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Prediction of Crystallization Temperature for HfO_2 Thin Film in High Temperature Annealing Process by Reaction Time Accelerating Molecular Dynamics

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1. Introduction

Due to the shrinkage of CMOS devices, the replacement of gate insulator film with a novel material with high dielectric constant has been considered. Among these high-*k* materials, HfO_2 is widely studied because of its high dielectric constant, a large band gap and good electrical property. However, HfO_2 film easily undergoes leaky phase because of the crystallization on high temperature annealing after deposition in device manufacturing processes. Because the thickness of HfO_2 is very thin, atomic level simulation is important to understand the realistic film structure. Concerning crystallization processes, molecular dynamics study has been performed for HfO_2 and its alloy systems, and the composition dependency of the crystallization and phase separation has been well discussed [1,2]. However, in this calculation, because simulation cell has nucleation region and is supposed to bulk structure at periodic boundary condition, it seems to be difficult to estimate the crystallization temperature of thin film structure.

In an attempt to overcome this gap, we have developed new calculation method by incorporating simple reaction rule [3] for nucleation growth model into molecular dynamics simulation and inserting SiO_2 layer to the bottom of HfO_2 layer (SiO_2/HfO_2/SiO_2 structure at periodic boundary condition) in order to consider the thin film phenomena. In this study, we have succeeded to estimate the film thickness dependency of the crystallization temperature using our methodology.

2. Methodology

We investigated the crystallization temperature for 2 nm and 3 nm HfO_2 thin film by reaction time accelerating molecular dynamics (RTA-MD) simulation [3] with simple nucleation growth model. Simulation cells of amorphous-HfO_2/SiO_2 were prepared by melting of crystal layers of HfO_2 and rapid quenching to room temperature. These procedures were also performed by molecular dynamics simulation and same parameters were used for 2 nm and 3 nm HfO_2 models. We prepared unit cells 1.0 nm × 1.0 nm × 2.7 nm and 1.0 nm × 1.0 nm × 3.7 nm containing 240 atoms and 336 atoms, respectively. Amorphous SiO_2 layer was *ca.* 0.7 nm (48 atoms). The initial simulation structures were shown in Fig. 1. The periodic boundary condition was applied on this simulation. The simulations were performed at a constant pressure of 1 atm.

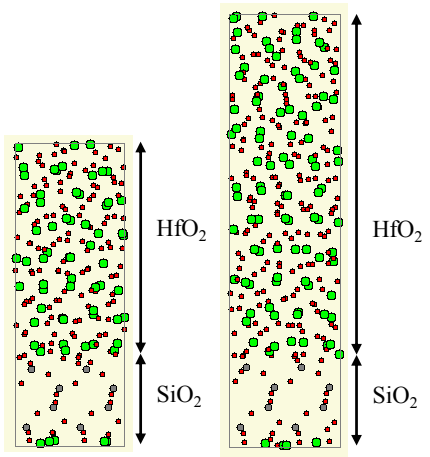

Fig. 1 Simulation models for 2 nm-HfO_2/SiO_2 and 3 nm-HfO_2/SiO_2

In order to consider the nucleation reaction from amorphous phase, we used two types of potentials and switched the potentials according to the atomic distance. Once atoms were approached within a certain distance, the potential was changed with a certain possibility to encourage crystallization process. Thus, we simply modeled nucleation reaction in the framework of classical molecular dynamics simulation. Both types of potentials were consisting of Columbic and Born-Mayer type interactions terms. Potential parameters for nucleation were referred to the previous work for similar materials system [2, 4]. Concerning poten-

tial for non-nucleation region (amorphous phase), parameters were slightly changed so as to represent amorphous structures. All the simulations were performed with a 1.0 fs of integration time step.

3. Results and discussions

The crystallization simulations of thin HfO_2 films were carried out. Fig. 2 shows the typical example of crystallization process. This figure shows that the crystallization was preceded from the nucleation region, which is spontaneously generated after some time steps. We have succeeded in the calculation of crystallization process without setting seed crystal in the simulation cell. The process time was underestimated compared with the realistic phenomena, because we ignored the reaction time to overcome the activation energy of nucleation by switching potential immediately. When we compare our results with experimental data, we used the simulation result of 1,000 ps, which is considered enough time for structural relaxation.

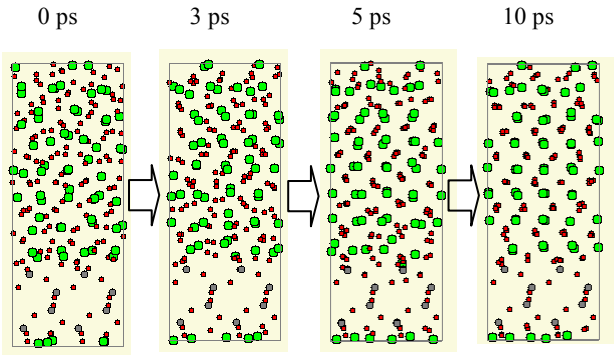

Fig. 2 Snapshots of crystallization process for 2 nm-HfO_2/SiO_2 at 700 °C.

To evaluate the crystallization temperature, we performed RTA-MD simulation with different temperatures. Fig. 3 shows the simulation results of 2 nm-HfO_2 and 3 nm-HfO_2 after 1,000 ps. For 2 nm-HfO_2/SiO_2, 600 °C was not sufficient to crystallize the thin film and the crystallization temperature was considered to be 700 °C. Similarly, for 3 nm-HfO_2/SiO_2, the crystallization temperature was considered to be 500 °C. In order to investigate the detailed structure, we calculated the radial distribution function (RDF). The typical result for 3 nm-HfO_2/SiO_2 and ideal monoclinic HfO_2 was shown in Fig. 4. This figure shows that the periodic structure was found for 500 °C and the structure was similar to the monoclinic phase. On the other hand, the experimental reported temperature was *ca.* 500 °C for 3 nm-HfO_2 and fully crystallization was found at 600-700 °C [5]. Furthermore, the majority of crystalline phase was reported to be monoclinic [5]. Our simulation results were consistent with these experimental results and the reported crystallization temperature was in good agreement with the predicted temperature.

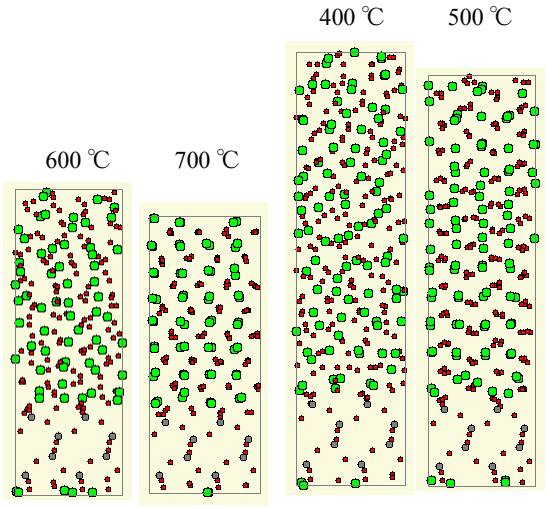

Fig. 3 Simulation results of crystallization process for 2 nm-HfO_2/SiO_2 and 3 nm- HfO_2/SiO_2

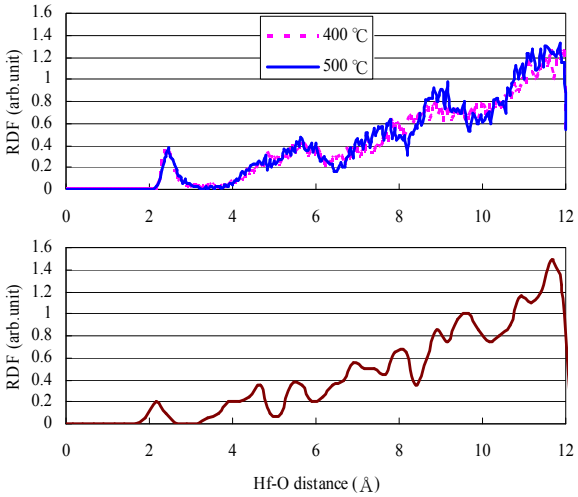

Fig. 4 Radial distribution function (RDF) for simulated 3 nm-HfO_2/SiO_2 (Top) and ideal monoclinic crystal (Bottom)

4. Conclusion

We can successfully estimate the crystallization temperature of HfO_2 thin film by molecular dynamics combined with simple nucleation growth model. The predicted temperature of 500 °C for 3 nm HfO_2 film was in fair agreement with the experimental value. Using our methodology, the estimation of thin film effect based on atomic level has been available.

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