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First principles molecular dynamics simulations for amorphous HfO_2 and $Hf_{1-x}Si_xO_2$ systems

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Amorphous phases of HfO_2 and $Hf_{1-x}Si_xO_2$ were obtained using the Projector Augmented Plane Wave method through the melt and quench technique. For the pure HfO_2 system, several pore channels appear in the structures. Changes to x in the $Hf_{1-x}Si_xO_2$ were also studied. As the concentration of Si increases, the size of the pore channels increases, much space appears and two-fold oxygen atoms increase. By calculating the heat of formation energy, it was found that phase separation between amorphous HfO_2 and SiO_2 occurs at $x>0.1$.

Key words: *HfO_2; $Hf_{1-x}Si_xO_2$; amorphous; first principles; molecular dynamics*

1. Introduction

Recently, hafnia (HfO_2) grown on Si substrates has been widely studied as a potential candidate for replacing silicon dioxide as the gate dielectric in scaled complementary metal oxide semiconductor(CMOS) devices [1]. To avoid the crystal orientation, misfit and grain boundary problems at the interface, good amorphous thin films are required for a high-k gate oxide like a SiO_2. In order to increase the crystallization temperature and improve the device performance, several ingredients such as Si, N and Al atoms are incorporated into the high-k gate oxides. Although many theoretical

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calculations are done for the monoclinic HfO_2 [2, 3], the amorphous HfO_2 has not been studied theoretically.

In this report, the amorphous phase of HfO_2 and $Hf_{1-x}Si_xO_2$ using the first principles molecular dynamics method is presented. The effects of the inclusion of Si atoms on the local structure and phase separation by changing the Si concentration was also analyzed.

2. Methodologies

Throughout this work, the Projector Augmented Plane Wave (PAW) method with the local density functional theory corrected by the generalized gradient approximation [4–6] was used. Using the first principles molecular dynamics method, amorphous structures of HfO_2 and $Hf_{1-x}Si_xO_2$ were obtained by employing the melt and quench method as shown in Fig. 1.

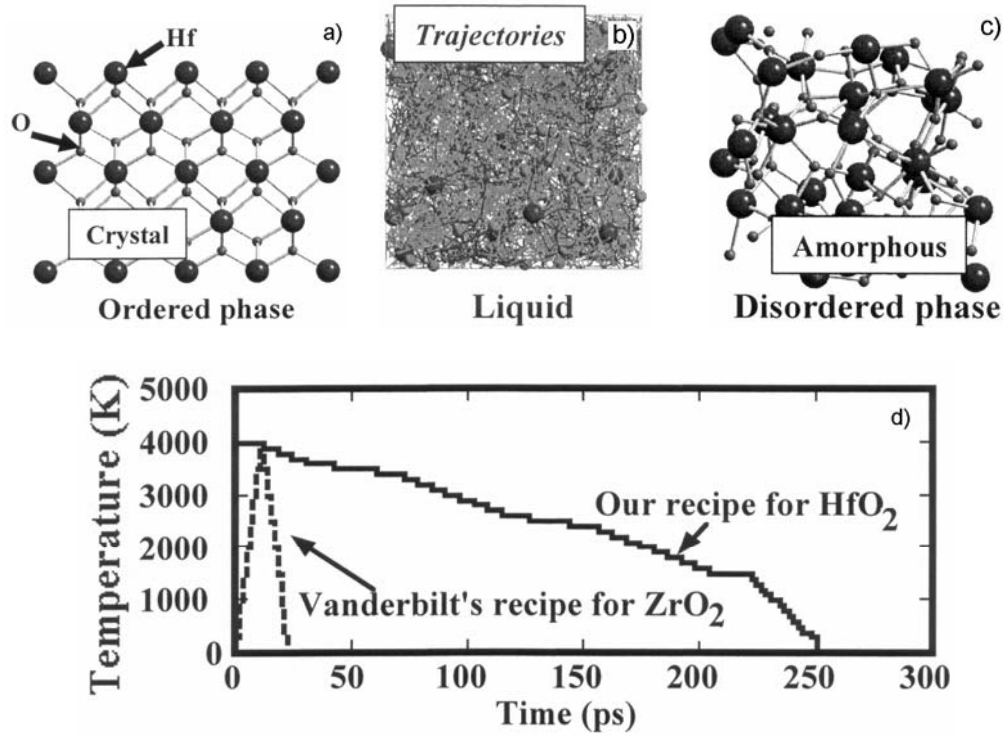

Fig. 1. The melt and quench method is schematically shown in (a) to (c). (a) shows the initial configuration in cubic cell. The atomic arrangements are tetragonal ones. (b) illustrates the trajectories of Hf (black lines) and O (grey lines) atoms at 4000 K during 12 ps. (c) shows the quenched disordered phase of HfO_2. The thermal recipe of this computer experiment is shown in (d). Our total simulation time is longer than Zao–Vanderbilt's by 10 times

The time step is 2 fs and the temperature is controlled by the Nose dynamics. The models consist of 96 and 117 atoms in the cubic cell. According to Zhao–Vanderbilt prescription [7], the volume of the cubic cell is increased by 7% to be able to melt the system at 4000 K.

3. Results and discussions

The temperature of the system was first raised to 4000 K and the system melted in 12 ps. Then the temperature was gradually decreased in 236 ps. The method is shown in Fig. 1d. After quenching the system, the cell volume was optimized. However, the volume change was within 1%, in contrast to the ZrO_2 case in which the volume reduction was as high as 9% [7].

Figure 2 shows the pair correlation functions between Hf and Hf for the crystal, liquids and amorphous phase. The amorphous phase obtained is very close to the liquid phase as shown in the figure.

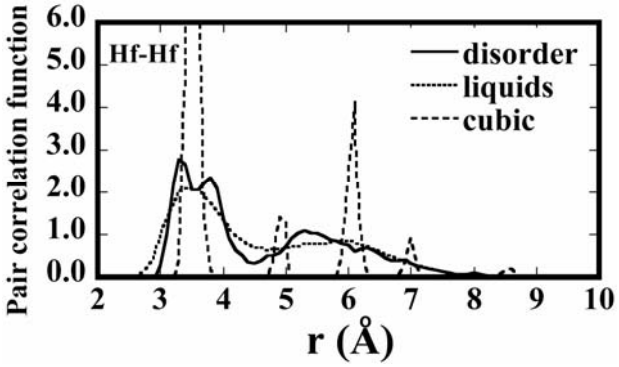

Fig. 2. The pair correlation functions of Hf and Hf in crystal (broken line), liquid (dotted line) and amorphous (solid line) phases are compared. The amorphous phase is very close to the liquid phase as shown in the figure

In the amorphous structures several pore channels exist as in the case of SiO_2. In pure hafnia, several pore channels exist with diameters 3–4 Å as indicated in Fig. 3a. If the Si concentration x of $Hf_{1-x}Si_xO_2$ is increased, the size of the pore channels increases and much space appears as can be easily seen from Figs. 3a–d.

In Figure 3c, a connected SiO_2 networks appears and the remaining HfO_2 molecules are also linked each other. It seems that the phase separation between HfO_2 and SiO_2 occurs at $Hf_{0.3}Si_{0.7}O_2$. The heat of formation energy of $Hf_{1-x}Si_xO_2$ was calculated using those of the amorphous HfO_2 and SiO_2 as reference energies according to the formula $H(x) = E(\text{am-Hf}_{1-x}\text{Si}_x\text{O}_2) - (1 - x)E(\text{am-HfO}_2) - xE(\text{am-SiO}_2)$ where am denotes amorphous form as shown in Fig. 3e. This graph shows that the phase separation between the amorphous HfO_2 and SiO_2 starts at $x > 0.1$.

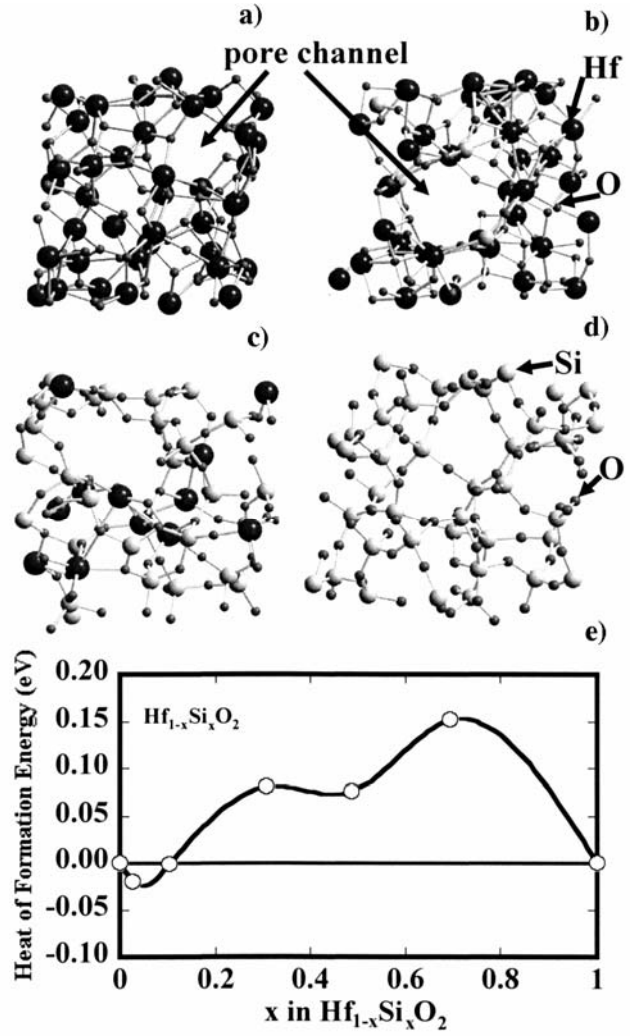

Fig. 3. The theoretically determined amorphous structures are shown in (a)–(d). The dark atoms denote Hf, whereas white ones indicate Si. The small atoms are oxygen. In obtaining these structures, we used 117 atoms in the cubic super cell; (a) is a pure amorphous HfO_2 structure, (b) and (c) are $Hf_{1-x}Si_xO_2$ structure with $x = 0.1$ and 0.7, respectively. (d) corresponds to the amorphous SiO_2. Pore channels are indicated by arrows in (a) and (b). In (e), the heat of formation energy is plotted as a function of Si concentration. The phase separation between amorphous HfO_2 and SiO_2 starts at $x > 0.1$

In Figures 4a–d, the coordination numbers of $Hf_{1-x}Si_xO_2$ with $x = 0$, 0.1, 0.3 and 1 are compared. The oxygen atoms with the coordination number 2 increase linearly with the Si concentration. If the configuration of Si in Figs. 3b and c are examined, the nearest neighbour atoms of Si are all oxygen atoms.

By using the pure amorphous hafnia model, the problem of boron atoms doped in the poly-Si gate penetrating into the Si substrate through the amorphous hafnia were

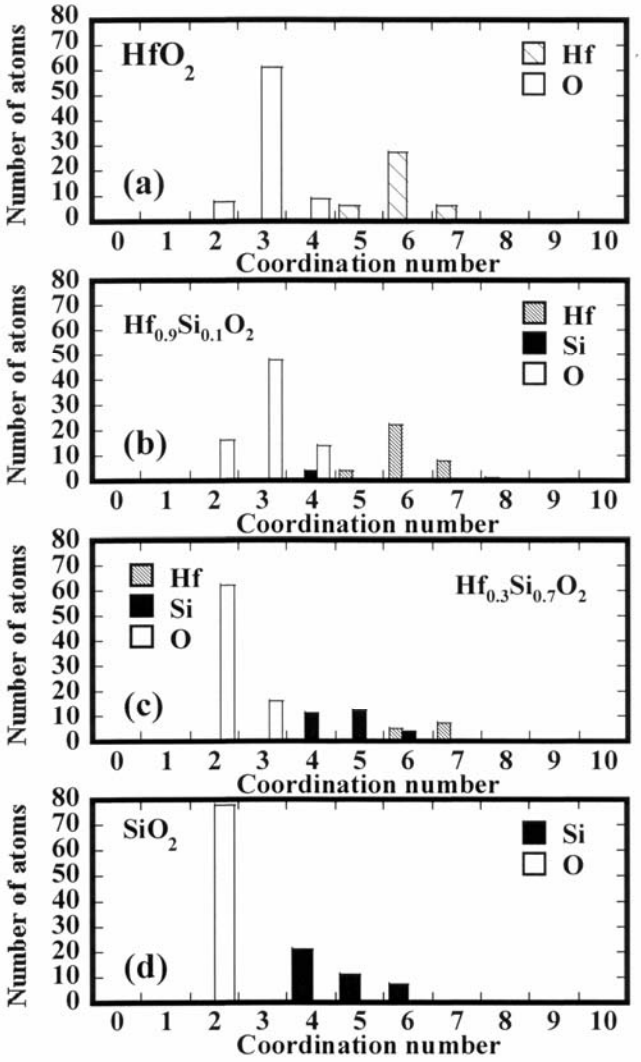

Fig. 4. The coordination numbers of $Hf_{1-x}Si_xO_2$ with x = 0, 0.1, 0.3 and 1 are illustrated in (a)–(d). (a) is a hafnia case, whereas (d) refers to the SiO_2 case. As the Si concentration x increases, then the number of oxygen with coordination number 2 increases

analysed. The fast diffusion of boron in amorphous HfO_2 can be explained successfully. In this analysis, the pore channel structures in HfO_2 which we found through the computer experiments, play a very important role [8]. Thus the amorphous structure models seem to be useful in understanding the actual systems.

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