# MD simulations of amorphous SiO<sub>2</sub> thin film formation in reactive sputtering deposition processes

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Silicon Dioxide  $(SiO_2)$  thin film deposition processes were studied with use of classical Molecular Dynamics (MD) simulations combined with Monte Carlo (MC) simulations. The MC simulations are shown to efficiently emulate thermal annealing processes during deposition. Dependence of various film properties on the incident atomic kinetic energies and incident angles is examined based on the numerical simulations.

#### 1. Introduction

Reactive sputtering deposition processes are widely used for the formation of dielectric thin films such as SiO<sub>2</sub> and TiO<sub>2</sub> [1]. Thin films formed in such processes tend to have stable film qualities suitable for, e.g., optical filter applications. For very fine optical filters such as gain flattened filters or band pass filters, however, thin film qualities (such as residual stresses) strongly affect their optical properties. One of the causes of such film stresses during deposition processes is the difference in thermal expansion ratios at various locations in the film. Another possible cause is the momentum transfer from impinging atoms to the deposited film surface, which makes the thin film denser and increases its stress. In order to clarify such stress generation mechanisms as well as modification of other film properties during deposition processes, we have simulated reactive sputtering deposition processes for amorphous SiO<sub>2</sub> thin films, using molecular dynamics (MD) [2-6] simulations combined with Monte Carlo (MC) simulations. In these processes, sputtered Si reacts with separately supplied oxygen gas to form SiO<sub>2</sub> near or on the surface. Energetic Ar ion bombardment is also used for the control of film qualities.

Classical interatomic potential functions used in our MD simulations are the same as those used in [2,3]. Effects of energetic Ar ion bombardment that "presses" the surface of deposited film [7] are also taken into account in our simulations. Thermal relaxation processes such as surface diffusion and thermal desorption processes are also effectively taken into account via Monte Carlo (MC) simulations. After sufficient amount of SiO<sub>2</sub> is deposited in the simulation, we evaluate various properties of the deposited film.

### 2. MD simulations

The structure of the initial substrate, which is a quartz plate, is shown in Fig.1. The horizontal cross section of this model substrate is  $2.4 \times 2.4$  nm<sup>2</sup>. Periodic boundary conditions are imposed in the x and y directions. The positions of bottom atoms are fixed during simulation, which prevents the entire substrate from moving downward when it is subject to incident atoms. The interatomic



Fig.1 The model substrate of quartz (450atoms) for MD simulations. A dark large sphere represents a silicon atom and a light small sphere represents an oxygen atom.

potential functions among Si, O, and Ar atoms are of Stillinger-Weber type. The numerical simulation procedures are as follows;

1. Before the first injection, the initial substrate is maintained in thermal equilibrium at 473K under NVT (i.e., the number of particles, volume, and temperature) constant (i.e., canonical) conditions. At time t = 0, a Si atom is injected and motions of all particles are followed in the MD simulation at NVE constant (i.e., microcanonical) conditions for a sufficiently long period (typically one pico second) until motions of most atoms in the system are "settled" near

thermal equilibrium.

2. Then the system temperature is brought to 473K and the system is maintained at this temperature for a while under NVT constant conditions again. Then 81 low-energy oxygen atoms are injected into the surface simultaneously at random horizontal positions. This phase of MD simulation is continued for a sufficiently long time under NVE constant conditions.

3. The system is again brought to thermal equilibrium at 473K. Into this surface an Ar atom is injected and the motions of all particles are followed under NVE constant conditions.

4. To emulate thermal relaxation processes before the next Si injection, the Monte Carlo (MC) simulation process based on the Metropolis algorithm is performed at 473K.

5. The cycle consisting of the 1 to 4 processes given above is repeated until the system accumulates 1500 atoms in the substrate.

A  $SiO_2$  film obtained in this manner is shown in Fig. 2. The structures of deposited films are analyzed with the radial distribution functions. The  $SiO_2$  film in Fig. 2 has



Fig.2 A snap shot of a deposited amorphous  $SiO_2$  thin film obtained from MD simulation.

been confirmed to be amorphous.

The MC simulation process is performed in the following manner. First we move one particle by a given small distance in an arbitrary direction and measure the change of the total potential energy. We adopt or do not adopt this atomic displacement, based on the usual Metropolis algorithm. We perform the same processes for all atoms in the entire simulation volume. We call this process of displacing all atoms, whether each displacement is adopted or not, one MC cycle. We have used approximately 800 MC cycles at each MC simulation process and confirmed that the system potential energy is sufficiently lowered by each MC simulation process. Figures 3 and 4 show the density and stoichiometry of deposited amorphous SiO<sub>2</sub> films as functions of Si incident energy.



Fig.3 The film density of a deposited amorphous  $SiO_2$  thin film as a function of Si incident energy, obtained from MD simulations.



Fig.4 Oxygen / Silicon number ratio and the coordination number around a Si atom in deposited amorphous  $SiO_2$  thin film as a function of Si incident energy, obtained from MD simulations.

### 3. Summary

We have developed a numerical scheme to simulate atomic-scale plasma surface interactions during reactive sputtering deposition processes based on classical MD and MC simulations and evaluated deposited film properties as functions of process parameters.

## References

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