Computational studies on atomic layer deposition mechanisms of Al2O3

(Konkuk University, Korea) Ki Chul Kim*

1. Introduction

Atomic layer deposition (ALD) has been a popular technique for efficiently depositing thin films of various materials with precise growth control for a variety of applications, such as semiconductor devices, lithium-ion batteries, fuel cells, and solar cells. Most studies highlight how the ALD technique can be commonly applied to a broad array of applications. These studies also emphasize that understanding the fundamental chemistry of the ALD processes would be needed to optimize the performance of the ALD-prepared thin films. In this presentation, we employ the DFT modeling approach to explore the chemisorption behaviors of TMA molecules on the active adsorption sites of the Al2O3 surfaces and to investigate the possibility of the dimeric adsorption of TMA during the TMA-dosed half-cycle. The thermodynamic characteristics associated with the subsequent H2O-dosed half-cycle are further investigated to understand the ALD chemistry.

2. Computational Methods

All the DFT calculations were performed using the Quantum Espresso package with Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation functional. The core electrons of each atom were described by ultrasoft pseudopotential. Energy cutoffs for wave function (680 eV) and charge density (6530 eV) were confirmed to be large enough to reliably predict the electronic structures. The bulk structure of the Al2O3 structure was geometrically optimized, allowing supercell and all atoms in the cell to fully relax until the forces on all atoms were less than 0.01 eV/Å. The Al2O3(0001) surface model was further developed through the cleavage of the optimized bulk structure followed by the hydroxylation of the surface dangling bonds. Note that the Al2O3(0001) surface was selected because the surface was the most stable in the thermodynamic point of view, exhibiting the lowest surface energy among possible low Miller index surfaces. The surface optimization was performed via the same procedure as the bulk optimization, except fixing the supercell. The resultant surface model contains six Al–O layers with a vacuum thickness of 30 Å. Such a large vacuum thickness would prevent the interaction between neighboring slab images, leading to the negligible effect of the dipole moment in the surface model.

3. Results and Discussion

We successfully identified the most stable formation for TMA chemisorption on the hydroxylated Al2O3 surfaces. As shown in Figure 1, in general, bidentate configurations are predicted to be more stable than monodentate configurations owing to the higher connectivity between Al and surface O atoms for the former. It is also unambiguous to see that the TMA species on the surface would thermodynamically prefer to be chemisorbed in a monomeric form rather than in a dimeric form. The formation energies for four MS-based models (MS2–MS5) are predicted to be ranged within −3.39 to −4.81 eV/2 TMA, which would be more negative than the values (−2.41 and − 2.89 eV/2 TMA) for DS-based models. It is further noted that the bond lengths (2.1 Å) of Al and C binding two monomeric species in the DS models are greater by 0.2 Å than the other Al–C bond lengths in the MS and DS models. Considering the relative thermodynamic stability of the models in terms of the bond geometry, the presence of a TMA molecule weakly maintained by these loose bonds for each DS model would be a critical indicator to describe the characteristics of the DS models less stable than the MS models.

The most striking observation from Figure 2 is that the energy profile for the sequential chemisorption of water molecules strongly relies on the configuration of TMA adsorbates on the surface at the early stage of the H2O-dosed half-cycle. The chemisorption of water molecules on the TMA (MS2)-chemisorbed surface exhibits a constant energy profile within the range of −1.32 to −1.35 eV/H2O, regardless of the number of chemisorbed water molecules (i.e., the number of the hydroxylation events in the sequential chemisorption of water). Considering that all the TMA species are uniformly chemisorbed on the bare surface in a bidentate configuration, all the active adsorption sites (monomethylaluminum groups) for the subsequent chemisorption of water molecules would be identical in the thermodynamic point of view. In addition, the space between neighboring TMA adsorbates is large enough to neglect the self-interaction between the water molecules chemisorbed on the neighboring TMA adsorbates. The constant energy profile for the TMA (MS2)-chemisorbed surface can be reasonably explained from all this evidence. In contrast to the MS2

configuration, the active adsorption sites for the chemisorption of water molecules on the TMA (MS3)-chemisorbed surface are not identical due to the co-existence of monodentate and bidentate configurations.
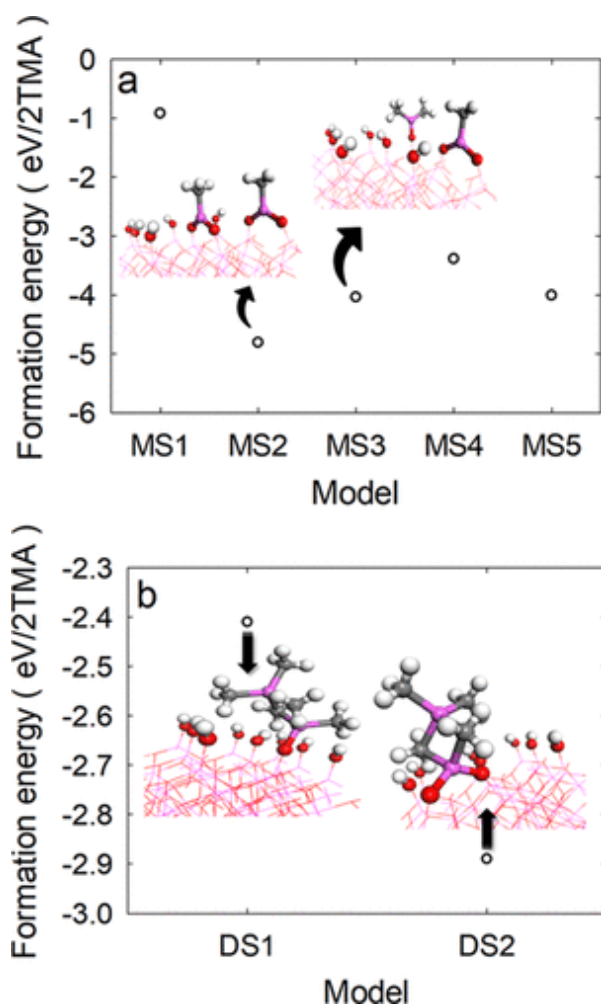

Figure 1. Thermodynamics of MS and DS. The DFT-calculated total energies of (a) five MS and (b) two DS models.
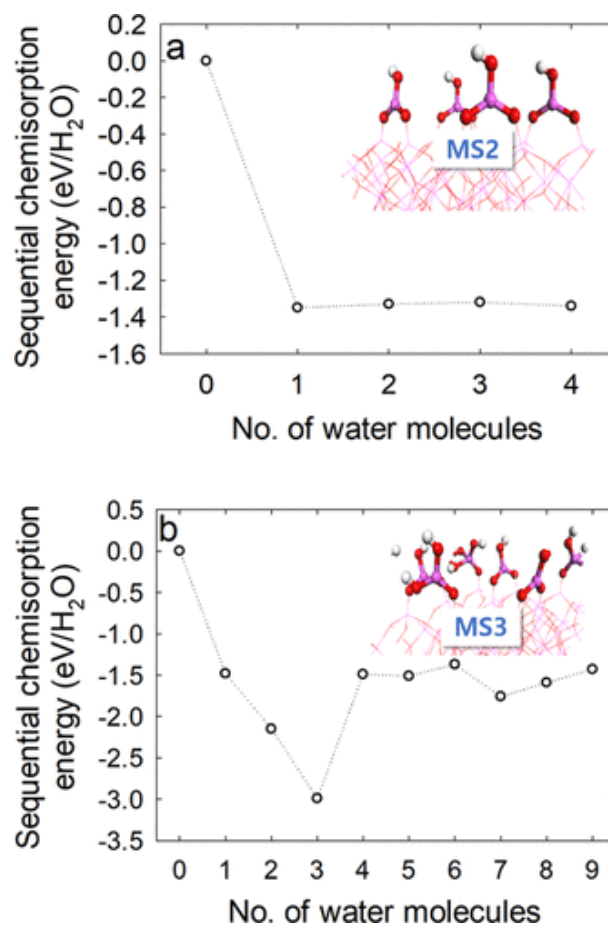

Figure 2. Thermodynamic energy profiles for atomic layer deposition processes. The change in the DFT-calculated sequential chemisorption energy during the water-based atomic layer deposition cycle for (a) MS2 and (b) MS3 models.