Atomic-Level Insight into Si-Cl₂-Ar Atomic Layer Etching from Molecular Dynamics Simulations

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Abstract: Classical molecular dynamics (MD) simulations of Si-Cl₂-Ar atomic layer etching (ALE) are performed to establish a more detailed understanding of the process. The amount of silicon (Si) etched and chlorine (Cl) present in the layer are carefully examined during the ion bombardment step. The etch yield and etch products vary greatly as a function of ion fluence. These insights can aid in developing more accurate mathematical models of ALE processes.

Keywords: atomic layer etching, molecular dynamics simulations, silicon, chlorine

1. Introduction

Moore's law is an empirical relationship that states that number of transiters on an integrated circuit will roughly double every two years. In order to achieve this, the characteristic features of transiters need to continually shrink. Our society is quickly approaching the stage where the relevant length scales for these features are nearing the atomic scale. Therefore, we are met with an unprecedented challenge, where atomic-level accuracy and fidelity need to be met within our microelectronics processing tools.

Atomic layer etching (ALE) processes is a promising technology that promises to achieve this during the etching of the relevant substrate.[1] An ALE cycle generally consist of two steps: a chemical modification step and an ion bombardment step. The first step is used to create a chemically modified near-surface layer with weakened bonds to the underlying material but ideally without any etching. The second step uses energetic ions to remove the modified layer with minimal or no alteration or loss of the non-modified material. Perhaps the most well-known ALE system is the etching of silicon (Si) by using chlorine (Cl) gas or plasma during the chemical modification step and argon ions (Ar^+) for the ion bombardment step.

Although the technique is now used industrially, research is needed to further refine and perfect ALE processes. Classical molecular dynamics (MD) is a useful computational technique to help build a fundamental understanding of ALE. In this work, we present MD simulations of Si-Cl₂-Ar ALE. Note that this corresponds to the case in which the chlorination step is done with Cl₂ gas dosing in the absence of plasma, and it is assumed that the Cl₂ gas is completely removed before the Ar⁺ plasma is applied.

We present calculations of etch per cycle and Cl uptake under various conditions. More interestingly, however, we demonstrate how the etch yield varies during the ion bombardment step and correlates with the near-surface Cl content. We also show how the distribution of etch products changes during the ion bombardment step.

2. Simulation Details

Classical MD simulations are performed using a custom code reported previously. [2,4] A recently reparametrized version of the Reactive Empirical Bond Order (REBO) potential is used to describe interactions between Si atoms and Cl atoms,[2] while the Molière potential is used for all interactions with Ar^+ ions.[3] The simulations are set up such that a semi-infinite Si slab is exposed to a vacuum space in the z-direction. Depending on which step of the ALE cycle is being modelled, Cl₂ molecules or Ar^+ ions are randomly placed in the vacuum space, just outside the interaction radius of the Si slab, and allowed to impact the Si surface. Impacts are modelled using microcanonical (constant number of atoms, volume, and energy) MD runs that last approximately 2 picoseconds.

The simulations are run to mimic Si-Cl₂-Ar ALE processes. The Si slab is subjected to a series of 300K Cl₂ molecule impacts, followed by a series of energetic Ar^+ ion impacts at normal incidence. The Cl₂ molecule impacts are the chemical modification step, and the Ar^+ ion impacts are the ion bombardment step. Both steps, make up one ALE cycle. Multiple cycles are run to allow the system to reach a cyclic steady state. Previous work has demonstrated the accuracy of our modelling procedure by comparison to Si-Cl₂-Ar ALE ion beam experiments. [4,5] More details of the simulation procedure are contained in previous references. [2,4]

3. Results and Discussion

Figure 1 shows the amount of Si etched and Cl uptake as a function of cycle number for various Si-Cl₂-Ar simulations. Results for four different cases are shown, each with a different Ar^+ ion energy.





As expected, the amount of Si etched (and equivalently the etch per cycle) increases with the Ar⁺ ion energy. The average Cl uptake shows the opposite dependence. While this result is also not surprising, it is interesting to examine this phenomenon in more detail. Figure 2 shows the amount of Si etched and Cl concentration in the subsurface region during the final ALE cycle for the simulations described in Figure 1. Focusing on the amount of Si etched during the last ion bombardment step, the etch yields can be calculated at various points during the step. The etch yields are shown at the beginning of the ion bombardment step (when the Cl concentration is the largest) and at the end of the ion bombardment step.



Fig. 2. Amount of Si etched (in units of equivalent monolayers) and Cl concentration in the amorphous region for the final cycle for the ALE simulations shown in Figure 1. Etch yields during ion bombardment step are calculated at the beginning (green) and end (purple) of the bombardment steps.

For the 15 eV case, the etch yield does not change dramatically during the ion bombardment. Similarly, there is not a large change in the Cl concentration. For the 25 eV, 50 eV, and 100 eV cases we see that the etch yields at the beginning of the cycle are larger by factors of 3, 5, and 8.5 respectively with respect to the etch yields at the end of the cycle. This demonstrates that a larger amount of Cl in the near surface region leads to a larger etch yield. For the 100 eV case, the etch yield at the end of the ion bombardment step (0.004) corresponds to the physical sputtering yield for bare Si. Therefore, given enough time during the ion bombardment step to deplete the amount of Cl, all ALE cycles reach the physical sputtering limit.

Figure 3 shows the etch products for the Si-Cl₂-Ar ALE simulations during the final ion bombardment step.



Fig. 3. Average product yields (per incident ion) as a function of Ar⁺ ion fluence during the final ion bombardment step for the ALE cycles shown in Figure 1.

The 15 eV case shows that this energy is near the threshold for ALE since well less than a monolayer of Si is removed per cycle. For the higher ion energies, a key feature is that a relatively large amount of atomic Cl is sputtered from the surface at the beginning of the ion bombardment step. Further, Cl is also mixed into the subsurface region. These effects tend to reduce the nearsurface Cl concentration and therefore the effective sputtering of SiCl_x products from the surface. This agrees with what is observed in Figure 2. SiCl₂ and to a lesser extent SiCl are predicted to be the primary silicon chloride etch products. For the 50 eV and 100 eV cases, atomic Si is a significant etch product throughout the cycle. At 100 eV the effective yield of atomic Si sputtering during the ion bombardment step is reduced somewhat initially and then remains roughly constant at the yield for pure Si through the rest of the cycle.

4. Conclusion

Classical MD simulations are performed to simulate a Si-Cl₂-Ar ALE process. The amount of Si etched and Cl uptake are monitored as a function of ALE cycle number. Four different ALE cycles are considered, each with a different Ar⁺ ion energy.

By closely examining the amount of Si etched during the final ALE cycle, it is shown that the etch yield varies as a function of ion fluence. The etch yield is the largest at the beginning of the ion bombardment step and decreases as the step progresses. There is a clear correlation between the etch yield and the amount of Cl in the subsurface region with the etch yield decreasing as the amount of Cl decreases. In the 100 eV case, the etch yield reaches the physical sputtering limit after about 10 ML of ion fluence. It is likely that this will also occur for the other three cases with a large enough ion fluence.

Etch products are also tracked during the ion bombardment step. It is observed that, generally speaking, a large amount of atomic Cl is removed from the surface during the beginning of the ion bombardment step. Atomic Cl sputtering declines steadily during the step. SiCl₂, the main silicon chloride product, follows a similar trend. For the 50 eV and 100 eV cases, a significant amount of atomic Si sputtering is observed throughout the cycle. Future work will focus on developing a mathematical model for the etch per cycle and Cl uptake for Si-Cl₂-Ar ALE as a function of relevant process parameters. These include, but are not limited to, ion fluence, ion energy, and angular distribution.

5. References

[1] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho, J. Vac. Sci. Technol. A **33**, 020802 (2015).

[2] J. R. Vella and D. B. Graves, J. Vac. Sci. Technol. A **40**, 063203 (2022).

[3] G. Molière, Z. Naturforschung A 2, 133-145 (1947).

[4] J. R. Vella, D. Humbird, and D. B. Graves, J. Vac.

Sci. Technol. B 40, 023205 (2022).

[5] S. Park, K. Min, B. Yoon, D. Lee, and G. Yeom, Jpn. J. Appl. Phys. **34**, 389-393.