Physics-Based Multi-Scale Modeling of Angled Reactive Ion Etching

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***Abstract*—We have developed a workflow to model reactive ion etching (RIE) that eliminates the need for experimental calibration by replacing empirical yield functions with data derived from molecular dynamics (MD) simulations. The MD simulations compute the angle- and energy-dependent sputtering yields, which are directly integrated into a feature-scale surface evolution model. Our approach captures the angular dependence of the etch process and qualitatively reproduces experimental profiles for blazed gratings fabricated using sequential ion beam exposures. The flexible and extendable workflow reduces reliance on time-consuming experiments and provides a pathway toward more predictive, physics-based process modeling.**

***Index Terms*—Molecular dynamics, Process simulation, Ion beam etching, Blazed gratings**

I. Introduction

The ongoing scaling of device features requires increasingly sophisticated fabrication techniques which are capable of achieving the necessary high precision and extreme aspect ratios. Reactive ion etching (RIE) is a widely used process to generate high aspect ratio structures, but accurately predicting feature-scale outcomes remains challenging due to the complex interplay of multiple plasma species, often in varying charge states. These species interact with surfaces in ways that are highly sensitive to plasma composition and process parameters, complicating the development of generalized models, which increasingly rely on expensive and time-consuming calibration from experiments.

In recent years, process emulation and simulation have become an important tool to predict etch profiles and to guide process development. However, such models typically rely on careful empirical fitting, using a combination of experimental data and theoretical knowledge from, e.g., atomistic simulations. Since the exact experimental conditions are not always fully known or reproducible, the applicability of such models to different plasma chemistries and conditions is often limited. We have recently introduced a feature scale model based on the level-set method and Monte Carlo ray tracing [1] to simulate the fabrication of blazed gratings using a novel dual-ion-beam technique [2]. A central component of this model is the angle-dependent etch yield function $\mathrm{f}(\theta)$, which is empirically fitted to match the angle-resolved etch rates obtained by Zhang et al. [2]. In that work, the yield peaked at an incident angle of approximately $65\,^{\circ}$, which was further used to calibrate the feature-scale simulation.

Molecular dynamics (MD) offers a powerful alternative to experimental fitting by providing atomistic-level insights into ion-surface interactions that are experimentally inaccessible. Earlier studies by Helmer et al. investigated the energy- and angle-dependent effects of Cl^+ and Ar^+ ions on silicon etching [3]. Belen et al. [4] used these results to model the reflection of ions as part of their feature-scale surface kinetics model. This model was then the foundation for the implementation of the blazed gratings model by Reiter et al. [1]. However, it is not entirely clear how well the results of chlorine ion interactions with silicon translate to fluorocarbon molecules.

In this report, MD simulations were performed to derive an angle-dependent yield function and the threshold energy for sputtering of a silicon dioxide substrate with $CF_3{}^+$ ions. This updated yield is integrated into the feature-scale model to investigate its impact on the resulting etch profiles, particularly in the fabrication of blazed gratings. By eliminating the need for empirical fitting, our approach enables more robust, transferable process simulations across a broader range of plasma conditions.

II. Methods

For the MD simulations, the LAMMPS software package was used [5], employing a ReaxFF potential developed by Du et al. [6] to describe interatomic interactions. This potential comprises several ReaxFF parameter sets, and as a result, it does not capture chemical reactions involving fluorine, silicon, and carbon with the highest accuracy permitted by the ReaxFF bond-order formalism. This limitation manifests as relatively large molecular fragments being desorbed during the etching process.

To investigate the chemical composition of the desorbed species, a post-processing analysis was conducted using the more recent ReaxFF potential from Zhong et al. [7], which is tailored for these elements. While the original simulations were performed prior to the availability of this potential, this analysis provides valuable chemical insight and highlights a clear path for further refinement in future work.

Post-processing and visualization of the simulation data were carried out using the OVITO software package [8]. The substrate, consisting of amorphous SiO_2, was generated through a melt-quench simulation with a quench rate of $10^{14}\,\frac{\mathrm{K}}{\mathrm{s}}$. To ensure computational efficiency, the dimensions of the

substrate were set to 34.5 Å × 34.5 Å × 68 Å, corresponding to a mass density of 2.47 g/cm^3. In simulation focused on low energy impacts, such as for the low energy ions in the threshold energy evaluation, the substrate size in the z-direction was reduced to 34 Å. This change improves computational efficiency by reducing the number of atoms in the system without compromising accuracy, as the shallow penetration depth of low-energy ions is fully captured within the thinner substrate.

Periodic boundaries were applied in the x- and y-directions, while a 30Å vacuum region was introduced above the substrate along the z-direction to account for an open surface. To suppress any drift of the simulation cell, the bottom 4 Å layer of the substrate was fixed. The upper 25% of the substrate atoms were integrated using a NVE ensemble, whereas the remaining atoms were coupled to a Nosé-Hoover thermostat (NVT ensemble) to dissipate excess heat generated by the incident ions and to maintain a substrate temperature of 300 K.

A CF_3^+ ion was introduced every 4.5 ps at a random lateral position, positioned 8-16 Å above the SiO_2 substrate surface. This time interval was selected to allow sufficient relaxation time for the substrate to dissipate the excess energy from the preceding impact. The ion's orientation was aligned such that its dipole moment pointed in the direction of motion, meaning the carbon atom was always the leading impact species. In total, 1200 ion impacts were simulated, corresponding to a dose of 10^{16}cm^{-2}. The angle of incidence, defined with respect to the surface normal, was varied from 0 ° to 80 ° while maintaining a constant ion energy of 200 eV. To estimate the threshold energy, the ion energy was varied from 10 eV to 200 eV, with all impacts oriented normal to the surface.

For the feature scale modeling, our in-house simulation tool ViennaPS was used [9]. The local etch rate was determined using Equation 1, which defines the yield as a function of the incident particle energy E and angle θ.

$$Y\left(E,\theta\right) = \left(\sqrt{E} - \sqrt{E_{\text{th}}}\right) f\left(\theta\right) \tag{1}$$

The primary modifications compared to the model from Reiter et al. were the adjustment of the initial energy of the ions to 200 eV (from 250 eV) and a reduction of the threshold energy E_{th} to 8.4 eV (from 20 V). The reduced ion energy better reflects the experimental conditions [2], while the reduced E_{th} is justified by the formation of a mixed layer of silicon, oxygen, carbon, and fluorine, which facilitates ion-enhanced chemical etching (see Section III-A). This modification is also consistent with the threshold energy of 4 eV for CF_3^+ ions reported by Gogolides et al. [10].

III. Results and Discussion

A central aspect in determining the angle- and energy-dependent yield is extracting the yield for each simulation setup. This was accomplished by subtracting the number of particles with a z-coordinate less than 75 Å from the initial particle count. The calculation was performed separately for silicon and oxygen atoms, yielding the number of etched particles as a function of the number of incident ions. By definition, the yield corresponds to the number of etched particles per incident ion. To quantify this, a linear function of the form $k \cdot x + d$ was fitted to the etch curves, where x represents the number of incident ions and k is the yield. In practice, the fit was applied only for ion impacts exceeding 500 to ensure the etching process had reached a steady state. An example of this fitting procedure is shown in Figure 1.

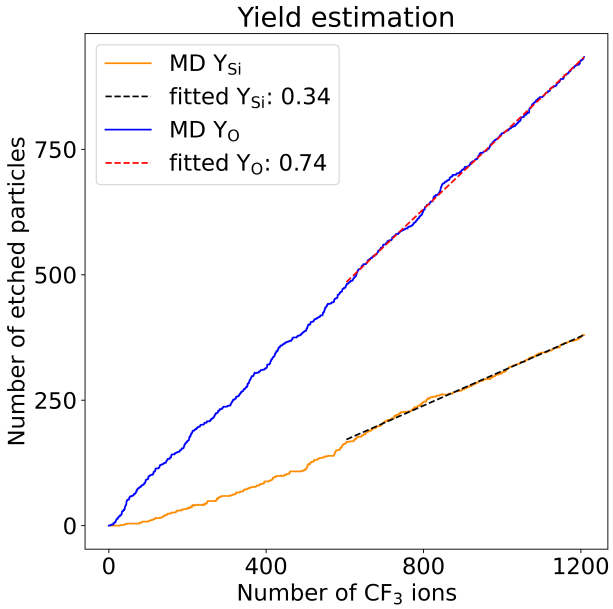

Fig. 1. Fitting of the yield by calculating the slope based on etched particles observed during ion impacts ranging from 500 to 1200.

A. Energy-Dependent Yield

Figure 2 illustrates the energy-dependent yield for CF_3^+ ions incident normally onto the silica surface.

A square-root dependent yield function, commonly used to describe ion-enhanced etching, was fitted to the simulation data. The resulting fit, as described by Equation 2, yielded a threshold energy of 8.4 eV and a prefactor A of 0.034. Although the threshold energy is significantly lower than the value of 20 eV used in the original model by Reiter et al., it aligns well with the ion-enhanced chemical etch rates reported by Gogolides et al. (E_{th}=4 eV and A=0.0454) [10].

$$Y_{\text{IEChE}}\left(E\right) = A\left(\sqrt{E} - \sqrt{E_{\text{th}}}\right) \tag{2}$$

The desorbed molecules from the simulation were then analyzed by employing the newly developed ReaxFF potential [7]. As shown in Figure 3, the number of desorbed CO and SiF_2 molecules increases with higher ion energies, indicating an increase in the breaking of Si–O bonds, followed by carbon binding to the freed oxygen and fluorine binding to the silicon. This observation is consistent with the ab-initio tight-binding study by Ito et al. [11], which reports increased formation of Si–F bonds at elevated energies for CF_3^+ ion impacts.

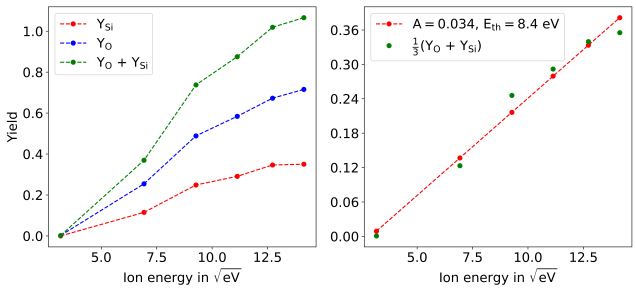

Fig. 2. Square-root dependent yield for ion beam experiments carried out by MD simulations.

Conversely, the number of CF_2 molecules decreases, suggesting that most of the incident carbon atoms are effectively incorporated into the formation of a fluorocarbon layer or contribute to the etching of oxygen. All these trends align well with experimental findings reported by Toyoda et al. [12] who observed similar behavior in the intensity of desorbed species.

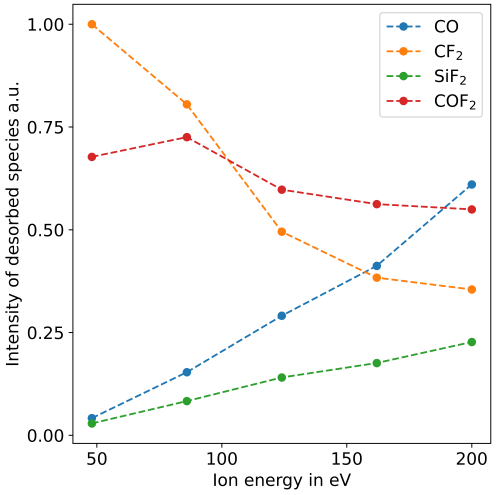

Fig. 3. Intensity of desorbed species for different ion energies. The intensity of desorbed CO and SiF_2 molecules increases with higher energies.

B. Angle-Dependent Yield

Figure 4 shows the resulting atomic structure and corresponding density profiles after 1200 ion impacts at an incident angle of 45 ° relative to the surface normal. A distinct fluorocarbon-rich layer is formed at the top of the substrate, supporting the assumption of a lower threshold energy of 8.4 eV. This fluorocarbon layer, often referred to as a steady-state reaction layer, effectively alters the target material from pure silicon dioxide to a mixed Si-O-C-F system. The chemical bonds within this layer are generally weaker and more readily broken by ion bombardment than the strong covalent bonds of the bulk SiO_2, which physically justifies a lower energy requirement for sputtering. Notably, the fluorocarbon layer exhibits a higher concentration of fluorine compared to carbon, which is consistent with experimental observations.

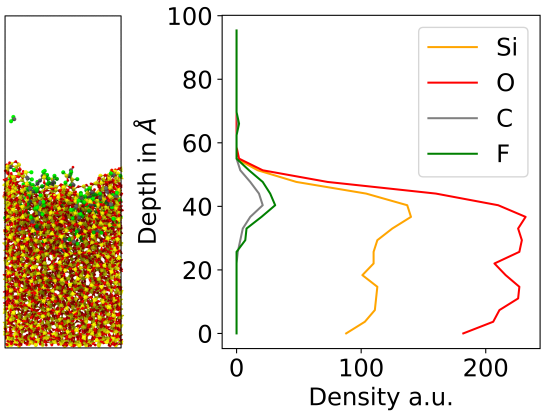

Fig. 4. (left) Atomic structure and (right) elemental density profiles after 1200 CF_3^+ ion impacts at an incident angle of 45 °. A fluorocarbon-rich layer forms at the surface, with higher fluorine concentration than carbon.

In Figure 5 the two angle-dependent yields, obtained from experiments [2] and MD (this work), are shown. The MD-derived yield peaks at slightly lower angles, indicating relatively enhanced etching for ions impacting the surface at an angle of approximately 50 °. To obtain a continuous representation for the yield, equation (3) was fitted to the MD data.

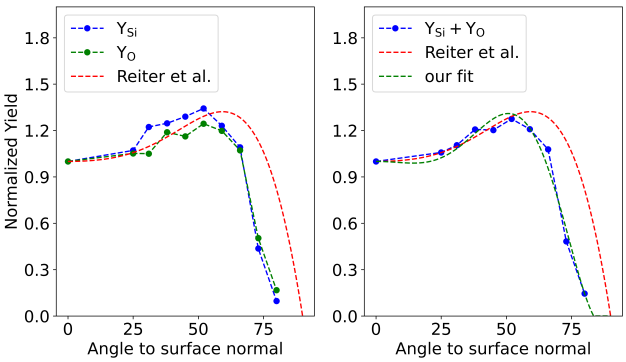

Fig. 5. Comparison of angular-dependent etch yields: MD-derived yields (Y_S, Y_0) versus the experiment-derived empirical yield used by Reiter et al. The right panel shows the total yield and fitted function used in the simulation model.

$$f(\theta) = \frac{\sum_{n=1}^{4} a_n \cos^n(\theta)}{\sum_{n=1}^{4} a_n} \quad (3)$$

Parameter	Value
a_1	-0.26
a_2	2.72
a_3	-4.3
a_4	1.95

C. Feature-Scale Model

The lower threshold energy affects particles with a reduced energy, such as reflected particles, more significantly than the initial high-energy ion beam. Physically, this leads to increased etching along the right vertical sidewalls, making the concave corner more pronounced. The shift in the yield peak towards

lower angles results in higher etching at flat surfaces. Since the top surface etches more quickly, the lower flat regions are exposed earlier to the primary ion flux, leading to a decreased final grating angle.

Figure 6 shows a comparison between the simulated etch profiles using ViennaPS with the original angular yield from Reiter et al. and the MD-derived yield from this work. Experimental profiles extracted from Zhang et al. [2] are also shown for reference.

After 140 s, the models match the experimental results equally well. Minor deviations are observed on the right sidewalls due to under-etching, which is attributed to ion reflection effects. This under-etching is a complex phenomenon tied to the simulation's reflection model. In the process, primary ions from the beam strike the sloped grating surface and scatter. A portion of these ions reflect with reduced energy and altered trajectories, subsequently bombarding the adjacent vertical sidewall. While the model captures this secondary etching mechanism, the slight deviation from the experimental profile suggests that the precise energy loss and angular distribution of the reflected particles may not be perfectly represented, highlighting a potential area for future model refinement. After 230 s well-defined blazed gratings have formed in all simulations. Our modified yield matches the steep surfaces of the experimental profile more accurately, although the final grating angle is slightly underestimated.

While both yield models reproduce the experimental results with good fidelity, the MD-derived yield shows a slightly improved match to the final grating angle and profile shape, particularly for the longer etch time.

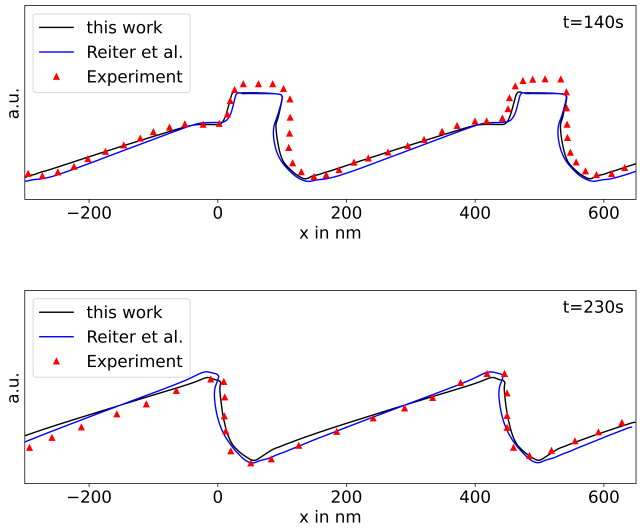

Fig. 6. Simulated etch profiles using ViennaPS at t=140 s and t=230s. The results from this work (black lines) and from Reiter et al. (blue lines) are compared to experimental profiles (red triangles) from Zhang et al. [2].

IV. Conclusion

In this work, we have successfully extracted the angle-dependent sputtering yield for CF_3^+ ions with a kinetic energy of 200 eV using molecular dynamics simulations. In addition the threshold energy for CF_3 molecules was determined and found to be lower than the initially proposed one. When combining both findings, the resulting yield function qualitatively reproduces experimental etch profiles. In contrast to previous studies, our multi-scale modeling approach eliminates the need for experimentally derived angle-dependent etch rates. Furthermore, the presented workflow is readily extendable. It can be extended to extract not only yield functions, but also ion reflection characteristics for different ion species. This incorporation of physically grounded input data enhances the predictive power of the model and improves its robustness when extrapolating to new process conditions.

Acknowledgement

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