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Initial reaction of HfO_2 atomic layer deposition on silicon surfaces with different oxygen levels: A density functional theory study

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Abstract

Density functional theory is employed to investigate atomic layer deposition mechanism of HfO_2 on hydroxylated silicon surfaces with different oxygen levels. Calculations show that the surface bridged oxygen can enhance the adsorption of $HfCl_4$ and weaken the adsorption of H_2O. In addition, temperature effects on the chlorine loss has been discussed. In particular, two possible pathways for the second chlorine loss at low temperature are explored. However, both of them are limited at higher temperature for two main reasons: (a) the decrease in the number of surface hydroxyl sites and (b) the dehydroxylation of as-grown HfO_2 surface.

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1. Introduction

SiO_2 as the traditional gate dielectric has been used widely in silicon microelectronic field. However, with continual miniaturization of metal oxide semiconductor field effect transistor, SiO_2 will reach its physical limitations where electron tunneling through the insulator is a serious problem [1,2]. As a result, the replacement of SiO_2 by high-κ oxides is inevitable to increase capacitance density and suppress electron tunneling [3,4]. In particular, HfO_2 has recently emerged as one of the most promising alternative dielectric materials due to its relatively high permittivity and good thermal stability [3,5–7].

Among various methods for growing high-κ dielectric films, atomic layer deposition (ALD) shows its unique ability in depositing ultra thin films with excellent conformity and uniformity over large areas [8,9]. In ALD, each precursor is pulsed to the reaction chamber alternately, and the reaction between the incoming precursors and surface species is self-terminating. Thus atomic level control of film growth can be achieved. Recently, HfO_2 has been grown by ALD using $HfCl_4$ and H_2O as precursors [10,11].

Experimental results have shown that the properties of the film strongly depended on the composition of the film in the interfacial region between the high-oxide and the silicon substrate. An interfacial layer of SiO_2 only one or two molecular layers thick can benefit to channel mobility although the total capacitance is lowered compared to the pure HfO_2 [12–14]. In addition, the formation of $HfSi_xO_y$ interfacial layer can also improve the thermodynamic stability of HfO_2 on silicon [15]. Experimental results have also shown that the starting surface is critical in initiating growth and assuring uniformity for ALD-grown high-κ dielectric films. For instance, many starting surfaces are non-uniform nucleation, followed by rapid island growth rather than the desired layer-by-layer growth with each half-reaction. It is thus critical to understand the initial reactivity of each precursor on all possible surface species [12]. Recently, certain first principle studies have started to focus on the ALD growth mechanism of HfO_2. In particular, Estève et al. [16] and Jeloaica et al. [17] have studied the $HfCl_4$ initial reactions on SiO_2 surface using the transition state (TS) search algorithm of bond constraint relaxation (BCR). In their work, the computational model $Si_9O_5H_{12}$–H–OH, where five oxygen atoms are

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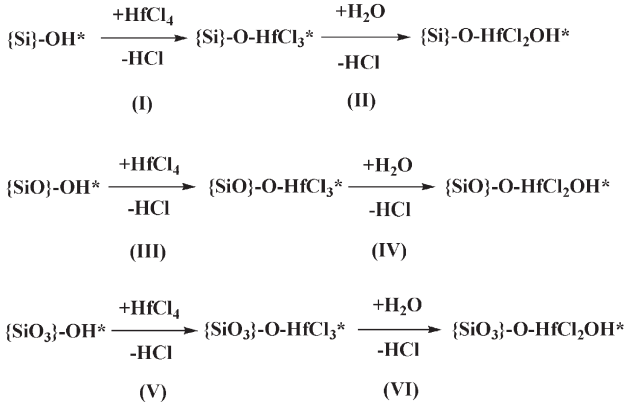
introduced within Si–Si bonds at the surface and upper subsurface, are presented. However, Han et al. [12] have referred to the BCR method is limited in nature due to its unable to fully explore the whole potential energy surface (PES) of the system to locate the TS. In Han's work, the reaction mechanism of ALD of ZrO_2 on SiO_2 surfaces based on some relatively small models rather than Si(100)-2 × 1 model has been proposed [12]. It is well known that ZrO_2 is extremely similar to HfO_2, so Han's results can be compared with that of ALD of HfO_2 on SiO_2 surface in our current work. Besides SiO_2 surface reactions mentioned above, Widjaja et al. have once predicted the structures, the reaction energies, and the reaction mechanism of $HfCl_4$ and H_2O on HfO_2 surface [18], and have also suggested that the mechanism of ALD of ZrO_2 on silicon surface [19]. Although some first principle studies of ALD of HfO_2 reactions on silicon, SiO_2 and as-grown HfO_2 surfaces have been reported, the thermochemistry and kinetics of silicon surface reactions with different oxygen levels still need to be explored in detail.

In this study, the detailed initial growth mechanism of ALD HfO_2 on hydroxylated Si(100)-2 × 1 surface using $HfCl_4$ and H_2O as precursors will be intensively studied. The ALD of HfO_2 cycle is achieved through two sequential half-reactions (i.e., $HfCl_4$ and H_2O half-reactions). The reaction sequence explored in this study is presented in Scheme 1. Reactions I, III and V belong to the $HfCl_4$ half-reaction, representing the reactions of surface hydroxyl with the precursor $HfCl_4$ molecule, and reactions II, IV and VI belong to H_2O half-reaction, in which H_2O reacts with the surface hafnium species.

2. Computational models and methods

Cluster approximation is used extensively due to the predominantly localized bonding of the Si(100)-2 × 1 surface. Most frequently, Si(100)-2 × 1 is modeled with a Si_9H_{12} one-dimer cluster (ref. Fig. 1a) in previous studies [16,17,19–21]. The Si_9H_{12} one-dimer cluster consists of four layer silicon atoms where the top two silicon atoms compose the surface dimer. The remaining seven silicon atoms compose three subsurface layers that are hydrogen terminated to prevent unrealistic charge transfer. In this study, to investigate the ALD of HfO_2 on the interfacial SiO_2, two model clusters, i.e., Si_9OH_{12}–H–OH and



Scheme 1. $HfCl_4$ and H_2O half-reactions on the Si_9H_{12}–H–OH, Si_9OH_{12}–H–OH and $Si_9O_3H_{12}$–H–OH surfaces.

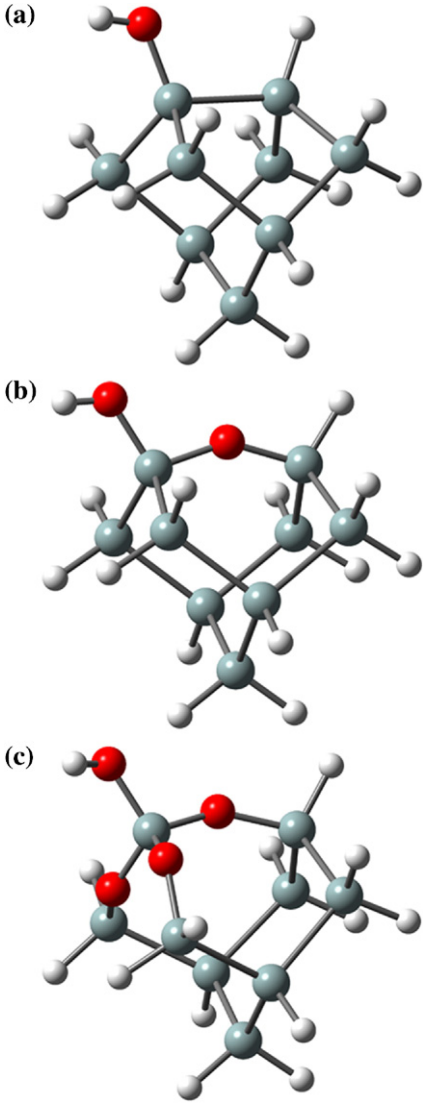


Fig. 1. The models (a) Si_9H_{12}–H–OH, the hydroxylated Si_9H_{12} one-dimer cluster, simulating Si(100)-2 × 1 surface, (b) Si_9OH_{12}–H–OH and (c) $Si_9O_3H_{12}$–H–OH, representing SiO_2 surface sites, oxygen atoms are red, silicon atoms are grey and hydrogen atoms are light grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

$Si_9O_3H_{12}$–H–OH clusters (Fig. 1b and c), are applied to represent the different oxygen levels in silicon surfaces, in which the central silicon atom has one hydroxyl surface active site, and the neighboring Si–Si bonds are introduced one and three oxygen atoms, respectively. The single OH-terminated model cluster Si_9H_{12}–H–OH (Fig. 1a) is also employed to investigate the influence of the SiO_2 interfacial layer on the initial growth of HfO_2. The structures of these model clusters will be fully optimized in all calculations.

The hybrid B3LYP method, as implemented in GAUSSIAN 03 [22], has been employed in all calculations, incorporating Becke's three parameter exchange functional [23,24] and the Lee–Yang–Parr gradient-corrected functional [25]. A mixed basis set scheme is used to minimize the computational time. The LANL2DZ basis set [26–28] and effective core potential for Hf