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Dissociation characteristics of proton release in a-SiO_2 by first-principles theory

Yunliang Yue[a], Pei Li[a], Yu Song[b,c], Xu Zuo[a,d,*]

[a] College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300071, China
[b] Microsystem and Terahertz Research Center, China Academy of Engineering Physics, Chengdu 610200, China
[c] Institute of Electronic Engineering, China Academy of Engineering Physics, Mianyang 621999, China
[d] Municipal Key Laboratory of Photo-electronic Thin Film Devices and Technology, Nankai University, Tianjin 300071, China

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ABSTRACT

Radiation-induced interface traps are the essential defects affecting the reliability of microelectronic devices, and it is generally agreed that protons play a key role in the reaction that generates the traps. We thus perform first-principles calculations to investigate the reactions that possibly release protons in amorphous SiO_2 (a-SiO_2). Two fundamental mechanisms are explored, namely the dissociation of hydrogen molecules at positive oxygen vacancies and the dissociation of hydrogenated defects. The calculations show that there are high energy barriers for the singly hydrogenated vacancies to generate protons, and that the barrier for the doubly hydrogenated vacancy is relatively low. The calculations also show that the dissociation of hydrogen molecule at the dimer configuration has a lower energy barrier and a more stable product than the dissociation at the puckered configuration. The energy barrier of the dissociation at the dimer configuration can be as low as 0.58 eV, which ensures that the reaction can take place quickly at room temperature. The details of the reactions are investigated at the atomic scale to provide a microscopic insight into proton release in a-SiO_2.

1. Introduction

Radiation-induced interface traps play an important role in the reliability of microelectronic devices [1–3]. By means of studying the interface traps, it could help to remove the defects and improve the quality of devices [4–6]. According to the consensus of the previous researches, the main process of the interface-trap buildup is that the protons induced by radiation depassivate the hydrogenated defects at the interface, creating the interface traps [7–9]. Thus, learning how the protons to generate in the oxide could increase the ability to understand and decrease the interface traps [10–12].

The experimental researches have demonstrated that the interface traps increase with the increasing molecular hydrogen concentration during irradiation, indicating that the molecular hydrogen can contribute to the interface-trap buildup and enhance the degradation of the electronic device [13–17]. At the same time, the interface traps could still be generated by irradiation in the absence of sufficiently high concentration of molecular hydrogen, implying that there are other sources of protons [13]. Generally, the hydrogenated defects could be treated as reactants to react with holes under the irradiation condition, which is recognized as the main reaction for the proton release especially at the low concentrations of molecular hydrogen [18,19]. Electron-hole pairs are stimulated by radiation, and the holes that escape from the initial recombination diffuse into the bulk amorphous SiO_2 (a-SiO_2). Some holes directly attack the Si—H bonds to release a proton [20]. Meanwhile, some of them should be trapped by the neutral defects, forming the positively charged centers. One of the most prevalent defects in a-SiO_2 is the oxygen vacancy [21]. The neutral oxygen vacancies are always present in the Si—Si dimer configuration, but the positive ones could form the puckered configuration other than the Si—Si dimer once trapping a hole. The molecular hydrogen that incorporates into a-SiO_2 may react with the positively charged oxygen vacancies to generate protons [22–24]. The amorphous nature of silicon dioxide makes it difficult to carry out experimental studies. However, many theoretical efforts have been devoted to the reactions on the proton release in the previous reports [25–27]. Tuttle et al. investigated the molecular hydrogen cracking at the positively charged oxygen vacancy defects by using the first-principles calculations, but their research ignored the hydrogenated defects as the reactants to release protons under radiation [28]. Rowsey et al. filled the vacancy of the research by covering the singly-hydrogenated and doubly-hydrogenated vacancy defects, whereas their research only listed the final

* Corresponding author at: College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300071, China.
E-mail address: xzuo@nankai.edu.cn (X. Zuo).

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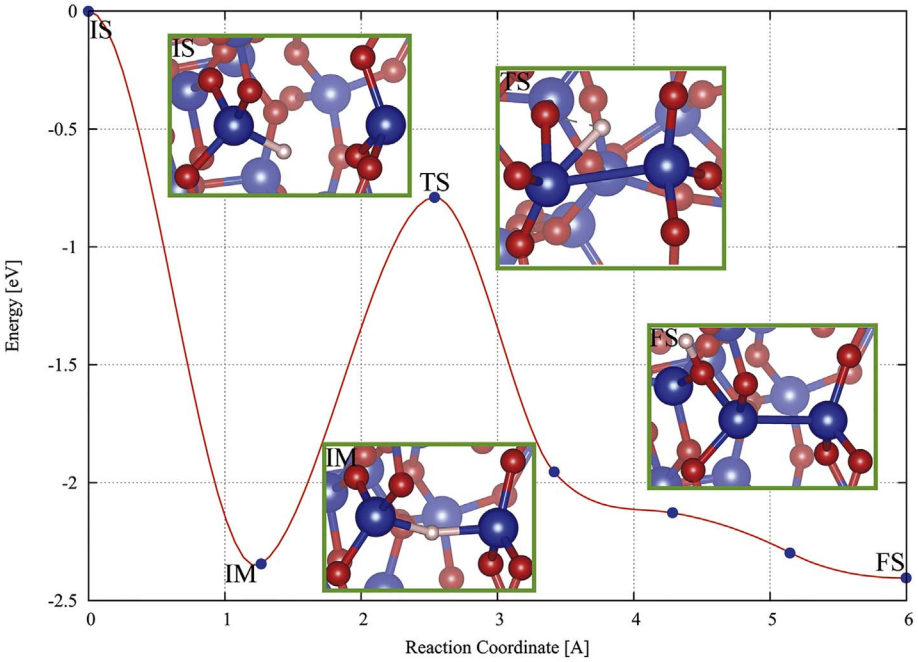

Fig. 1. The reaction curve of the dissociation of the hydrogenated back-projected oxygen vacancy. The structures of the initial, transition and final states are illustrated in the insets.

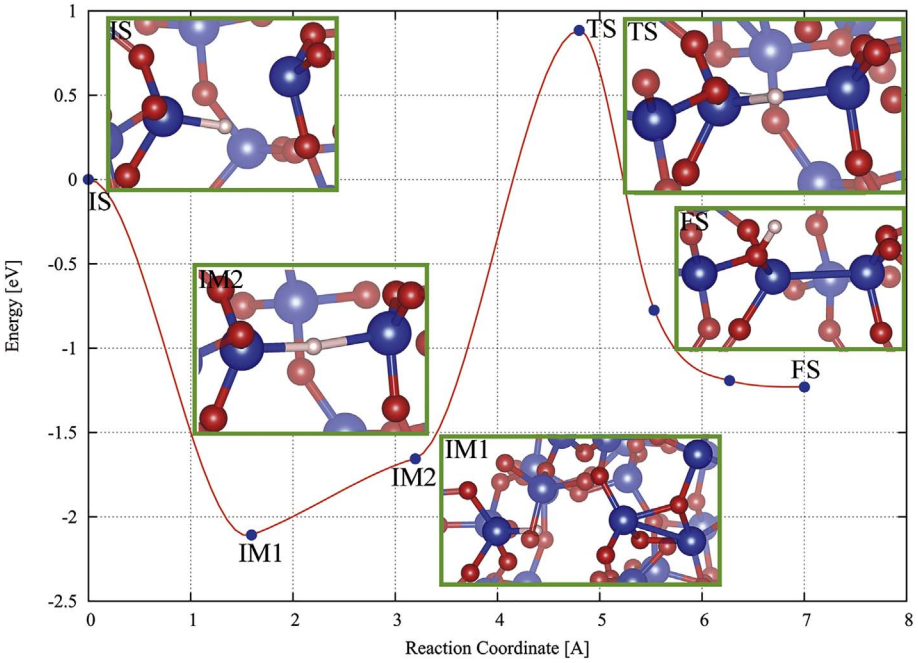

Fig. 2. The reaction curve of the dissociation of the hydrogenated forward-projected oxygen vacancy defect.

barrier energies of a series of reactions without their details such as the minimum-energy path and transition state [29]. More importantly, the method of structural optimization and some significant parameters of the first-principles calculations including the cutoff energy and convergence threshold are not given in these reports, which makes it hard to reproduce and verify their results [28,29].

In this research, we perform the first-principles calculations to investigate the reactions associated with proton generation in the a-SiO_2. The two sources of protons in a-SiO_2 are considered. One of them is the hydrogenated defects reacting with the hole, and three kinds of singly-hydrogenated defects and one kind of doubly-hydrogenated defects are considered as the reactants to generate protons. The other is the molecular hydrogen dissociating at the positively charged oxygen vacancies including the dimer and puckered configurations. From this research, we can find out the dominant reactions to release protons in a-SiO_2.

2. Computational methods

The calculations have been performed within the framework of density functional theory (DFT) by using the plane wave pseudopotential code VASP (Vienna ab initio simulation package) [30–32]. The electronic exchange and correlation interaction are described by Perdew–Burke–Ernzerhof (PBE) parameterization of general gradient approximation (GGA) [33]. The cut-off energy of plane wave expansion is set to be 520 eV. There are 216 atoms in the defect-free a-SiO_2 cell, and