Theoretical Analysis of Interstitial Boron Diffusion and Its Suppression Mechanism with Nitrogen in Amorphous HfO₂

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1. Introduction

Recently, HfO_2 deposited on Si substrates has been widely studied as a potential candidate for replacing silicon dioxide as the high-k gate dielectrics in scaled CMOS. The boron doped poly-Si gate on HfO_2 is used for fabricating p MOSFETs, in which the flat-band voltage shift due to boron penetration has been reported [1]. Various efforts have been done to circumvent this anomalous diffusion of boron by incorporating nitrogen into high-k gate dielectrics as in the case of SiO₂. However, the detailed mechanism of boron diffusion suppression with nitrogen incorporation into high-k materials such as HfO_2 remains unknown. This paper presents a new theoretical analysis to explain the mechanism of boron (B⁺, B⁰ and B⁻) diffusion suppression, by introducing nitrogen in HfO_2 .

2. Methodologies

Throughout this work, we used the Projector Augmented Plane Wave (PAW) method with the local density functional theory corrected by the generalized gradient approximation [2-4]. Amorphous structures of high-k materials are obtained by employing the melt and quench method according to the Zhao-Vanderbilt prescription as shown in Fig. 1 [5]. Our model employed 96 and 117 atoms in the cubic cell. The details of our amorphous structures are well described elsewhere [6]. Other computational details are similar to the analysis of the oxygen diffusion in monoclinic HfO₂ [7-8].

3. Results and Discussion

First of all, it must be pointed out that if we use the monoclinic crystal HfO_2 model to analyze the boron diffusion our estimated barrier heights for B^+ , B^0 and B^- are 2.75eV, 2.63 and 2.42 eV respectively. These higher values mean that boron diffuses hardly in monoclinic HfO_2 and contradicts with the very fast diffusion. These higher values originate from the results that two bond breakings are necessary for boron atom to jump to the next stable position as shown in Fig.2

An amorphous HfO_2 structure is theoretically synthesized through first melting of the cubic crystal structure and quenching it as already shown in Fig. 1(b) and (c). The obtained amorphous structure contains 3-fold-sites and 4-fold-sites oxygen atoms in the cell although the starting cubic structure only has 4-fold-sites oxygen atoms. The amorphous HfO₂ has atomic scale pore structure with a diameter of 0.3nm as illustrated in Fig.3(a) and (b). The atomic boron B^+ (B^0 and B^-) diffuses through this pore structure channel with a barrier height of 1.22 eV (1.24 and 1.14 eV) as shown in Fig. 4. Nitrogen atoms (N^0) diffuse through the pore channel with a barrier height of 1.4 eV as shown in Fig. 5. The obtained barrier heights are about one half of the values calculated for monoclinic crystal model. In Fig. 3(c), we schematically illustrate the boron atom diffusion in the atomic scale pore channel. Boron (nitrogen) atom can move from the stable to the next stable position by just breaking one bond only. Another effect, "bonding and rebonding", being popular in amorphous phase also assists the diffusion of boron (nitrogen) atoms. It should be noted that the diffusion path of boron and nitrogen atoms are the same. Therefore, boron and nitrogen atoms can easily meet at the pore channel.

In order to analyze the effects of the nitrogen, after setting the nitrogen atom at the most stable configuration, we study the boron atom diffusion in the pore channel as shown in Fig. 6. Boron and nitrogen atoms form very rigid bonds of $(O)_3$ -B-N-(Hf)₃ with a barrier height 6eV as shown in Fig 7. And thus the boron diffusion is suppressed. Of course, B-N molecule can move in this pore channel, however, from geometrical reason B-N must break two bonds at the same time when B-N moves. If we also consider the strain effects due to the formation of such a molecule, its energy increase is 0.8eV. Rough energy estimation indicates 2.8 eV for the barrier height of B-N diffusion. Therefore B-N molecule never diffuses very fast.

4. Conclusions

In the amorphous phase of HfO_2 , boron atoms diffuse through atomic scale pore channels in the network, and the nitrogen atoms also diffuse through the pore channels. The boron and the nitrogen meet together to form the energetically stable (O)₃-B-N-(Hf)₃ configuration in amorphous HfO₂, resulting in boron diffusion suppression.

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Fig. 1. Initial configuration of HfO_2 for our simulation is shown in (a). The trajectories during 12 ps for liquids HfO_2 at 4000K are illustrated in (b). Final structure for amorphous HfO_2 (c) is obtained using the melt and quench method.



Fig. 2. The most stable configuration of B^+ in monoclinic HfO₂ is shown in (a). Two nearest neighbor oxygen atoms take 4-fold sites by forming extra bonds with B^+ . Saddle point configuration is illustrated in (b). At this point, nearest neighbor oxygen atoms break the Hf-O bonds at the same time and forms two 3-fold sites.



Fig. 3. The amorphous HfO_2 is shown in (a). The pore channel is pointed out by an arrow. In (b) pore channels are schematically illustrated. B and N diffuse through the same pore channel. The bond breaking of B (N) in pore channel is shown in (c).



Fig. 4. The energy dependences are plotted against the movement of boron (B^+ , B^0 and B^-) in the pore like space. The energy barrier height for B^+ (B^0 and B^-) is 1.14eV (1.24 and 1.22eV).



Fig. 5 The energy along the diffusion path is illustrated as a function of diffusion length for the interstitial nitrogen. The barrier height energy of the diffusion is also shown.



Fig. 6. The energy dependences against the movement of boron in amorphous HfO_2 with nitrogen are plotted. Nitrogen atom is placed at the most stable position. In region I, boron and nitrogen exist separately in the pore, whereas boron and nitrogen bind in region II. The energy gains are also illustrated in the figure.



Fig. 7. This configuration is the lowest energy configuration of B^0 and N^0 inside the pore channel. Boron and nitrogen atoms form the rigid bond as well as boron binds with 3 oxygen atoms, whereas nitrogen couples with the 3 nearest neighbor Hf atoms.