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Molecular dynamics simulations of silicon dioxide atomic layer etching using fluorocarbon and oxygen plasmas

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Abstract: Molecular dynamics simulations were used to study the fluorocarbon-assisted etching of silicon dioxide. The interaction of C, F, and O species on the surface was studied for a better understanding of the mechanisms involved in ALE. The C accumulation was also analyzed and observed that it could be minimized with the additional supply of O atoms during the Ar ion desorption step.

Keywords: Atomic layer etching, silicon dioxide, fluorocarbon

1. Introduction

The semiconductor industry continues to advance its technologies as the demand for more powerful devices keeps growing. The fabrication processes of semiconductor devices must also keep up with the fast-paced technological advancement. New technologies such as atomic layer deposition (ALD) and atomic layer etching (ALE) have been incorporated into such fabrication processes [1]. The ALD is a method to grow a thin film atomic layer by atomic layer and the ALE is its reverse process to remove a material atomic layer by atomic layer. In reality, in typical ALD and ALE, a few nm thick layers are deposited or etched layer by layer.

To achieve the atomic-scale control of such processes, we must understand their surface reaction mechanisms. Recently, Kaler and co-workers studied the SiO_2 ALE using an alternating C_4F_8 and energetic Ar ion beam in an ICP plasma reactor [2]. In this process, the etched depth per cycle was observed to be a few angstroms. On the other hand, lowering the Ar ion energy led to surface fluorination and a decrease in the removal rate of surface species. Moreover, C atoms from the decomposed fragments of the C_4F_8 plasma beam were found to form a C-rich accumulated layer, which can be remedied by a short exposure to an oxygen-containing plasma beam.

In our study, we use molecular dynamics (MD) simulations to emulate the SiO_2 ALE process. A similar system was studied to understand the etching and formation mechanisms earlier [A]. In this study, we focus on the surface modification in the fluorocarbon adsorption step, the penetration depths of fluorine (F), oxygen (O), and C atoms during the desorption step, and the thickness of the mixed layer formed during the process.

2. Methods

A rectangular simulation box with a surface area of 2.09 × 2.09 nm^2 and an initial depth of 2.79 nm represented the SiO_2 model system used in our study, as shown in Fig. 1. A detailed description of the MD simulations of beam surface interactions was presented in detail by Miyake *et al.* [3]. The modified Stillinger-Weber (SW) type potential sets with bond-order properties were used to integrate the equations of motion of each atomic species present in the system [4-5]. Periodic boundary conditions were applied in the horizontal directions, representing an infinitely large surface layer. The depth in the *z*-direction of the material is also assumed to be infinite in the sense that additional layers of SiO_2 atoms are added from the bottom as the etching proceeds. All species injected with pre-defined incident energies approach the surface at a normal angle and hit at random positions. The adsorption step was simulated by depositing chemically reactive species such as CF_3 radicals on the surface. These radical species were adsorbed and formed a fluorocarbon (FC) layer on the SiO_2 surface. After this, the desorption step was simulated by exposing the FC-covered SiO_2 surface to low-energy Ar ions (40 eV). During the desorption step, the Ar ions bombard the FC-covered layer, forming a mixed layer of F, C, Si, and O atoms, which may eventually etch the SiO_2 surface.

The addition of O species during the desorption step was also studied. The parameters used in the adsorption and desorption steps are summarized in Table 1.

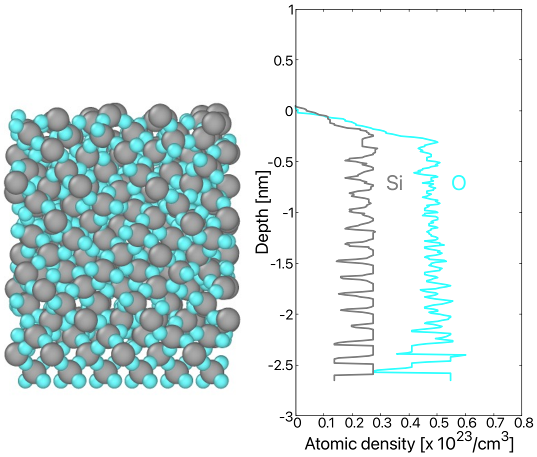

Fig. 1. Actual picture of the SiO_2 model system and its corresponding depth profiles of atomic concentrations. The 0 nm represents the initial top layer of the SiO_2.

Table 1. Simulation parameters

Parameters		Values
CF3	Radical dose	2.3×10^{15} cm^{-2}
	Incident energy	0.5 eV
Ar	Ion dose	11.4×10^{16} cm^{-2}
	Incident energy	40 eV
Ar:O (5:1)	Ion dose	2.3×10^{15} cm^{-2}
	Incident energy	40 eV

3. Results and Discussions

Figure 2 shows the depth profiles of atomic concentrations of each specie present in the system. The horizontal axis represents the atomic density per unit volume, and the vertical axis represents the depth or height in nm. The 0 nm is the position of the initial top layer of the SiO_2 model. The penetration depths of the surface species can be seen, as well as the atomic density at a specific position after the desorption step. Comparing the two figures, the thickness of C atoms is found to be higher in the Ar-only bombardment case and lower in the case with the addition of O. Moreover, the density of O atoms increased in the case of O addition.

Figure 3 shows the total number of atoms and molecules desorbed during the desorption step of the SiO_2 ALE in the simulation. Here, the total number corresponds to the number of species removed from the surface per Ar ion injection. The number of species desorbed due to the Ar ion bombardment is shown in red, and the case where O atoms were mixed with the ratio of Ar:O = 5:1 is shown in blue. At the same Ar ion dose, it is seen that the surface atoms removed with the additional O atoms are higher compared to that in the case of Ar bombardment only. More C atoms were removed due to the formation of CO and CO_2 species, which explains the lower C atomic density observed in Fig. 2.

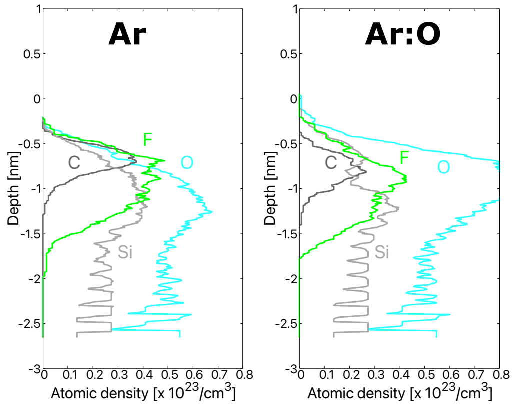

Fig. 2. The depth profiles of atomic concentrations after the desorption step with an ion incident energy of 40 eV. The 0 nm represents the initial top layer of the SiO_2.

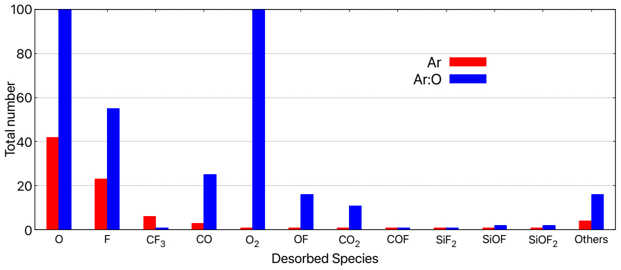

Fig. 3. The total number of the desorbed species during the desorption step with an Ar ion dose of 11.4×10^{16} cm^{-2} obtained from the simulation. The category "Others" refers to the sum of the other desorbed atoms and molecules not listed in this figure

4. Conclusions

The formation mechanisms and surface etching during the SiO_2 ALE process were studied using MD simulations. The adsorption of C and F fragments from CF_3 radicals, the desorption of the modified surface layer with Ar ions, and the mixed Ar and O ions were investigated. The simulation results showed the penetration depths of the FC species and an accumulation of the FC layer during the desorption step. The FC layer contains a high density of C atoms. The simulation results revealed that the thickness of the C layer could be minimized with the mixture of Ar:O ions during the desorption step due to the formation of CO and CO_2 volatile byproducts.

5. References

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