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The Effect of Nitrogen on Thermal Diffusion in HfO$_2$-based Gate Dielectrics

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1. Introduction

In recent years, high-k materials such as HfO$_2$ and Hf-silicate have been expected to be the new gate dielectrics for MOS devices [1]. For practical use of the high-k gate dielectrics, some problems should be solved such as the crystallization, the formation of grain boundaries, and the oxidation of the substrates during the deposition or annealing processes. In order to overcome these drawbacks, nitrogen atoms are incorporated into the HfO$_2$ and Hf-silicate [2,3].

In this study, we focus on the atomic diffusion between dielectrics and substrates depending on the composition of the alloys or the condition of annealing. Classical molecular dynamics (MD) simulations have been performed to investigate the effect of nitrogen on thermal diffusion in HfO$_2$-based gate dielectrics.

2. Calculation method

In our MD approach, the potential energy of the system is calculated by the sum of pairwise potentials [4,5]:

$$V(r_{ij}) = f\,b_{ij}\exp\left(\frac{a_{ij}-r_{ij}}{b_{ij}}\right) - \frac{c_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}} \ , \qquad (1)$$

where r_{ij} is the distance between atoms i and j, q_i is the net charge of atom i, f is a constant, and a_{ij}, b_{ij}, and c_{ij}, are the parameters determined for each pair of atoms. We modified the Si and O potential parameters optimized by Matsui [4,5] and added the Hf [5] and N parameters. This parameter set reproduces the experimental values of the lattice constants of crystal HfO$_2$, Si$_3$N$_4$, Si$_2$N$_2$O, and Hf$_2$N$_2$O , the Si-N and Hf-N bond lengths [6-9].

Our MD simulations are performed under the condition of constant temperatures and volumes. The equations of motion are solved numerically with the time step of 1.0 fs.

3. Results and Discussions

In the fabrication process of the high-k gate dielectrics, a thin SiO$_2$ interfacial layer (IL) is formed between the Si substrates and the high-k materials. Thus, we prepared the amorphous Hf$_{1-X}$Si$_X$O$_{2(1-Y)}$N$_{1.33Y}$ layer containing ~1200 atoms (2.5nm×2.5nm×3.0nm in size) on the amorphous SiO$_2$ interfacial layer containing 900 atoms (2.5nm×2.5nm ×2.0nm in size). The composition parameters are taken as X=0, 0.1, 0.2, 0.3 and Y=0, 0.1, 0.3, 0.5 in this study. Although the Hf-N metal phase can be formed due to the incorporation of too much nitrogen atoms, we have chosen these composition parameters to understand the atomic

diffusion systematically. For incorporation of nitrogen atoms into the Hf$_{1-X}$Si$_X$O$_2$, three oxygen atoms are replaced with two nitrogen atoms so that the charge of the system is conserved to be neutral before and after the replacement. Our simulations are performed at 1200~1600°C, which are higher than the usual annealing temperature. The reason for this is that the simulation time can be saved at these higher temperatures.

Figure 1 shows the atomic configurations of HfO$_{2(1-Y)}$N$_{1.33Y}$/SiO$_2$ (Y=0 and 0.5 for Figs. 1(a) and 1(b)). The diffusion of Si atoms into high-k materials is apparently suppressed by the incorporation of N atoms. It is found that the more N atoms are incorporated, the less Si
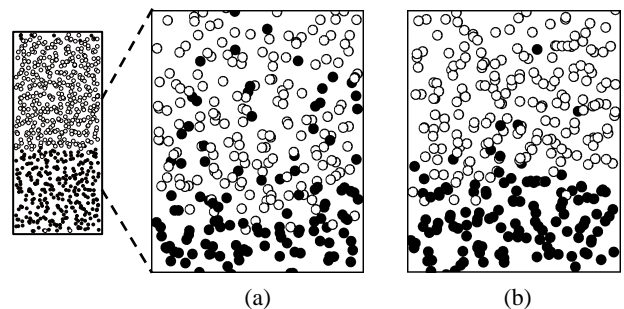

Fig. 1 The atomic configurations of (a) HfO$_2$/SiO$_2$ and (b) HfON$_{0.67}$/SiO$_2$ after 10ns annealing at 1300°C. The open and closed circles denote Hf and Si atoms, respectively. O and N atoms are not shown for clarity.
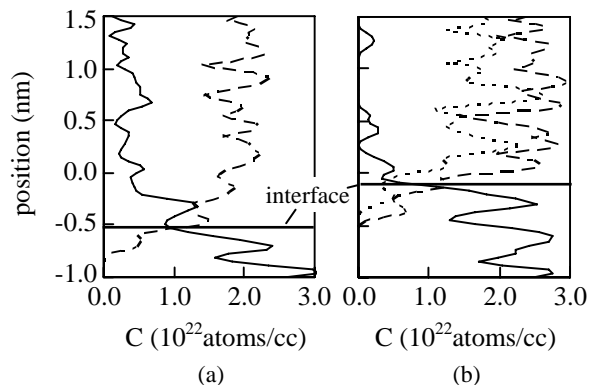

Fig. 2 Distributions of atomic concentration (C). (a) HfO$_2$/SiO$_2$ and (b) HfON$_{0.67}$/SiO$_2$ after 10ns annealing at 1300°C. Solid, dashed, and dotted lines denote concentrations of Si, Hf, and N atoms, respectively.

atoms diffuse. On the other hand, it seems that few Hf atoms diffuse into SiO_2 even if N atoms are not incorporated. Similar results were obtained for other temperatures.

The more Si atoms diffuse into high-k materials, the thinner SiO_2 layer becomes. Thus, the position of the interface between $HfO_{2(1-Y)}N_{1.33Y}$ and SiO_2 moves toward the SiO_2, which should be taken into consideration for counting the Si atoms in the high-k materials. We define the interface as the position at which the concentration of Hf atoms is half of the average one in the high-k materials (Fig. 2). The amount of Si atoms diffused into the high-k materials (n_{si}) is obtained by integrating Si concentration in $HfO_{2(1-Y)}N_{1.33Y}$ for Y=0, 0.1, 0.3, 0.5 (Fig. 3). Figure 3 shows that the incorporation of N atoms into high-k materials effectively suppresses the diffusion of Si atoms.

The slopes of the solid lines shown in Fig. 3 ($\Delta n_{si}/\Delta t$) represent the amount of Si atoms diffused into the high-k materials per unit time. Figure 4 shows the Arrhenius plots of $\Delta n_{si}/\Delta t$. In this case, the value obtained from the slope of the line for the Arrhenius plots (activation energy ΔE in the Arrhenius equation) corresponds to the diffusion barrier between $HfO_{2(1-Y)}N_{1.33Y}$ and SiO_2. The more N atoms are incorporated, the steeper the slope of the line for the Arrhenius plots becomes. The diffusion barriers are obtained as ΔE=1.57, 1.69, 1.76, 2.10 eV for Y=0, 0.1, 0.3, 0.5, respectively. Therefore, the decrease in the amount of Si atoms diffused into the high-k materials is quantitatively shown as the increase of diffusion barriers by the incorporation of N atoms.

Finally, the initial thinning rates of the SiO_2 layer due to the diffusion of Si atoms at the usual annealing temperature (1000°C) were estimated by extrapolating the line shown in Fig.4. For example, the initial thinning rate of the SiO_2 layer for the case of Y=0.1 is about half of that for the case of Y=0. These results are helpful in estimating the initial conditions of the composition, annealing temperature, and annealing time required in the fabrication process of the high-k gate dielectrics.

4. Summary

We investigated the effects of nitrogen on thermal diffusion in HfO_2/SiO_2(IL) gate dielectrics by using classical molecular dynamics simulations.

(1) The more N atoms are incorporated into the high-k materials, the less Si atoms diffuse from SiO_2 into $HfO_{2(1-Y)}N_{1.33Y}$.

(2) The effect of N atoms on the diffusion of Si atoms from SiO_2 into the high-k materials is quantitatively shown by the increase of diffusion barriers.

(3) In contrast to the diffusion of Si atoms into high-k materials, few Hf atoms diffuse into SiO_2 even if N atoms are not incorporated.

(4) From the results of Arrhenius plots of $\Delta n_{si}/\Delta t$, the initial thinning rate of the SiO_2 layer (1000°C) for the case of Y=0.1 is estimated to be about half of that for the case of Y=0.
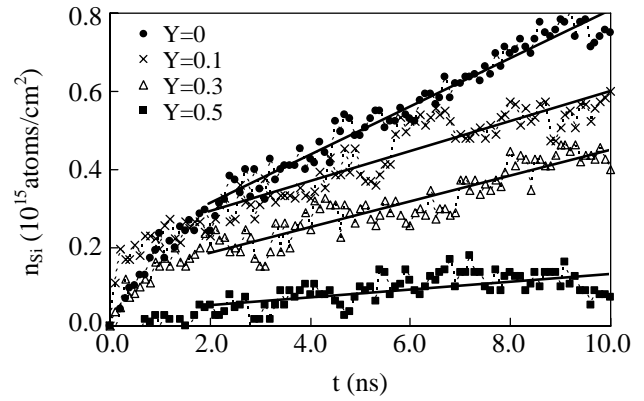

Fig. 3 The amount of Si atoms diffused from SiO_2 into $HfO_{2(1-Y)}N_{1.33Y}$ for Y=0, 0.1, 0.3, 0.5 (1300°C). Solid lines are drawn by least squares fit for each series of plots.
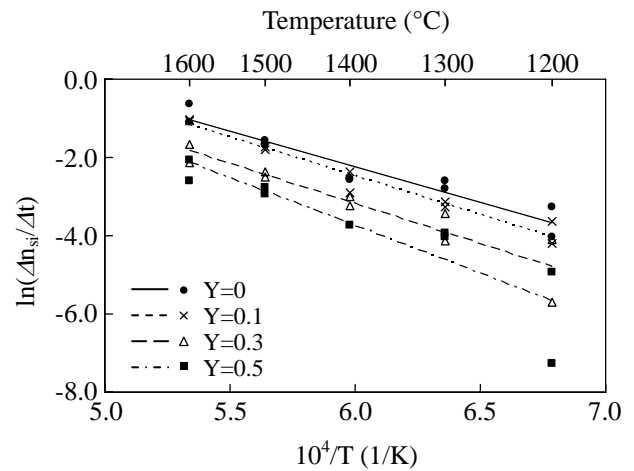

Fig. 4 Arrhenius plots of $\Delta n_{si}/\Delta t$. For each Y and temperature, the results of two cases in which initial conditions differ are shown. Lines are drawn by least squares fit for each series of plots.

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