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Surface roughness in XeF$_2$ etching of a-Si/c-Si(100)

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Single wavelength ellipsometry and atomic force microscopy (AFM) have been applied in a well-calibrated beam-etching experiment to characterize the dynamics of surface roughening induced by chemical etching of a ∼12 nm amorphous silicon (a-Si) top layer and the underlying crystalline silicon (c-Si) bulk. In both the initial and final phase of etching, where either only a-Si or only c-Si is exposed to the XeF$_2$ flux, we observe a similar evolution of the surface roughness as a function of the XeF$_2$ dose proportional to $D$(XeF$_2$)$^\beta$ with $\beta\approx0.2$. In the transition region from the pure amorphous to the pure crystalline silicon layer, we observe a strong anomalous increase of the surface roughness proportional to $D$(XeF$_2$)$^\beta$ with $\beta\approx1.5$. Not only the growth rate of the roughness increases sharply in this phase, also the surface morphology temporarily changes to a structure that suggests a cusplike shape. Both features suggest that the remaining a-Si patches on the surface act effectively as a capping layer which causes the growth of deep trenches in the c-Si. The ellipsometry data on the roughness are corroborated by the AFM results, by equating the thickness of the rough layer to 6 $\sigma$, with $\sigma$ the root-mean-square variation of the AFM’s distribution function of height differences. In the AFM data, the anomalous behavior is reflected in a too small value of $\sigma$ which again suggests narrow and deep surface features that cannot be tracked by the AFM tip. The final phase morphology is characterized by an effective increase in surface area by a factor of two, as derived from a simple bilayer model of the reaction layer, using the experimental etch rate as input. We obtain a local reaction layer thickness of 1.5 monolayer consistent with the 1.7 ML value of Lo et al. [Lo et al., Phys. Rev. B 47, 648 (1993)] that is also independent of surface roughness. © 2005 American Vacuum Society. [DOI: 10.1116/1.1830499]

I. INTRODUCTION

Plasma etching is the standard etching technique in the production of integrated circuits, MEMS devices, and photonic devices. The main advantage of plasma etching is the directionality that is imposed by the ions that bombard the surface of the device. However, the etch process gives rise to surface roughness depending on the various plasma parameters, such as ion energy and ion-to-etchant flux ratio. As device dimensions continue to shrink, any roughness, caused by the device production process, plays a key role in eventual device performance.

In optimizing plasma etch processes, the main problem one comes across is the tremendous complexity of the plasma environment. This makes it exceedingly difficult to get an understanding of the reaction mechanisms involved. To circumvent the difficulties associated with plasma etching, many experiments have been performed$^2$ that give a picture of the processes involved. In several beam etching systems, fairly complete and accurate models have been developed. The present system has also been studied intensively by etch product analysis.$^3$–$^{12}$ However, surface roughness caused by the etching has never been characterized in detail, although various authors$^7$–$^{13}$ mention the importance in fully understanding the obtained models inspired by etch product analysis.

Ellipsometry is by far the most commonly used in situ surface diagnostic to look at the surface roughness. Therefore, ellipsometry is applied to a beam etching experiment to characterize the surface roughness. The fact that ions and etchant can be manipulated independently helps in revealing the role of ions and etchant in the roughening process on a more fundamental level. Aliev et al.$^{14}$ looked into the initial stage of c-Si surface roughening caused by XeF$_2$ etching with ellipsometry. This work will report on the roughness caused by XeF$_2$ etching of an amorphous silicon (a-Si) layer and subsequently the underlying crystalline silicon [c-Si(100)] sample. The a-Si layer is produced by 2.5 keV Ar$^+$ ion bombardment. The amorphization of c-Si has been studied quite intensively in terms of roughness, damage profiling, and simulations by Refs. 15–21 and many others, although most studies are done by surface probe measurements, such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM), and for ion energy ranges other than 0.5–2.5 keV as presented here. In Sec. III the ellipsometric characterization of the a-Si layer will be addressed and also the surface roughness caused by the impinging ions. This information is required in Sec. IV, addressing the subsequent chemical XeF$_2$ etching of the a-Si layer and the underlying c-Si sample. A comparison will be made between the roughness determined with in situ ellipsometry and the roughness of samples which have been analyzed ex situ with atomic force microscopy (AFM). The surface roughness caused by the XeF$_2$ etching affects the interpretation of the existing reaction layer models for XeF$_2$ etching of...
silicon deduced from product analysis. A discussion based on the bilayer model will address the issue of silicon-fluoride reaction layer thickness in Sec. V. In this section only the two modifications that have been made recently will be discussed. These are the addition of a sample exchange mechanism and the addition of an ellipsometer. A brief description of ellipsometry and measurement interpretation will also be given.

A. Vacuum apparatus

A schematic view of the setup and relative orientation of the beams onto the sample is shown in Fig. 1. The sample holder has been replaced by a rotatable two-slot sample holder. This sample holder has two slots in order to enable the calibration of the mass spectrometer. In the standard position of the sample holder, the sample surface is oriented toward the multiple-beam setup. The sample can be rotated to be in the path of a magnetic linear drive in the vacuum. With this linear drive, the sample can be transported to the load lock. The load lock has a capacity of six samples and a base pressure of $1 \times 10^{-8}$ mbar, achieved by a turbomolecular pump of 56 l/s. A valve separates the loadlock from the main chamber. The sample chamber has a base pressure of $10^{-8}$ mbar and is pumped by turbomolecular pumps. All fluxes impinging on the sample are measured in monolayers per second (ML/s); one monolayer corresponds to $6.86 \times 10^{18}$ m$^{-2}$, the surface density of Si(100). The Ar$^+$ ion flux can be varied from 0 to 0.11 ML/s and the ion energy ranges from 0.5 to 2.5 keV. The ion beam impinges at a $45^\circ$ angle of incidence. The XeF$_2$ flux can be varied from 0 to 3.6 ML/s and impinges at a $52^\circ$ angle of incidence.

B. Ellipsometry

This section gives a brief outline of ellipsometry. A full theory can be found in the book by Azzam and Bashara. Ellipsometry is a surface diagnostic that uses the change in ellipticity that a light beam undergoes during reflection at a surface. The Fresnel equations require that reflection coefficients for polarization parallel ($R_p$) and perpendicular ($R_s$) to the plane of incidence differ. This is usually expressed as a reflectance ratio $\rho$:

$$\rho = \frac{R_p}{R_s} = \tan(\Psi) \times e^{i\Delta}.$$  \hspace{1cm} (1)

Equation (1) defines the ellipsometric angles $\Psi$ and $\Delta$. The factor $\tan(\Psi)$ is the ratio of the reflected amplitudes of the $p$ and $s$ waves. The phase difference between the reflected $p$ and $s$ waves is called $\Delta$. Both angles are traditionally expressed in degrees.

The reflectance ratio $\rho$ that is measured depends on the refractive index and the morphology of the surface under investigation, as well as on the wavelength used, the angle of incidence, and the presence of thin films on the surface. A medium consisting of a mixture of two different substances (labeled 1 and 2) is modeled as an effective medium. The dielectric constant $\varepsilon_i$ of the effective medium is found by solving the Bruggemann equation:

$$0 = \nu_i \left( \frac{\varepsilon_1 - \varepsilon_r}{\varepsilon_1 + 2\varepsilon_r} \right) + \nu_2 \left( \frac{\varepsilon_2 - \varepsilon_r}{\varepsilon_2 + 2\varepsilon_r} \right) + \nu_s \left( \frac{\varepsilon_s - \varepsilon_r}{\varepsilon_s + 2\varepsilon_r} \right).$$  \hspace{1cm} (2)

Here the (complex) dielectric constants of media 1 and 2 are called $\varepsilon_{1,2}$ and $\varepsilon_r$, respectively. Medium $i$ ($i=1,2$) occupies a volume fraction $\nu_i$, with $\sum \nu_i = 1$. The complex refractive index of a medium is given by $e = \varepsilon + i\kappa$. In the case of a rough top layer, one of the media is vacuum with $\varepsilon_r = 1$.

The interpretation of the measured $\Psi$ and $\Delta$ is quite cumbersome. The Fresnel equations have no easy proportionality in them. In the case of a substrate with a film on top, all internal reflections in the film have to be taken into account, further complicating matters. This is why the interpretation of the data measured is done by comparison with computer simulations. For this work, a computer program based on the impedance algorithm was used. This allows the interpretation of measurements on substrates that have several thin layers stacked on top of one another. The refractive indices used in the analysis of these measurements are given in Table I.

C. Rotating-compensator ellipsometer

The setup for the ellipsometry is a rotating-compensator ellipsometer in the polarizer-compensator-sample-analyzer configuration. The laser light used is linearly polarized...
632.8 nm light from a He–Ne laser. The angle of incidence onto the sample was chosen to be around 74° for maximum sensitivity on silicon. The light is made circular with a λ/4 retarder. The polarizer and analyzer used are dichroic sheet polarizers with an extinction coefficient of 10^4. They can both be manually adjusted to within 0.05° of the desired settings. The rotating compensator is driven by a synchronous motor at line frequency, with a 2:3 transmission in both settings. The rotating compensator is driven by a synchronous motor at line frequency, with a 2:3 transmission in both settings.

**Table I. Numerical values of the refractive indices for the various layers assumed for data analysis and for reference.**

<table>
<thead>
<tr>
<th>Used for</th>
<th>Material</th>
<th>Assumed n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modeling</td>
<td>Crystalline silicon (c-Si)</td>
<td>3.88–0.02</td>
</tr>
<tr>
<td></td>
<td>SiO2</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>Amorphized silicon (a-Si)</td>
<td>4.58–0.72</td>
</tr>
<tr>
<td>Reference</td>
<td>Amorphized silicon (a-Si)</td>
<td>4.63–0.76</td>
</tr>
<tr>
<td></td>
<td>Rough SiF4</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>SiCl</td>
<td>1.66</td>
</tr>
</tbody>
</table>

Reference 32.
Reference 33.
Reference 26.
Reference 15.
Reference 29.
Reference 30.

D. Product flux calibration

To calibrate the pulse counting system of the mass spectrometer to absolute values of the flux leaving the sample an inert Ni sample is used, which does not interact with XeF2. For this purpose the sample holder is rotated such that a Ni sample is in the focus of the beams and the detector acceptance. The XeF+ count rate is calibrated with the absolute value of the impinging XeF2 flux of 0.9 ML s⁻¹ (=6.2 × 10¹⁴ cm⁻² s⁻¹). Rotating the Si sample back into position, the loss of XeF2 flux due to etching (as visible in the loss of XeF⁺ count rate) is equal to the SiF4 flux leaving the sample, because SiF4 is known to be the only etch product at room temperature. This absolute flux is used to calibrate the SiF3⁺ count rate which is used as a fingerprint of SiF4. Now, the mass spectrometer count rates directly represent an absolute flux of reagents and products, an essential condition for understanding etch dynamics. The etch rate is now expressed in the production coefficient δ defined as

\[ \delta = \frac{2\Phi(\text{SiF}_4)}{\Phi(\text{XeF}_2)} \]  

with Φ(\text{XeF}_2) the impinging flux on the sample and Φ(\text{SiF}_4) the product flux leaving the sample. The production coefficient or etching efficiency is defined such that δ=1 corresponds to the full conversion of reactant into products. The etch rate of silicon at the sample is given by

\[ \frac{d[\text{Si}]}{dt} = \frac{\delta}{2} \Phi(\text{XeF}_2), \]

which reflects that we need two reactant molecules to form a product molecule. By inserting the thickness as_{Si} =0.138 nm/ML of a monolayer of Si, the Si etch yield Y_{Si} (nm) is related to the total dose D(XeF2) (ML) of reactant delivered to the surface, as given by

\[ Y_{\text{Si}} = \frac{\delta}{2} D(\text{XeF}_2). \]

This relation allows tracking of the total amount of Si removed during our experiments. Further details concerning the mass spectrometer and the product analysis have been reported in the past.

III. AMORPHIZATION OF c-Si

The production of the amorphized (a-Si) layer by Ar⁺ ions will be described briefly, since ellipsometry has never been performed on Ar⁺ sputtering with ion energies in the range of 1.0–2.5 keV. Furthermore, this information is required to described the XeF2 etching in the following section. A more elaborate treatise will be published elsewhere.
Fig. 2. Ψ-Δ plot of a measurement of Ar\(^+\) sputter etching (connected dots). The drawn lines are simulations on the basis of Fig. 3. The large dot represents (Ψ, Δ) for a clean c-Si sample. At t = 0 the c-Si is covered by a 2.1 nm native oxide layer. When Ar\(^+\) ions are switched on steady state (Ψ, Δ) situations are reached for the various ion energies. A corresponding amorphized layer thickness \(d_{a-Si}\) and a rough layer thickness \(d_r\) is found by matching the simulations to the measurement.

A. Model

In Fig. 2 an ellipsometry measurement of the Ar\(^+\) etching of c-Si is shown (connected dots). The large dot represents the model values of Ψ and Δ of a clean c-Si sample, i.e., no native-oxide layer, roughness or amorphized Si layer. At \(t = 0\) the c-Si sample is covered by a thin native oxide layer. By matching the simulation of an increasing native oxide layer thickness on top of a c-Si bulk layer [Fig. 3(a)] to the measured Ψ and Δ the native oxide layer thickness is obtained. In this case the native-oxide layer thickness is found to be 2.1 nm. The refractive indices required for the simulations are listed in Table I.

Next, Ar\(^+\) ions with an energy of 0.5 keV and a flux of \(0.011 \text{ ML s}^{-1} (= 7.5 \times 10^{12} \text{ cm}^{-2} \text{s}^{-1})\) are switched on resulting in an increase of Ψ and Δ. The ions initially remove the native-oxide layer. Simultaneously the ions generate an a-Si layer with a rough layer on top, eventually going to a steady state values of Ψ and Δ. Subsequently the ion energy is increased with steps of 0.5 keV up to 2.5 keV keeping the ion flux constant. The ellipsometric parameter Ψ increases with increasing ion energy whereas little variation can be observed for Δ. At each energy a steady state situation is reached.

Next, a multilayer model is required to obtain a-Si layer thickness \(d_{a-Si}\) and rough layer thickness \(d_r\) in which the rough layer is constituted from 50\% void and 50\% a-Si via the Bruggemann equation Eq. (2). The complex refractive index used for a-Si is mentioned in Table I and has been determined in a more extensive study.\(^{26}\) Note that the values for \(n\) and \(k\) used here are in good agreement with the values reported by Fried et al.\(^{15}\) (See Table I), although they used 20 keV Ar\(^+\) ions to amorphise a Si sample. The simplest model to describe the measurement is shown in [Fig. 3(b)]. Two simulations by means of this model are shown in Fig. 2. Both simulations result from increasing the a-Si layer from 0 to 15 nm keeping the rough layer thickness constant at 0 and 1 nm, respectively. The following sections will show that this multilayer model gives a good description of the Ar\(^+\) etching of c-Si.

B. a-Si layer thickness

The a-Si layer thickness is determined by matching measurement and simulation at the steady state Ψ and Δ for each ion energy. The resulting a-Si layer thickness as a function of ion energy is shown in Fig. 4. The errors are derived from ten measurements on ten different samples. The a-Si layer thickness for 1.05 keV Ar\(^+\) ions determined by Buckner et al.\(^{16}\) is also included. buckner used the complex refractive index determined by Fried et al.\(^{15}\) (Table I). The difference between his result and ours is an indication of the difference in a-Si layer thickness resulting from the difference in complex refractive index.

With increasing ion energy the a-Si layer thickness increases, because the ions penetrate deeper into the silicon sample. Note that the a-Si layer thickness is in fact an effec-
tive layer thickness, since the amorphous to crystalline transition is not discrete but gradual. A comparison with, e.g., (SRIM) is therefore not straightforward. Here, a comparison is made by looking at the distribution of vacancy-causing collisions (vacancies/nm/ion) as a function of depth. The solid line in Fig. 4 represents the depth in SRIM that corresponds to a level of vacancy-causing collisions equal to 0.1 vacancy/nm/ion, which is in good agreement with the measured effective a-Si layer thickness. These conditions clearly define the depth of the effective discrete transition from a-Si to c-Si.

C. Roughness

The rough layer is simulated using the Bruggemann effective medium approximation [Eq. (2)] using a mixture of 50% voids and 50% a-Si. The rough layer thickness is on the order of 0.65±0.05 nm and shows no clear dependence on the ion energy. A similar degree of roughness caused by ion etching was reported by various authors not only on Si but also on other materials. The minor differences can be easily related to the difference in diagnostic tool or experimental conditions such as ion angle of impingement, ion flux, ion dose, and ion energy differences. Note that here the ions are still switched on when the roughness is determined. Surface probe measurements (AFM/STM) afterward might give a different roughness due to surface relaxation once the ions are switched off. More importantly, surface probe measurements give a different measure for surface roughness (root-mean-square roughness $\sigma$) than the rough layer thickness from ellipsometry which makes a quantitative comparison not straightforward.

The rather low roughness result can be explained by surface smoothing. After impact of the energetically incident ions, a heat spike of 1 ps melts the surface locally, allowing the surface to relax. One would expect this surface smoothing process, thus also the surface roughness, to be ion energy dependent. Here, the surface roughness shows no clear dependence on the incident ion energy. The energy deposited at the surface by the impinging ions with energies between 0.5 and 2.5 keV results in a lowering of the binding energy of surface atoms and consequently in an improvement of the sputter yield. A higher sputter yield may lead to a higher roughness. But simultaneously more energy is available for surface relaxation. Apparently, the two effects cancel out. Hence, a pronounced ion energy dependence of the surface roughness is not observed.

To conclude, the ion damage layer thickness and surface roughness obtained with ellipsometry can be explained and the results are in good agreement with literature. This insight in the amorphization process provides the necessary information to study the chemical XeF$_2$ etching of a 2.5 keV Ar$^+$ created, 12 nm a-Si layer and subsequently the underlying c-Si bulk.

IV. CHEMICAL XeF$_2$ ETCHING

In this section the ellipsometric characterization of the XeF$_2$ etching of a 12 nm a-Si layer and the underlying c-Si bulk sample will be addressed. The different models used to analyze the ellipsometry data are discussed, elaborating on the approximations made. The evolution of the roughness in time will be compared to AFM measurements and the amorphous-to-crystalline transition region will be discussed in detail.

A. Model

To obtain the surface roughness, again (multi-)layer models describing the surface are required. The used models are shown in Fig. 5. In time, the a-Si layer will be etched away and in the process the roughness increases [Fig. 5(a)]. When the a-Si layer is completely removed, the etching continues on the underlying bulk c-Si [Fig. 5(b)]. In general, a ratio of 50% void/50% material is used to model the roughness. Here, the percentage void $x$ is used as an additional fit parameter.

These models lack the presence of a SiF reaction layer contribution. The question therefore is whether this is a valid representation of the surface layers. In literature no reference can be found on the optical properties of SiF except for a complex refractive index for a rough SiF layer of $n=1.6$ determined by Oehrlein. Layadi and coworkers determined a complex refractive index for a SiCl layer of $n=1.66$, which should be somewhat similar to SiF considering the nature of F and Cl. However, since the reaction layer is known to be just a few monolayers thick, here a first approach will be to consider the contribution of the SiF layer to be negligible in contrast to the surface roughness. Hence, no SiF contribution will be incorporated in the layer models.

B. Results ellipsometry

In Fig. 6, simulations are shown in which the rough layer is assumed to have a certain thickness and the thickness of the underlying a-Si layer has been varied (along each thin line). At a given point in time, the measurement matches a
gives = 15 and 20 nm, respectively. Matching the simulation to the measurement, the rough layer thickness as a function of time is derived. 

In Fig. 7, the measurement (thick line) and simulations for three %void/% c-Si ratios are shown as a function of the rough layer thickness $d_{r, c\text{-Si}}$, originating in the point $d_{r, c\text{-Si}} = 0$ (dot). For the two cross lines the %void/% c-Si ratio has been varied in the range of 20%/80% to 70%/30% for $d_{r, c\text{-Si}}$=15 and 20 nm, respectively. By matching the simulation to the measurement, the rough layer thickness as a function of time can be derived. Note, that for $\Psi$ between 6° and 9°, the measurement comes close to the simulation with a 40% void/60% c-Si ratio, then going back to the 50% void/50% c-Si simulation. A 40%/60% ratio for %void/% c-Si can be seen as a surface that has a cusplike shape as is illustrated in Fig. 8. Such a rough layer can only arise from a process that etches faster in the direction parallel to the etch direction than in the lateral direction, perpendicular to the etch direction.

C. Evolution of roughness

The recorded ellipsometry trace in $(\Psi, \Delta)$-space for the XeF$_2$ etch process in time is shown in Fig. 6 (thick line). At $t=0$ the etch process starts. First both $\Psi$ and $\Delta$ decrease as a function of time [region (a)] followed by a region [region (b)] where $\Psi$ increase again but $\Delta$ keeps decreasing. In Fig. 9 the results of the analysis of the ellipsometry data as a function of the dose $D$(XeF$_2$) of the impinging reactant flux is shown. On the left-hand side, the thickness $d_r$ of the rough layer is shown and on the right-hand side, the measured SiF$_4$ production coefficient $\delta$ is shown. The letters (a) and (b) corresponds to which model from Fig. 5 has been used for curve-fitting the data. Initially, the roughness slowly increases followed by an intermediate phase starting at $D$(XeF$_2$) $\approx 2 \times 10^3$ ML, in which the roughness shows a rapid increase. Finally, at $D$(XeF$_2$) $\approx 1.2 \times 10^4$ ML, the roughness increases slow again. In the initial and final phase
an increase of $d_r \sim D(XeF_2)^{0.1}$ up to a dose $5 \times 10^3 \text{ML}$ of $XeF_2$. Next, a switch to an increase of $d_r \sim D(XeF_2)^{0.7}$ can be seen, which then levels off at $D(XeF_2) \approx 0.6 \times 10^4 \text{ML}$. By etching through the amorphous-to-crystalline transition the total surface area increases significantly. A significantly larger surface area would imply that more sites are available to the incoming etchant. Etch products can be created more easily, hence the etch rate goes up.

D. AFM data

To have an independent measurement of the surface roughness, samples are prepared for various $XeF_2$ doses and are analyzed ex situ with an atomic force microscope (NT-MDT Solver P47) in noncontact mode. Here, the AFM results are compared to the ellipsometry results.

In Fig. 10 both the rough layer thickness from ellipsometry and the roughness $\sigma$ from the AFM measurements are shown as a function of the $XeF_2$ dose. Two series of AFM measurements are shown, taken at different positions of the sample with $1 \times 1 \mu m$ scan size. Both show a similar trend in roughness evolution. Comparing AFM and ellipsometry measurements is not straightforward since the measure for roughness is defined differently for both diagnostics. The root-mean-square roughness $\sigma$ (or interface width $w$) measured by AFM is the standard deviation of the heights measured in the rough layer, whereas ellipsometry measures the total thickness of the rough layer $d_r$. An illustration of the two measures is shown in Fig. 11.

Fig. 10. Roughness as a function of $XeF_2$ dose in terms of rough layer thickness $d_r$ from ellipsometry and root-mean-square roughness $\sigma$ from AFM measurements. All samples have been measured twice, resulting in the two series of points.

Here, $d_r$ is assumed twice the $3\sigma$ interval of heights distribution, hence

\[ d_r = 6\sigma. \] (6)

This definition is based on the statistical statement that a height data point outside the $3\sigma$ interval is most probably erroneous.\(^1\) This way the statistically relevant part of the height distribution function is taken into account. Thus, by plotting the rough layer thickness against the corresponding root-mean-square roughness $\sigma$ a comparison on basis of Eq. (6) can be made (Fig. 12).

The comparison seems valid for the long dosed samples. However, at short-term and mid-term ($a$-Si to $c$-Si transition) the measurements show $d_r \geq 6\sigma$. This is related to the way
Underestimation of the roughness occurs when AFM tip radius $\xi_{tip}$ is larger or on the order of lateral dimension $\xi$ and $\xi < d_r$. Consequently, the sampled roughness $d_{r,AFM}$ is smaller than the real roughness $d_r$.

If the roughness develops more rapidly in etch direction but lateral dimension $\xi$ stays smaller or is on the order of the AFM tip radius ($\xi_{tip} = 10$ nm), the AFM is not able to sample the surface properly (Fig. 13). The consequence is an underestimation of the roughness obtained with AFM. In the long term, the lateral dimension grows and becomes larger than the AFM tip radius $\xi_{tip}$, which results in a proper sampling of the surface by AFM, hence the comparison on basis of Eq. (6) shows good agreement with the experiments. In addition, a $d_r = 4\sigma$ comparison line is added, which merely illustrates how sensitive is the comparison on the basis of Eq. (6).

**E. Anomalous roughening**

All independent diagnostics for the surface roughness, i.e., the ellipsometry data, the AFM data and the etch efficiency show anomalous behavior roughly centered at the transition from the $a$-Si top-layer to the c-Si bulk. Here, an attempt is done to qualitatively explain this behavior. First, a simple plot to define the extent of the transition region is introduced. The average thickness of the layer removed by etching is given by the integral version of Eq. (5), equal to

$$Y_{Si}(t) = \frac{1}{2}a_{Si} \int_0^{t'} \delta(t')\Phi_d(XeF_2)dt'$$

where $t' = D(XeF_2)/\delta(t')/\Phi_d(XeF_2)$.

In Fig. 14 the Si etch yield $Y_{Si}$ is shown as a function of $D(XeF_2)$ for easy comparison with our earlier plots. Additionally, plots of the functions $Y_{max} = Y_{Si} + d_r/2$ and $Y_{min} = Y_{Si} - d_r/2$, which represent the upper and lower bounds of the structures on the roughened surface. The dose (or point in etching time) where $Y_{max} = 12$ nm, the thickness of the $a$-Si layer at $t=0$, represents the time where the first c-Si patches start to become “visible” to the reactant. Conversely, the dose where $Y_{min} = 12$ nm, determines the point in time where the last cap of $a$-Si disappears from the sample. These two values $D(XeF_2)_1 = 4 \times 10^3$ ML and $D(XeF_2)_2 = 8 \times 10^3$ ML determine the region where both $a$-Si and c-Si have to be considered, the transition region. The anomalous behavior of roughening is contained in this transition region. In this region the shape of the structures, i.e., the surface morphology, changes.

To conclude, in the analysis of the ellipsometry data with model Fig. 5(b) in this transition region the best description is obtained for a 40% void/60% c-Si ratio, while a 50%/50% ratio is relevant for the final phase of pure c-Si etching for $D(XeF_2) > 1.2 \times 10^4$ ML. This suggests a cusplike shape of the pits in the surface in the transition region. Both features suggest that the remaining $a$-Si patches on the surface effectively act as a capping layer which causes the growth of deep and narrow trenches in the bulk c-Si. As a result the number of surface sites, i.e., the total surface area, increases. More sites are available to the incoming etching and, hence, the etch rate increases. The ellipsometry data on the roughness are corroborated by the AFM data, where in this transition region the measured variation $\sigma$ of the height distribution function is way too small as compared to the thickness $d_r$. This again suggests narrow and deep surface pits that cannot be tracked by the AFM tip in the transition region. Figure 15 illustrates the full etch process in the three phases.

**V. ROUGHNESS IN REACTION LAYER MODELS**

A severe surface area increase will have consequences for the kinetic reaction dynamics models that have been proposed in the past. Some issues concerning the reaction layer during XeF$_2$ etching, such as the “real” or local reaction layer thickness, are still open for debate, hence a discussion in the following section is an attempt to explain the local reaction layer thickness on basis of surface area increase due to roughening.

The local reaction layer thickness is the reaction layer thickness at the atomic scale, which is the parameter of most interest. However, when the surface area increases significantly, the reaction layer thickness obtained with almost all diagnostics tools is an area-integrated layer thickness. There-
Therefore, this measure is no longer equal to the local reaction layer thickness $d_{\text{local}}$, but is an effective reaction layer thickness $d_{\text{eff}}$.

$$d_{\text{eff}} = \rho d_{\text{local}},$$

where $\rho$ is the ratio of the area along the ragged peaks and valleys of the rough surface as compared to the effective area by looking at the bulk of the sample. Thus $\rho$ is the relative increase in available surface sites due to the roughening.

Some experiments in the past have led to the interpretation that the SiF reaction layer should be several monolayers (up to 10 ML) thick in order to explain the observations. However, Lo et al. concluded from x-ray photoemission spectroscopy (XPS) measurements that the SiF layer thickness is only 1.7 ML and the observed thick reaction layer is a consequence of surface roughness and not as suggested due to fluorine diffusion into the silicon. Vugts et al. arrived at the same conclusion by estimating the roughness on the basis of accurate (TDS) measurements with a mass spectrometer.

In this article, the surface roughness has been characterized: all information is present to review the available reaction layer models.

A simple but adequate model for XeF$_2$ etching of Si, the bilayer model, is used here for the discussion. A fast fluorination of Si–Si* surface sites results in Si–SiF and Si–SiF$_2$ species. Next the Si–Si back bonds are broken, leading to SiF$_3$ species at the surface. Then, the last bond can be broken leading to SiF$_4$ etch products. Basically, a simple description to visualize the reaction layer is a subsurface monolayer of SiF and SiF$_2$ species (partially) covered by a layer of SiF$_3$ species. The rate equations for the bilayer model are as follows:

$$\frac{d[\text{SiF}_{1,2}]}{dt} = k_f \Phi(XeF_2) \left(1 - \frac{[\text{SiF}_{1,2}]}{\rho N_0}\right)$$

$$- k_g \Phi(XeF_2) \frac{[\text{SiF}_3]}{\rho N_0},$$

in which $k_f$ is the fluorination probability, $k_b$ is the back-bond breaking probability and $k_e$ the etching probability. Here, $[\text{SiF}_{1,2}]$ and $[\text{SiF}_3]$ are the surface concentrations of the corresponding species in ML on a flat surface. The parameter $N_0$ is the Si surface concentration for a flat surface ($\rho=1$, $N_0 = 1$ ML). The formation of etch products is expressed in $\delta$ as

$$\delta = 2k_e[\text{SiF}_3],$$

which has already been shown in Fig. 9. With the proper parameter values for $\rho$, $k_f$, $k_b$, $k_e$, and $N_0$, the value of $\delta$ can be calculated and fitted to the measured $\delta$. In Fig. 16 again $\delta$ is shown as a function of XeF$_2$ dose, together with $\rho$ and coverage of SiF$_{1,2}$ and SiF$_3$ species (ML).

A discrimination is made between short-term and long-term parameter values. The bilayer model simulations are obtained as follows. For a XeF$_2$ dose below $10^3$ ML (=short term) the surface area increase $\rho$ is assumed to be close to 1. The true reaction layer growth can be observed. The SiF$_{1,2}$ species first start to generate a monolayer coverage. This layer gets covered for about 50% by SiF$_3$ species leading to the steady state reaction layer. To perform the simulations, $k_f$ is taken from Vugts et al., $k_g$ and $N_0$ are fixed, whereas $k_b$ and $k_e$ are used to fit the calculated $\delta$ to the measured $\delta$. The fixed and fitted parameter values are listed in Table II. For a XeF$_2$ dose above $10^3$ ML due to the etch process the roughness increases, which results in an increase of the surface area. Therefore, $k_f$, $k_b$, $k_e$, and $N_0$ are kept fixed to their values derived from the short term fit to the measured $\delta$. Only $\rho$ is used to fit the increase in the measured $\delta$. The concentration of SiF$_{1,2}$ species grows with the same factor as the surface area increase, thus also more sites are available to harbor SiF$_3$ species. Hence, more SiF$_3$ species
VI. SURFACE MORPHOLOGY

With the rough layer thickness \( d_r \) obtained from ellipsometry and the surface area increase \( \rho \) obtained from the product coefficient \( \delta \), a detailed description of the surface morphology can be derived. A three-dimensional geometric representation for the rough layer is required. The chosen geometry is a repetitive pattern [Fig. 17(a)] of the unit cell, which is constructed of a pyramid pointing upwards and a pyramid pointing downwards [Fig. 17(b)]. Now, the surface area increase \( \rho \) can be geometrically calculated by

\[
\rho = \sqrt{1 + \frac{d_r^2}{\xi^2}},
\]

where \( d_r \) is the peak-to-peak height difference. Dimension \( \xi \) equals the peak-to-peak lateral dimension. Actually, this formula is valid for both the three-dimensional and two-dimensional cases. Thus, the lateral dimension \( \xi \) here is equal to \( \xi \) defined in Fig. 13. Since \( \rho \) and \( d_r \) have been experimentally determined the lateral dimension \( \xi \) can be calculated.

At the beginning of the transition \( [D(XeF_2)] = 4 \times 10^3 \text{ ML}, \) Fig. 14] \( \xi \) is found to be equal to 6.6 nm with \( d_r = 5.9 \text{ nm} \) and at the end of the transition \( [D(XeF_2)] = 8 \times 10^3 \text{ ML}, \) Fig. 14] \( \xi = 12.9 \text{ nm} \) with \( d_r = 18.7 \text{ nm} \). In the transition phase \( \xi \) becomes smaller than \( d_r \) and is smaller than the AFM tip radius \( \xi_{\text{tip}} = 10 \) nm. Again this substantiates the fact that this type of surface roughness cannot be properly tracked with the AFM. In the final phase at \( D(XeF_2) = 2 \times 10^4 \text{ ML}, \) the value of \( \xi \) is found to be 15 nm with \( d_r = 27.8 \text{ nm} \). Here, \( \xi \) is significantly larger than the \( \xi_{\text{tip}} \); hence the roughness cannot be tracked properly.

Now, the average surface-slope angle can be determined, as given by the angle \( \gamma \) as defined in Fig. 17(b). For \( D(XeF_2) = 2 \times 10^4 \text{ ML}, \) the angle is found to be 62°. At 54° with respect to the Si(100) crystal plane lies the Si(111) plane, which is close to the 62° that is found here. This suggests that the roughness growth in the final phase has

---

**Table II.** Bilayer model parameters used for short and long term simulations, including the indication whether the parameter is used as fit parameter or as fixed value.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Short term values</th>
<th>Long term values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_f )</td>
<td>0.03 (fixed)*</td>
<td>0.03 (fixed)*</td>
</tr>
<tr>
<td>( k_o )</td>
<td>0.03 (fit)</td>
<td>0.03 (fixed)</td>
</tr>
<tr>
<td>( k_e )</td>
<td>0.03 (fit)</td>
<td>0.03 (fixed)</td>
</tr>
<tr>
<td>( N_o )</td>
<td>1 ML (fixed)</td>
<td>1 ML (fixed)</td>
</tr>
<tr>
<td>( \rho )</td>
<td>1 (fixed)</td>
<td>var. (fit)</td>
</tr>
<tr>
<td>( \Phi (XeF_2) )</td>
<td>0.9 ML s(^{-1})</td>
<td>0.9 ML s(^{-1})</td>
</tr>
</tbody>
</table>

*From Reference 7.
arrived at a steady state, i.e., surface area increase remains constant, which is governed by the etching of the Si(111) plane.

VII. CONCLUSIONS

Single wavelength ellipsometry has been successfully employed to characterize the surface roughness caused by physical Ar⁺ etching and chemical XeF₂ etching. The proposed ellipsometry layer models give a good representation of the etch process. Preliminary results with spectroscopic ellipsometry show a similar behavior. Thus, for the Ar⁺/XeF₂/c-Si system single wavelength ellipsometry has proven to be a good tool to monitor surface roughness. For XeF₂ etching of the a-Si layer and subsequently the c-Si bulk sample, the roughness evolution shows an anomalous roughening. When etching through the amorphous to crystalline transition the roughness increases proportional to $D(\text{XeF}_2)^{1.5}$ and, simultaneously, the etch rate shows an increase. Since etching is faster in the direction parallel to the etch direction than in the lateral direction, the surface shows a cusplike shape and hence the surface area increases severely. Presently, studies are devoted to answer the question why the etching goes faster in the etch direction as opposed to the lateral direction. In the a-Si to c-Si transition region the remaining a-Si patches act as a capping layer, which might suggest an etch rate difference between a-Si and selected crystal faces of c-Si. A comparison with AFM measurements substantiates the anomalous roughening. On the basis of the bilayer model for XeF₂ etching of silicon an estimation of the surface area increase yields an increase of a factor of 2. The resulting local reaction-layer thickness of 1.5 ML is in agreement with the 1.7 ML reported by Lo et al.\(^{13}\) Such a thin SiF reaction layer can be considered transparent to the ellipsometer and can therefore be disregarded in the ellipsometry layer models. Due to surface area increase this SiF layer becomes effectively 3 ML, but this is still negligibly small in comparison to the roughness. These separate studies of Ar⁺ and XeF₂ etching will facilitate a basis for studying the surface roughness caused by the Ar⁺ ion assisted XeF₂ beam etching of silicon.

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