

Simulation of Dilute Hydrofluoric Acid Etching of Silicon Dioxide Films in Constrained Spaces

制約条件下のSiO₂薄膜に対する、希釈フッ化水素酸による湿式エッチングのシミュレーション

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Control of lateral etching of films that are constrained by non-etching films is an area of great interest in the manufacturing of semiconductor devices such as 3-D NAND memory. In this paper, lateral etching of very thin silicon dioxide films sandwiched between silicon films in dilute hydrofluoric acid has been simulated using COMSOL Multiphysics modeling software. Specifically, using literature equations for the etch rate of 'standalone' oxide films, a time-dependent moving-boundary simulation that takes into account the electrical charging of wetted surfaces has been used to determine the effect of thickness of constrained oxide films on their etch rate. The results have been compared with experimentally measured etch rates for very thin oxide films reported in the literature.

薄膜の横方向のエッチングを、それが接するエッチングされない薄膜からの拘束を利用して制御する手法は、3次元 NANDメモリー等の半導体デバイスの製造プロセスにおいて非常に注目されている分野である。我々はこの論文で、Si 薄膜で挟まれたSiO₂超薄膜の希釈HFによるエッチングを、COMSOL Multiphysicsソフトウェアを用いてシミュレーションした結果について報告する。特記すべき点として、“拘束を受けていない”SiO₂薄膜について文献記載のエッチングレートを用い、濡れ表面の帯電を考慮した時間依存境界条件の下でシミュレーションすることによって、拘束を受けている薄膜の膜厚がそのエッチングレートにおよぼす効果を決定できた。またこれらの結果を、実験的に求められた超薄酸化膜のエッチングレートの文献報告とも比較した。

Introduction

Dilute hydrofluoric acid is commonly used in the fabrication of semiconductor and MEMS devices during steps that involve etching of silicon dioxide (SiO₂) in the presence of other materials such as silicon. Specifically, in the MEMS area, nanoscale trenches are created by etching thin SiO₂ layers sandwiched between two silicon layers. The size of the trench created is controlled by the thickness of the oxide layer. The type of HF (regular or buffered) used will affect the relative concentration of

different fluoride species in the solution. These species include HF, H₂F₂, HF₂⁻ and F⁻. Because surfaces immersed in aqueous solutions can develop a surface charge, the concentration of the charged etching species near the surface can be different from their bulk concentration. Silicon dioxide etch rate equations reported in the literature for acidic fluoride systems^[1, 2] have focused on free-standing films. In the case of SiO₂ films sandwiched between Si films, as the SiO₂ film is etched away, surface charge developed on exposed Si films is likely to affect the concentration profile of the charged fluoride species in

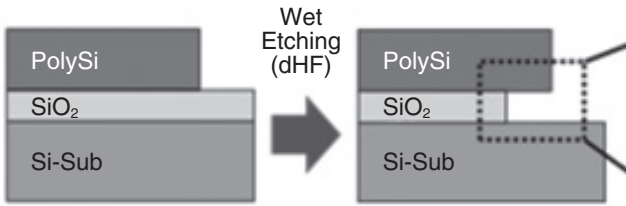


Figure 1 Schematic of channel formed between silicon as the sandwiched layer of SiO₂ is etched away^[3]

solution and hence the etch rate.

The work of Okuyama et al. was one of the early attempts to study the impact of interfacial electrical phenomena on the etching of thin silicon dioxide films constrained by silicon films.^[3] They utilized the Nernst-Planck equation and the Poisson-Boltzmann equation, in a finite element model to predict the concentration profile of ions in a channel schematically shown in Figure 1. They assumed a negative surface charge on Si, zero charge on SiO₂, and considered HF₂⁻ as the only active etchant species. *Equilibrium* simulations were carried out to determine the average HF₂⁻ concentration at the SiO₂/solution interface with varied SiO₂ film thicknesses. As expected, the calculations showed reduced concentration of HF₂⁻ near the oxide/solution interface as compared to the bulk concentration.

By comparing the calculated average concentration of HF₂⁻ in the channel to the experimental etch rate of SiO₂ films determined by an SEM technique, they concluded that thinner films etched at a much slower rate than the thicker films due to the reduction of HF₂⁻ at the SiO₂/solution interface. They did not do any dynamic etching simulations to validate this correlation.

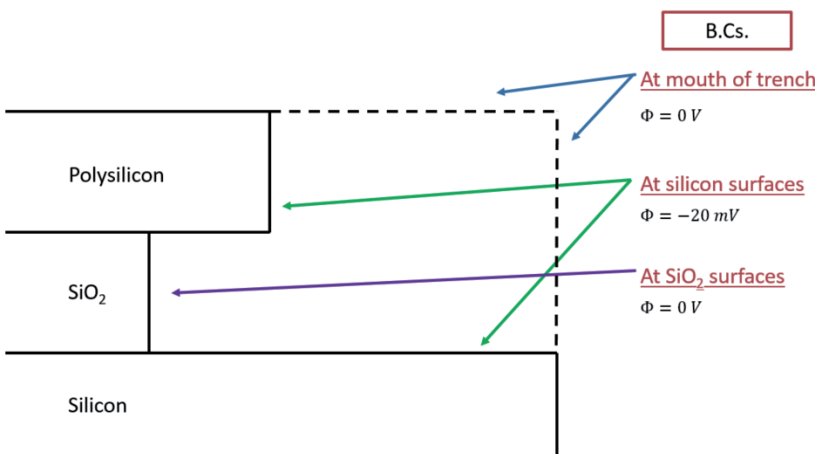


Figure 3 Boundary conditions for equilibrium simulation

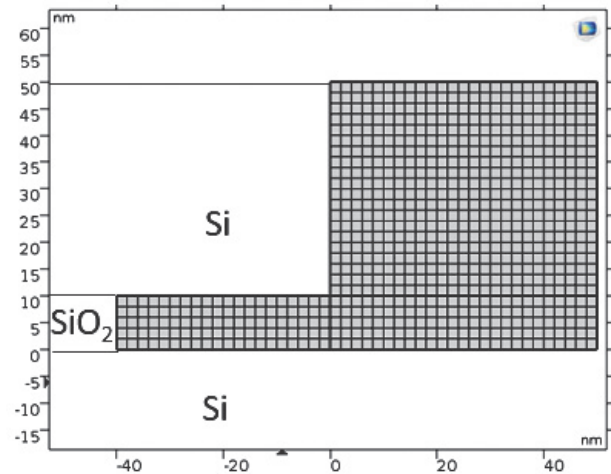


Figure 2 Meshed simulation geometry in COMSOL Multiphysics

Simulation

In this work, we have attempted to address the aforementioned shortcoming of the work of Okuyama et al. by creating a time-dependent moving-boundary simulation in COMSOL Multiphysics 5.3a. Utilizing species concentration-dependent etch rate equations from published literature and surface chemistry principles, the etching process was simulated.

To create a moving-boundary simulation of SiO₂ etching by dHF solutions in an Si/SiO₂/Si stacked structure, a simple 2D model was used. The volume of the hydrofluoric etching solution was used as the simulation area. A 2x2 nm free quadrilateral mesh was used in the simulation area where the finite element calculations were carried out. This mesh was chosen because it handles mesh element deformation better than the standard triangular mesh. The simulation geometry and meshing are shown in Figure 2.

For simulations, a *two-step method* was utilized. First, an equilibrium study was performed to develop the initial species concentration profiles as a function of X and Y position in the solution volume (This step is similar to the work of Okuyama et al.). The concentration profile from the equilibrium study was then used as the initial condition for a time-dependent study in which the etching process was modeled as a *moving-boundary problem*.

In the equilibrium study, the two governing equations, stationary Nernst-Planck equation and the Poisson equation, are solved to determine the position-dependent concentration profiles. The simulation area includes a slightly pre-etched SiO₂ layer, creating a small

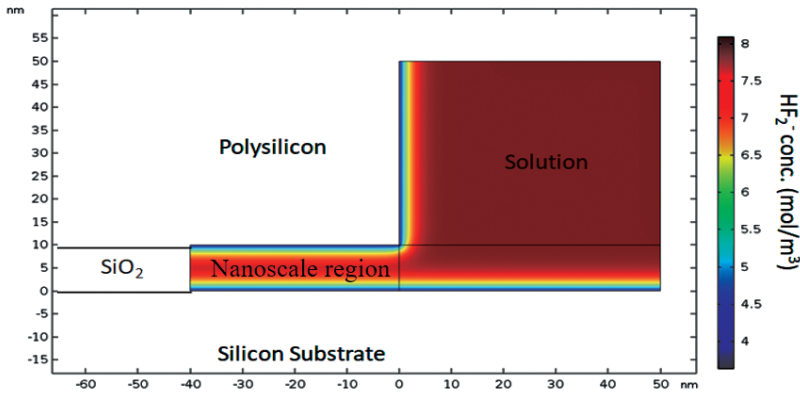


Figure 4 Equilibrium concentration profile of HF_2^- with -20 mV at the silicon/solution interface

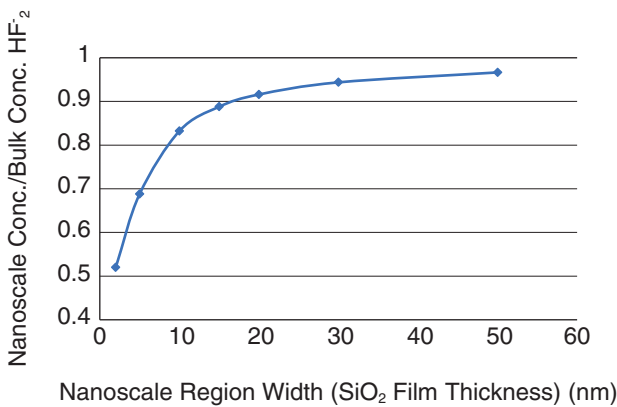


Figure 5 Simulated concentration of HF_2^- in the nanoscale region normalized to the bulk concentration vs. nanoscale region width

channel between the two silicon layers, which is shown in Figure 3. At the silicon/solution interface, a constant potential of -20 mV was used to represent the surface charging that would occur on silicon in a 0.5 wt% solution (~pH = 2). (The surface potential on silicon was approximated by its measured zeta potential at pH = 2 by the authors). At the SiO_2 /solution boundary as well as the remaining outer solution boundaries, a 0 mV boundary condition was applied. The SiO_2 /solution boundary was set to 0 mV because the isoelectric point (IEP) of SiO_2 typically occurs around a pH of 2.

Equilibrium simulations were carried out for channels with different widths. The result of one of these studies with a 10 nm SiO_2 film is shown in the HF_2^- concentration map in Figure 4. The repulsion of the HF_2^- away from the silicon surfaces leads to an overall reduced concentration in the nanoscale region. Average concentrations in the nanoscale region were calculated for SiO_2 film thicknesses of 2 nm – 50 nm. These

average concentration values were then normalized to the bulk concentration of HF_2^- and plotted as a function of nanoscale region width in Figure 5. The results of these equilibrium simulations agree with the simulations done by Okuyama et al.

In the time-dependent studies, the equilibrium concentration profile that was determined by the stationary study is used as the initial condition. Additional boundary conditions were applied to the SiO_2 /solution boundary and the outer solution perimeter boundaries. At the

SiO_2 /solution interface, a boundary velocity as a function of local species concentrations was used to represent the etching of SiO_2 in HF solutions. At the same interface, a flux boundary condition related to the etch rate was used to represent the consumption of species due to the etching reaction. At the outer solution boundaries, a constant concentration condition was used to represent the bulk HF solution that replenishes the simulation area as species are consumed due to the etching reaction.

The time-dependent simulations were carried out using two commonly used etch equations in published literature. These are the Judge Equation 1 and the Verhaverbeke et al. Equation 2. The mathematical forms of these equations that relate etch rate (R) to different fluoride species are as follows:

$$\text{Judge: } R = A[\text{HF}] + B[\text{HF}_2^-] + C \dots\dots\dots (1)$$

$$A = 2.5 * 10^{-13} \quad B = 9.66 * 10^{-13} \quad C = -1.4 * 10^{-11}$$

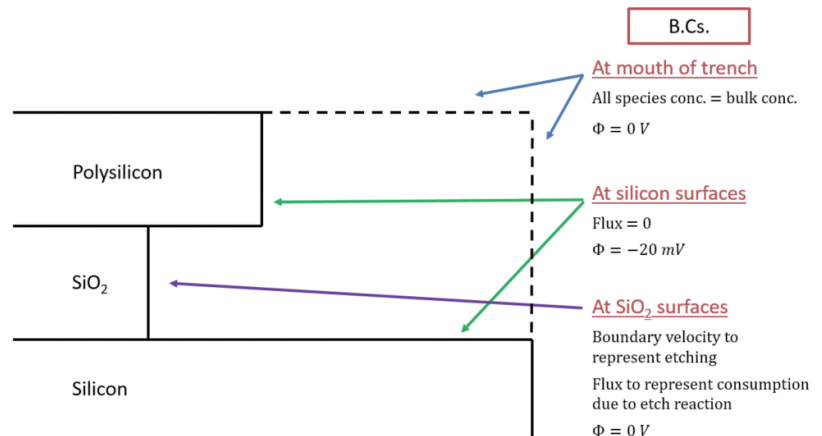


Figure 6 Boundary conditions for time-dependent simulations

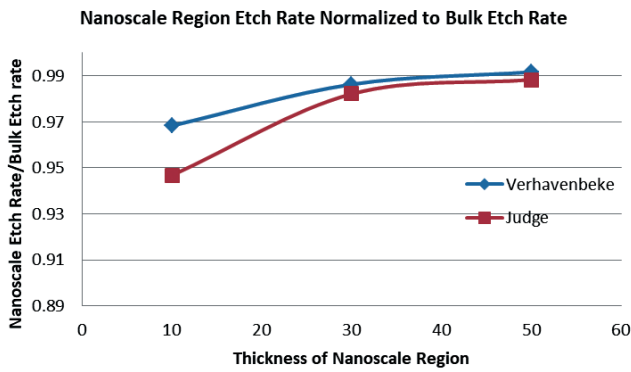


Figure 7 Comparison of the simulated etch rates using the Judge model and the Verhaverbeke model

$$\begin{aligned}
 \text{Verhaverbeke: } R = & a[(HF)_2] + b[(HF)_2]^2 + c6[HF_2^-] - \\
 & + d[HF_2^-] * \log\left(\frac{[H^+]}{[HF_2^-]}\right)
 \end{aligned}
 \tag{2}$$

$$\begin{aligned}
 a = & 3.73 * 10^{-13} \quad b = 1.22 * 10^{-16} \quad c = 2.14 * 10^{-12} \\
 d = & 3.53 * 10^{-12}
 \end{aligned}$$

In these models, the etch rate is in units of *m/s*, and the concentrations of the individual species are in units of *md/m³*. Both models have individual contributions to the etch rate from neutral and ionic species. The Judge model considers the monomer HF to be the neutral species responsible for etching while the Verhaverbeke model regards the dimer H₂F₂ to be the active neutral species. Three time-dependent simulations were performed for different nanoscale region width (SiO₂ layer thickness) of 10, 30, and 50 nm. The etch rate for each of these SiO₂ thicknesses was simulated and normalized to the bulk etch rate (no electrostatic effects), as shown in Figure 7.

Conclusion

The use of either model did not show a significant reduction in etch rate with film thickness. The simulation results do not agree with the experimentally measured etch rates reported by Okuyama et al. It may be recalled that neutral HF species (including the dimer) and HF₂⁻ ions are considered etchant species in these two models. Since neutral HF and H₂F₂ species dominate speciation in 0.5 % HF solution at a pH of 2 and electrostatic effect is likely to have an impact only for charged specie, HF₂⁻, the simulation results appear to make sense. The discrepancy between our simulation results and Okuyama et al.’s experimental results may be because the literature etch rate equations used in the simulation were developed for oxide films that were very different from the films used by Okuyama et al. A research project aimed at establishing etch rate expressions for well characterized thin oxide films in dilute HF solutions would immensely help in

testing the validity of the correlation put forth by Okuyama’s group.

References

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