous etching in our case. In the case of a high dangling bond concentration, chemisorption cannot be neglected anymore.

C. Influence of ion flux

It is assumed that, with increasing ion flux, the Si surface changes from a totally fluorinated surface with only SiF_2 species $[SiF_2]=1$ ML to a surface covered with only dangling bonds with $[Si]=1$ ML. Because of Si surface-site conservation we can write

$$[Si]+[SiF_2]=1\ \text{ML}. \tag{12}$$

The reaction probability ϵ is given by the sum of the reaction probabilities on fluorinated sites and dangling bonds

$$\epsilon=2k_ec(R,T)[SiF_2]+kc(R,T)[Si], \tag{13}$$

with $c(R,T)$ given by Eq. (11). For spontaneous etching ($[SiF_2]=1$ ML) and ion-assisted etching in the high flux ratio limit ($[Si]=1$ ML), Eq. (13) again yields Eqs. (7) and (8), respectively.

We now can use Eq. (13) to describe the experimental results of ϵ. The values τ_0k_e and τ_0k are fixed by two boundary conditions

$$T=150\ \text{K and}\ [Si]=0:\quad \epsilon=\epsilon_0=1, \tag{14}$$

$$T=300\ \text{K and}\ [Si]=1:\quad \epsilon=\epsilon_{ion}=0.88. \tag{15}$$

The first condition corresponds to a spontaneous reaction probability of unity at 150 K and the second condition corresponds to the maximum reaction probability in the high R limit at room temperature [Eq. (8)]. These boundary conditions result in $\tau_0k=2.1$ and $\tau_0k_e=0.043$.

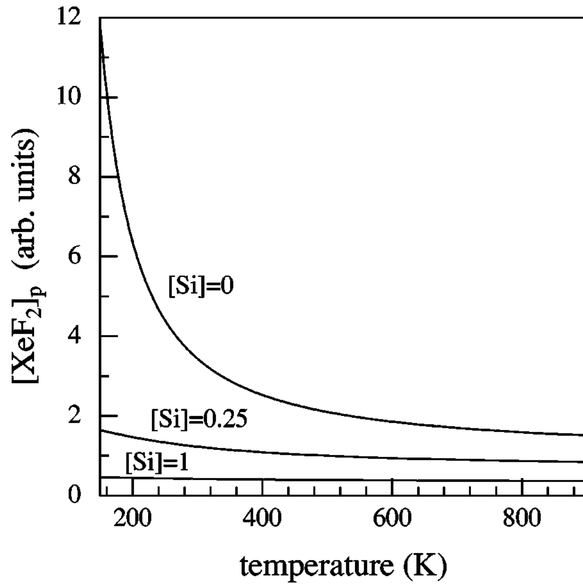

FIG. 6. Precursor concentration $[\mathrm{XeF_2}]_p$ for fixed $\Phi_s(\mathrm{XeF_2})$ as a function of temperature for a dangling bond concentration of [Si]=0 ML, [Si]=0.25 ML, and [Si]=1 ML.

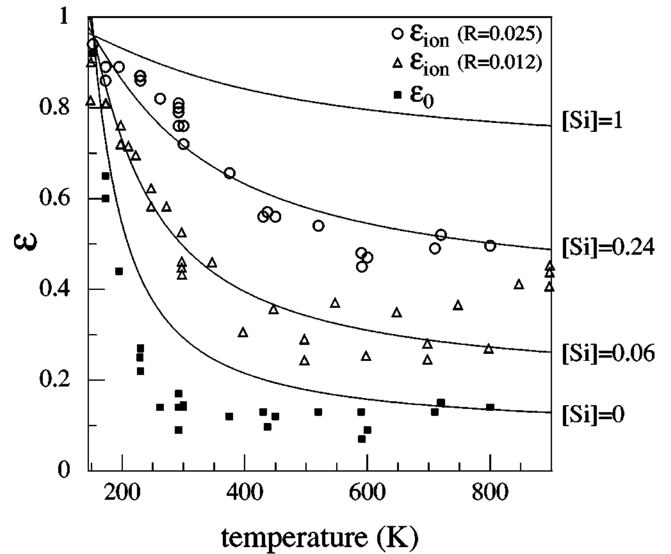

FIG. 7. Experimental values of ϵ as a function of temperature compared to the results of the precursor model. The measured values of ϵ_{ion} at a flux ratio $R=0.012$ and $R=0.025$ are compared to the model with a dangling bond concentration [Si]=0.06 ML and [Si]=0.24 ML, respectively. For the sake of completeness also the curves for [Si]=0 ML and [Si]=1 ML are shown.

Before comparing the model to the experimental results, first the precursor concentration $[\mathrm{XeF_2}]_p$ in Eq. (11) is plotted in Fig. 6 as a function of temperature for different values of the dangling bond concentration [Si]. It is seen that the precursor concentration decreases a factor five in the range $T=150-800$ K for spontaneous etching at [Si]=0 ML. When going from a dangling bond concentration [Si]=0 to a concentration [Si]=0.25, the precursor concentration drops by a factor of 2.5 at room temperature, and by more than a factor of 6 at 150 K. It is stressed that this decrease is *not* the result of sputtering of the precursor but results from a higher probability for $\mathrm{XeF_2}$ to react with the reaction layer on dangling bonds.

When these results are applied to our experiments, a higher precursor concentration must be released from the surface at lower temperatures when switching from spontaneous to ion-assisted etching than at room temperature. Of course, a larger concentration also has to rebuild when the ions are switched off again.

Now, our model can be used to describe the experimental results. The concentration $0<[\mathrm{Si}]<1$ ML of dangling bonds on the surface is the only scaling parameter of our model: it is assumed to be independent of temperature. The temperature dependence is given by the model once a value of the dangling bond concentration is chosen.

V. REACTION PROBABILITY: EXPERIMENTS VERSUS MODEL

In Fig. 7 the model is compared to the experimental results of ϵ_{ion} for a flux ratio $R=0.012$ (Ref. 13) and a flux ratio $R=0.025$ (this work) as well as those for ϵ_0. For the model calculations, in addition to the limiting cases [Si]=0 ML and [Si]=1 ML, also the curves for [Si]=0.06 ML and [Si]=0.24 ML are shown, being the best fits to the experimental results for the lower and the higher flux ratio, respectively. This indicates that flux ratio's of $R=0.012$ and $R=0.025$ produce dangling bond concentrations of [Si]=0.06 ML and [Si]=0.24 ML, respectively. For ion-assisted etching, we see that the model describes the measured temperature dependence very well for both flux ratios. The model fit for spontaneous etching ([Si]=0) is not so good which may be due to surface roughness.[13]

Despite the good trend of our model compared to the experimental results, we still see some small deviations for ion-assisted etching at higher temperatures. At $T>600$ K an increase in ϵ_{ion} is measured (especially for $R=0.012$) while our model predicts a decrease. This is explained by the fact that above 600 K also spontaneous $\mathrm{SiF_2}$ release becomes important, which results in a new mechanism for creating dangling bonds besides the ion bombardment. Thus, the assumption that the dangling bond concentration is independent of the temperature breaks down at $T>600$ K and low flux ratios. For high flux ratios (see $R=0.025$), the creation of dangling bonds by thermal desorption of $\mathrm{SiF_2}$ seems to become less important.

A. Dangling bond concentration

The value [Si]=0.24 ML for the dangling bond for the measured flux ratio of $R=0.025$ concentration may seem very low, since at room temperature $\epsilon_{\mathrm{ion}}\approx 0.7$, which is close to the maximum reaction probability for high flux ratios [Eq. (8)]. However, a second look reveals that the spontaneous contribution to the reaction probability on fluorinated sites has dropped over a factor of 3, which is caused by a lower precursor concentration and a somewhat lower $\mathrm{SiF_2}$ concentration [Eq. (13)]. Thus, despite the apparently low dangling

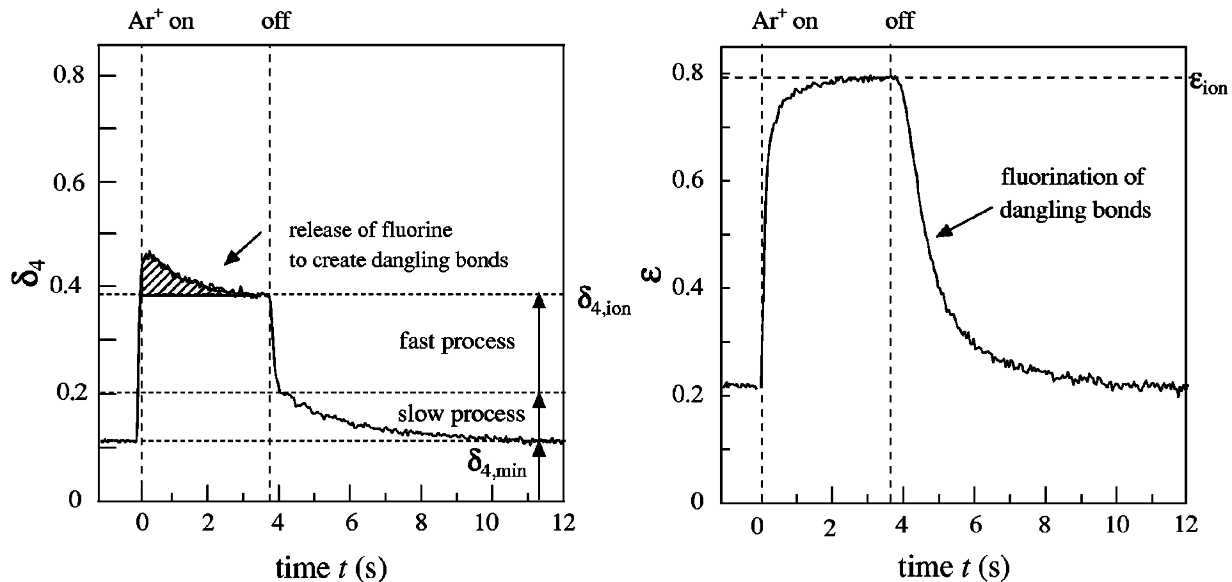

FIG. 8. Typical response of ϵ and δ_4 to a short pulse on the time scale of seconds at room temperature. The transient at ion switch-on is attributed to the creation of dangling bonds. Upon ion switch-off, a fast and a slow response are observed which are related to the formation of SiF_4 within the reaction layer and from excited surface species, respectively. At ion switch-off, it is seen that ϵ has a slower response than δ_4 which is attributed to the fluorination of the dangling bonds.

bond concentration, the reaction probability on dangling bonds is responsible for about 90% of the total reaction probability.

A good way to interpret the dangling bond concentration [Si] is to consider the residence time of SiF_2 surface species.[19] Before a reaction product (SiF_4 and SiF_2) can be formed (which results in the creation of a dangling bond), Si sites have to be fluorinated first. The calculated bare and fluorinated sites concentration is an average surface coverage during the ion bombardment. During ion-assisted etching the SiF_2 residence time is much shorter than during spontaneous etching. Thus, a dangling bond concentration $[Si]=0.24$ ML should be interpreted such that 24% of the time the surface site has dangling bonds and the rest of the time the site is fluorinated to produce the reaction products. It is clear that a very high ion flux is needed to assure that, on the average, a surface site is never fluorinated ($[Si]=1$ ML). Since the ion-to-neutral flux ratio R determines the time a site is fluorinated, it is also clear that the dangling bond concentration will only be a function of this ratio. At room temperature this was shown for ion-assisted etching by Vugts *et al.*[14] Thus, at second thought, a dangling bond concentration of 24% seems very reasonable for a flux ratio $R=0.025$.

B. SiF_4 production

We can also use the model to calculate the SiF_4 production. Let us assume that the SiF_4 contribution to the total reaction product formation is independent of temperature. At room temperature this contribution of δ_4 is 40%. In Fig. 2, the model curve $\delta_{4,\mathrm{ion}}=0.4\epsilon_{\mathrm{ion}}$ is plotted for our measurements at a flux ratio $R=0.025$. It is seen that at $T<600$ K the SiF_4 production is described very well with this simple assumption.

VI. SHORT-PULSE MEASUREMENTS

In Sec. III it was shown that the precursor concentration is reconstructed on a much shorter time scale than the reaction layer. Therefore, the dynamics of the precursor concentration should be studied using short ion pulses. The response of ϵ and δ_4 is now studied as a function of temperature on a time scale of seconds by using ion pulses having a duration of 3.75 s and a time between subsequent pulses of 8.75 s. These measurements also serve as a validation for the model, in which the precursor concentration was described both as a function of ion flux and temperature. This model shows that at lower temperatures a higher precursor concentration has to be rebuilt after the ion bombardment has ceased (Fig. 6). From these measurements, also conclusions can be drawn about the mechanisms for SiF_4 production during ion-assisted etching as a function of temperature.[10]

In Fig. 8 a typical response of ϵ and δ_4 at room temperature is shown. When the ions are switched on, a transient peak in SiF_4 production is measured, similar to the response to pulses of 180 s (Fig. 1). This peak, however, decays on a time scale of seconds. Here, the interpretation is that fluorine is released and dangling bonds are created: the reaction layer changes from a monolayer fluorine coverage to a submonolayer fluorine coverage. When the ions are switched off, first a fast decrease in SiF_4 production is observed, followed by a slower decay to $\delta_{4,\mathrm{min}}$. These responses reflect two mechanisms which enhance the SiF_4 production on a depleted reaction layer during ion-assisted etching. The fast decay reflects the formation of SiF_4 within the reaction layer, modeled as the reaction of two SiF_2 surface species to form SiF_4. The slow decay reflects the enhanced formation of SiF_4 from physisorbed XeF_2 and excited SiF_2 surface spe-

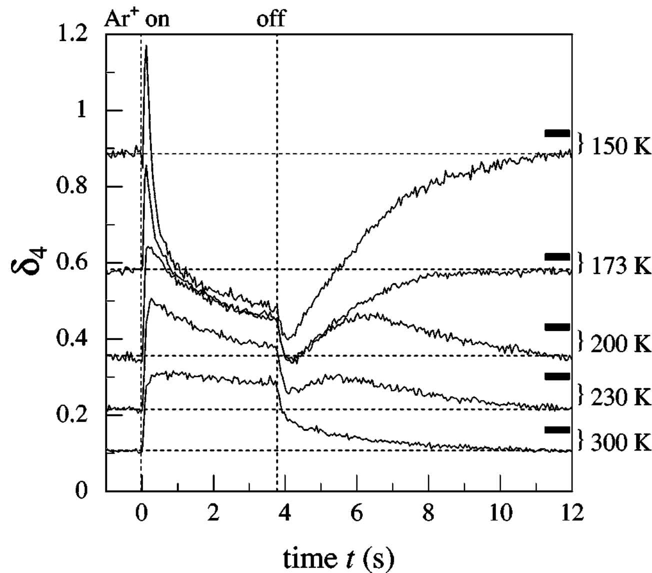

FIG. 9. Response of the SiF_4 production coefficient δ_4 to an ion pulse of 3.75 s at $T<300$ K. At lower temperatures a temporary peak in the SiF_4 production is observed, as explained in the running text. The marks on the right-hand y axis indicate the steady-state values $\delta_{4,0}$ at each temperature which are reached on the time scale of hundreds of seconds.

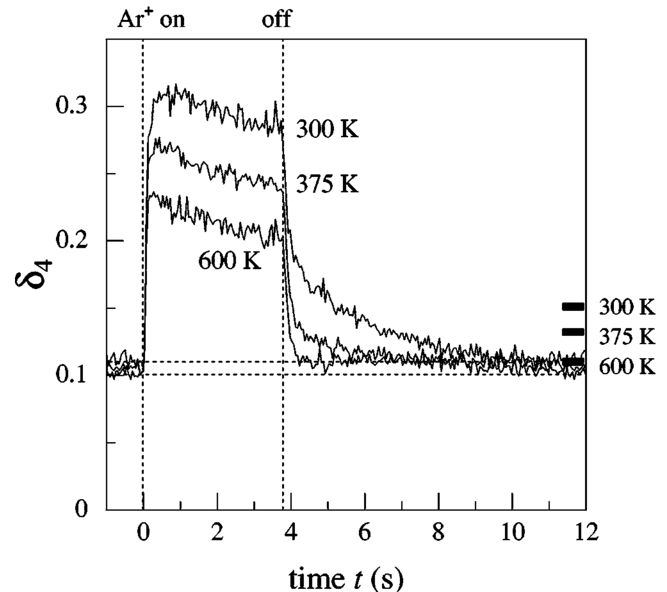

FIG. 10. Response of the SiF_4 production coefficient δ_4 to an ion pulse of 3.75 s at $T>300$ K. At higher temperatures the slow response after ion switch-off disappears and a steady-state situation is reached directly after the fast decay. The marks on the right-hand y axis indicate the steady-state values $\delta_{4,0}$ at each temperature which are reached on the time scale of hundreds of seconds.

cies, which decay during the slow process to SiF_2 species with a low reaction probability.[10]

In the response of ϵ no transient peak is observed. During the increase of ϵ at ion switch-on, the higher reaction probability is attributed to the increasing dangling bond concentration (cf. the response of δ_4). The difference between ϵ and δ_4 during steady state is explained by the production of SiF_2. The response of ϵ at ion switch-off is much slower than the response of δ_4. This difference is explained by the fluorination of dangling bonds. The difference in the amount of fluorine that reacts with the dangling bonds during ion switch-off (from the behavior of ϵ) and the much smaller amount that is released in the transient peak (hatched area in Fig. 8) is explained by an additional transient peak in the SiF_2 production.

The response of δ_4 at temperatures below and above room temperature is shown in Figs. 9 and 10, respectively. On the time scale of these measurements, no steady-state situation of spontaneous etching is reached during the ion switch-off period. The corresponding steady-state values are indicated in Fig. 9. The response of ϵ as a function of temperature is shown in Fig. 11. In the following sections, first the temperature dependence of ion switch-off and next the transient at ion switch-on is discussed.

A. Temperature dependence of switch-off behavior

At ion switch-off, a fast decay of SiF_4 production is observed over the whole temperature range in Figs. 9 and 10. Thus the production of SiF_4 in the reaction layer is a valid ion-assisted mechanism for enhanced SiF_4 production at all temperatures.

After this initial fast decrease in δ_4, a temporary peak in δ_4 is measured for $T=200$ and 230 K (Fig. 9). This temporary peak after the ion switch-off increases with decreasing temperature. It is explained by a competition of a decreasing excited SiF_2 concentration (slow decay) and an increasing precursor concentration. The broad peak in the SiF_4 production is observed because the reconstruction takes place on a shorter time scale than the decay of excited SiF_2 surface species. At 230 K, the precursor concentration is only lowered slightly by the ion bombardment and thus is recon-

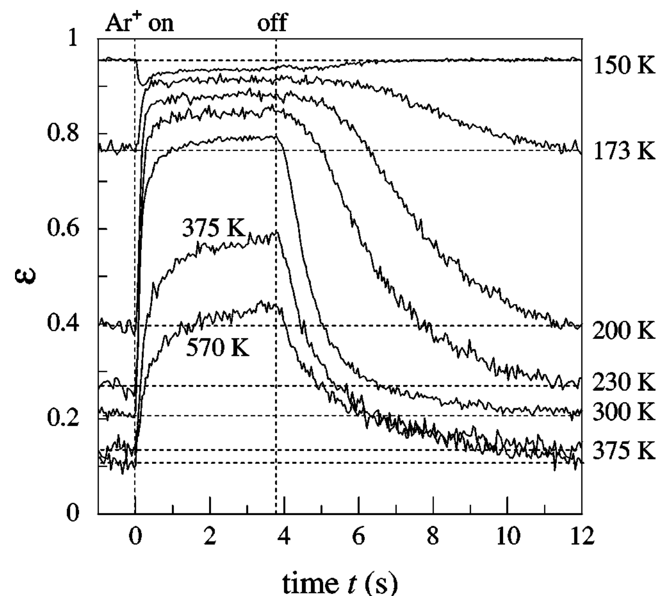

FIG. 11. Response of the XeF_2 reaction coefficient ϵ to an ion pulse of 3.75 s. In contrast to the response at $T>300$ K, the reaction probability ϵ does not decrease immediately when the ions are switched off at $T<300$ K.

structed again after a few seconds. For even lower temperatures $T \leq 173$ K, a higher precursor concentration has to be rebuilt, which takes longer. Here, no temporary peak is observed but the SiF_4 production increases monotonically.

Above 300 K (Fig. 10), the slow response decreases at higher temperatures. Above 600 K no slow response is observed and constant SiF_4 production is reached directly after the fast decay. However, above 600 K roughening plays an important role as can be concluded from the fact that ϵ_0 does not increase significantly at these temperatures (Fig. 2), in contrast to the measurements by Vugts *et al.*[11] The effect of roughening on ion-assisted etching at these temperatures is not known and could result in a decrease of the slow response. For this reason we choose not to discuss this feature further.

Now, the response of the reaction probability ϵ is discussed (Fig. 11). Similar to the response on a long time scale, ϵ increases and decreases monotonously when the ions are switched on and off, respectively. An interesting feature is observed when the ions are switched off. Above room temperature ϵ starts to decrease at the moment that the ions are switched off (discontinuity in first derivative). At lower temperatures, however, ϵ decreases more slowly (continuous behavior of first derivative). At $T=173$ K it is seen that ϵ stays constant for about 2 s after the ions have been switched off before it starts to decrease, in stark contrast to the immediate response at room temperature.

This behavior of ϵ at ion switch-off is attributed to the rebuilding of the precursor concentration. According to the model, a thicker precursor layer has to be rebuilt (Fig. 6) and thus more XeF_2 will be physisorbed after ion switch-off at lower temperatures. This can be seen in the response of ϵ, since it takes longer for the reaction probability to drop at lower temperatures.

B. Temperature dependence of switch-on behavior

Now that the decay of the SiF_4 signal upon ion switch-off has been discussed, the transient peak upon ion switch-on will be discussed. In the temperature range 300–600 K (Fig. 10) a small transient peak is observed. This is attributed to the release of fluorine when dangling bonds are created on the surface; at the time of ion switch-off these dangling bonds are fluorinated again.[10] At lower temperatures the magnitude of this transient increases significantly (Fig. 9). This is attributed to the removal of the precursor layer which has been reconstructed during the ion switch-off period. Thus, the excess precursors react to form SiF_4. This is another indication that a thicker precursor concentration is present at lower temperatures.

C. Conclusions from short pulses

Summarizing, for the whole temperature range 150–800 K, the SiF_4 formation on a depleted reaction layer is enhanced by the same mechanisms as identified at room temperature. Also from the response of both ϵ and δ_4 we conclude that at lower temperatures a thicker precursor layer is formed. This is in agreement with our model.

From the short-pulse experiments, the decrease of SiF_4 production under ion bombardment below 210 K can be understood in some more detail. The reason is that the spontaneous contribution decreases due to a lower precursor concentration. This is only partially offset by the fact that the ion bombardment enhances the SiF_4 production again by the same mechanisms as at room temperature.

VII. CONCLUSIONS

Based on ion-pulse measurements on the time scale of 1–100 s, we conclude that the mechanisms for ion-assisted Si etching by XeF_2 and Ar^+ ions are independent of temperature in the range 150–800 K. During ion bombardment, a reaction layer is formed with a submonolayer fluorine coverage, which is independent of temperature. The dangling bond concentration is the key parameter to describe the reaction layer. Below 600 K the dangling bonds are created by ions only: a higher ion flux results in a higher dangling bond concentration. Above 600 K there is also a small contribution to the creation of dangling bonds from thermal desorption of SiF_2 from the reaction layer. It is also concluded that the mechanisms of SiF_4 formation are independent of temperature.

The temperature dependence of the XeF_2 reaction probability ϵ is now described by the transition of XeF_2 from the precursor state to the reaction layer. In steady state, the incoming XeF_2 flux is balanced by chemisorption to fluorinate the dangling bonds plus thermal desorption. During ion bombardment, dangling bonds are created on which XeF_2 reacts with a high probability. Because of this high chemisorption probability, thermal desorption of XeF_2 process is not important and thus the temperature dependence of ϵ becomes less with increasing ion flux. During spontaneous etching, when no dangling bonds are presented in the reaction layer, the chemisorption probability is low which results in a strong temperature dependence of ϵ.

A simple model describes the observed temperature dependence of ϵ as a function of the ion fluxes (and thus the dangling bond concentrations) very well. From this model also the precursor concentration is calculated as a function of both temperature and the dangling bond concentration.

[1] H. F. Winters, J. Appl. Phys. **49**, 5165 (1978).
[2] G. S. Oehrlein and H. L. Williams, J. Appl. Phys. **62**, 662 (1987).
[3] M. J. M. Vugts, M. F. A. Eurlings, L. J. F. Hermans, and H. C. W. Beijerinck, J. Vac. Sci. Technol. A **14**, 2780 (1996).
[4] C. B. Mullins and J. W. Coburn, J. Appl. Phys. **76**, 7562 (1994).
[5] H. F. Winters and J. W. Coburn, Surf. Sci. Rep. **14**, 161 (1992).
[6] D. C. Gray, I. Teppermeister, and H. H. Sawin, J. Vac. Sci. Technol. B **11**, 1243 (1993).
[7] F. R. McFeely, J. F. Morar, N. D. Shinn, G. Landgren, and F. J. Himpsel, Phys. Rev. B **30**, 764 (1984).
[8] F. R. McFeely, J. F. Morar, and F. J. Himpsel, Surf. Sci. **165**, 277 (1986).
[9] C. W. Lo, D. K. Shuh, V. Chakarian, T. D. Durbin, P. R. Varekamp, and J. A. Yarmoff, Phys. Rev. B **47**, 15648 (1993).
[10] P. G. M. Sebel, L. J. F. Hermans, and H. C. W. Beijerinck, J. Vac. Sci. Technol. A **17**, 3368 (1999).
[11] M. J. M. Vugts, G. L. J. Verschueren, M. F. A. Eurlings, L. J. F. Hermans, and H. C. W. Beijerinck, J. Vac. Sci. Technol. A **14**, 2766

(1996).
[12]M. J. M. Vugts, G. J. P. Joosten, A. van Oosterum, H. A. J. Senhorst, and H. C. W. Beijerinck, J. Vac. Sci. Technol. A **12**, 2999 (1994).
[13]M. J. M. Vugts, L. J. F. Hermans, and H. C. W. Beijerinck, J. Vac. Sci. Technol. A **14**, 2820 (1996).
[14]M. J. M. Vugts, L. J. F. Hermans, and H. C. W. Beijerinck, J. Vac. Sci. Technol. A **14**, 2138 (1996).
[15]V. M. Bermudez, J. Vac. Sci. Technol. A **10**, 3478 (1992).
[16]J. A. Dagata, D. W. Squire, C. S. Dulcey, D. S. Y. Hsu, and M. C. Lin, J. Vac. Sci. Technol. B **5**, 1495 (1987).
[17]D. A. King, CRC Crit. Rev. Solid State Mater. Sci. **7**, 167 (1978).
[18]D. J. D. Sullivan, H. C. Flaum, and A. C. Kummel, J. Phys. Chem. **97**, 12051 (1993).
[19]J. W. Coburn, J. Vac. Sci. Technol. A **12**, 1417 (1994).