Energy barriers for trimethylaluminum reaction with varying surface hydroxyl density

Dae-Hee Kim, Seung-Bin Baek, Yeong-Cheol Kim*

School of Energy, Materials & Chemical Engineering, Korea University of Technology and Education, Cheonan 330-708, Republic of Korea

1. Introduction

Since its successful introduction to semiconductor sector as an inner layer of ZrO2/Al2O3/ZrO2 (ZAZ) capacitor dielectric thin-films to suppress the leakage current [1,2], the Al2O3 thin-film has recently been actively studied in solar cell sector to utilize its negative fixed charge to suppress the recombination rate of minority charge carriers as passivation layers [3–8]. Atomic layer deposition (ALD) that is a deposition technique based on sequential chemical reactions of precursors and gases has been employed to deposit the Al2O3 thin-films due to its accurate thickness controllability and excellent conformality [9–11]. Trimethylaluminum (Al(CH3)3, TMA) among many Al precursors have been frequently employed to deposit the Al2O3 thin-films for the ALD process [2,4,5,11–20].

The Al2O3 thin-films have been experimentally deposited on fully H-, half H- and half OH-, and fully OH-terminated Si (0 0 1) surfaces using TMA [16,17,20]. These surfaces could be prepared by dipping Si wafers in aqueous HF solution, dissociating H2O molecules on clean Si surfaces, and reacting H2O molecules with Cl-terminated Si (0 0 1) surfaces, respectively. The Al2O3 thin-films were deposited at above 350 °C on fully H-terminated Si (0 0 1) surfaces, while they were deposited at 200 °C on fully OH-terminated Si (0 0 1) surfaces. Namely, the presence of –OH on the surfaces greatly enhanced the reaction between TMA and the surfaces.

Energy barriers for TMA reaction with varying surface –OH density on Si (0 0 1) surfaces have been theoretically studied using density functional theory (DFT) [21–24]. Halls et al. reported the TMA reaction that produced a dimethylaluminum (–Al(CH3)2), DMA group and CH4 on fully H-terminated Si (0 0 1) surfaces using GAUSSIAN98 [21]. The adsorption energy of TMA on the surface and its reaction energy barrier were 0.03 and 1.22 eV, respectively. They also reported the TMA reaction on half H- and half OH-terminated Si (0 0 1) surfaces that were prepared via the dissociation of H2O using GAUSSIAN03 [22]. The adsorption energy of TMA and its reaction energy barrier were 0.59 and 0.40 eV, respectively. The increase of the adsorption energy might be partly due to the consideration of the van der Waals interaction. Ghosh et al. reported the initial reaction mechanism of TMA on fully OH-terminated Si (0 0 1) surfaces using general atomic and molecular electronic system structure (GAMESS) with the van der Waals interaction [23]. The adsorption energy of TMA and its reaction energy barrier were 1.08 and 0.72 eV, respectively. Recently, Kim et al. reported the TMA’s adsorption energy of 0.70 eV and its reaction energy barrier of 0.50 eV on fully OH-terminated Si (0 0 1) surfaces using Vienna ab initio simulation package (VASP) without the van der Waals interaction [24]. No consideration of the van der Waals interaction reduced the adsorption from 1.08 to 0.70 eV, and the difference in energy barriers was mainly due to different structures of the transition states that were determined by different codes to find minimum energy paths for surface reaction.

In this study, adsorption energies and energy barriers for TMA reaction with varying surface –OH density on Si (0 0 1) surfaces were investigated using a DFT-D2-based code. Additionally, an α-SiO2 (0 0 1) surface on TMA reaction was considered to investigate...
the effect of higher surface –OH density on adsorption energies and energy barriers for TMA reaction.

2. Calculation details

All DFT calculations were performed using VASP code [25–28]. Electron wave functions were described using the projector augmented wave (PAW) method of Bloch [29] implemented to the VASP code by Kresse and Joubert [30]. The exchange correlation energy was described by Perdew, Burke, and Ernzerhof (PBE) based on the generalized gradient approximation (GGA) [31]. All calculations considered van der Waals interactions based on Grimme’s DFT-D2 approach in PAW [32]. Since geometric configuration was not well optimized with DFT-D2, all geometric configurations were first optimized using DFT. The cutoff energy of 500 eV was used, and 2 × 2 × 1 k-points mesh with zero shift for a slab structure including a 2-nm thick vacuum layer was used to generate the plane wave basis set using the Monkhorst–Pack grid method [33]. Partial wave occupancies were calculated with the Gaussian smearing method, and its factor was 0.05 eV. Electronic and geometry optimizations were converged when the total energy difference between successive calculations steps was less than 10^{-3} and 10^{-2}, respectively. All atoms were allowed to relax until the force on each atom was below 0.2 eV/Å.

Fig. 1 shows fully H- [21], half H- and half OH- [22], fully OH-terminated Si (001) surfaces [23], and a fully OH-terminated α-SiO₂ (001) surface [34]. Si and α-SiO₂ (001) surface size are 4 × 4 (1.53 nm × 1.53 nm) and 2 × 3 (1.73 nm × 1.50 nm), respectively. The bottom Si layer among the four Si layers and the H atoms bonded to the bottom Si atoms were fixed, and three top Si layers with H atoms and/or –OH’s on top were fully relaxed in Si (001) surfaces, as shown in Fig. 1(a)–(c). In the case of the fully OH-terminated α-SiO₂ (001) surface, as shown in Fig. 1(d), the bottom Si layer in the bottom α-SiO₂ layer and the H atoms bonded to the bottom Si atoms were fixed, and the rest α-SiO₂ layer and two top α-SiO₂ layers with –OH’s on top were relaxed. A relaxed energy is set to 0 eV as reference, when TMA is located further away from each surface with a distance of 10 Å. When TMA was adsorbed on each surface, energy barriers for TMA reaction were calculated using the nudged elastic band (NEB) tool implemented in the VASP code. Six images including the initial and final states were used for the energy barrier calculations. Inoms in ‘Relaxed layers’ shown in Fig. 1 and TMA were allowed to relax during the energy barrier calculations. Electron density images were drawn using the visualization for electronic and structural analysis (VESTA) tool [35]. An iso-surface level is the amount of electron charge per a₀³ (a₀ = Bohr radius), and the used value is 0.07 in this study.

3. Results and discussion

Energy barriers for TMA reaction on the fully H-, half H- and half OH-, fully OH-terminated Si (001) surfaces, and the fully OH-terminated α-SiO₂ (001) surface will be discussed. TMA reacts with –H or –OH on a surface to produce a DMA group and CH₄ during the first half cycle in ALD process, and its chemical reaction equation with –OH is given below:

\[ \text{Al(CH}_3)_3 + \text{–OH} \rightarrow \text{–O–Al(CH}_3)_2 + \text{CH}_4. \]

When one –CH₃ of TMA (–CH₃(TMA)) reacts with the H atom of –OH (H₃–OH) to produce CH₄ as a by-product, the Al–CH₃ and H–O bonds break, and the Al–O and H–CH₂ bonds are made. The bond breaking and making occur almost simultaneously, and the required energy for the reaction is therefore minimized. Since the reaction energy barrier is significantly affected by the relative distances between atoms during bond breaking/making, we will describe energy barriers for TMA reaction on different surfaces with varying distances between atoms.

Fig. 2 shows the adsorption energy of TMA and its reaction energy barrier on the fully H-terminated Si (001) surface that contains no –OH’s; The surface –OH density is 0/nm². TMA was adsorbed on the surface with no energy barrier, and its adsorption energy was 0.36 eV. The adsorption energy was 0.12 eV without the van der Waals interaction. The Al atom of TMA (Al(TMA)) was attracted to a H atom on the surface (Hsurface) by a distance of 2.27 Å. This is because Al(TMA) is deprived of electrons, while Hsurface still retains some, as shown from the electron density image in the red box. Due to the attractive interaction between Al(TMA) and Hsurface, Al–C bonds of the adsorbed TMA were weakened, indicated by an increased bond length of 1.97 Å. The Al–C bond length of TMA is 1.96 Å as a reference, when TMA is located further away from the surface. TMA reacts with Hsurface on the surface to produce a DMA group and CH₄, and its chemical reaction equation is given below:

\[ \text{Al(CH}_3)_3 + \text{–SiH} \rightarrow \text{–Si–Al(CH}_3)_2 + \text{CH}_4. \]

When one –CH₃(TMA) reacted with Hsurface to produce CH₄ at a distance of 3.34 Å between the atom of –CH₃(TMA) and Hsurface for bond making, Al(DMA group) bonded to the exposed Si atom with an
Al–Si bond length of 2.49 Å and a reaction energy barrier of 1.14 eV. In the transition state, the Al atom of the broken DMA group moved to the exposed Si atom for bond making at a distance of 1.87 Å, and $H_{\text{surface}}$ moved to the broken –CH$_3$(TMA) for bond making. The distance between the C atom of –CH$_3$(TMA) and $H_{\text{surface}}$ is shown in the upper right corner with a different viewing angle in the red box. The bond between the Si and the neighboring Si atom that formed a Si dimer had lower electron density relative to that in a neighboring Si dimer that did not bond to a DMA group, as shown in the blue box.

Fig. 3 shows the adsorption energy of TMA and its reaction energy barrier on the half H- and half OH-terminated Si (0 0 1) surface with the surface –OH density of 3.4/nm$^2$. $A_{\text{CH}_3}$ was located on $O_{\text{(OH)}}$ on the surface at a distance of 2.06 Å. Its adsorption energy of 1.00 eV was higher than that of 0.36 eV on the fully H-terminated Si (0 0 1) surface, because Al(TMA) strongly interacted with $O_{\text{(OH)}}$ due to the lone pair electrons of $O_{\text{(OH)}}$, as shown in the red box. Due to the strong attractive interaction between Al(TMA) and $O_{\text{(OH)}}$ on the half H- and half OH-terminated Si (0 0 1) surface, Al–C bonds of the adsorbed TMA on the surface were weakened, indicated by an increased bond length of 1.98 Å. When one –CH$_3$(TMA) reacted with $H_{\text{(OH)}}$ to produce CH$_4$ at a distance of 2.64 Å between the C atom of –CH$_3$(TMA) and $H_{\text{(OH)}}$ for bond making, Al(DMA group) bonded to the exposed O atom with an Al–O bond length of 1.72 Å and a reaction energy barrier of 0.62 eV. In the transition state, the Al atom of the broken DMA group moved to the exposed O atom for bond making at a distance of 1.89 Å, and $H_{\text{(OH)}}$ moved to the broken –CH$_3$(TMA) for bond making. The lower reaction energy barrier (0.62 eV) than that on the fully H-terminated Si (0 0 1) surface (1.14 eV) was due to the weakened Al–C bonds of the adsorbed TMA for bond breaking, the shorter distance of $C_{\text{TMA}}$–$H_{\text{(OH)}}$ from 3.34 to 2.64 Å, and a short distance of $A_{\text{CH}_3}$–$O_{\text{(OH)}}$ for bond making.

Fig. 4 shows the adsorption energy of TMA and its reaction energy barrier on the fully OH-terminated Si (0 0 1) surface with the surface –OH density of 6.8/nm$^2$. $A_{\text{CH}_3}$ was located on $O_{\text{(OH)}}$.
at a distance of 2.05 Å due to lone pair electrons of O_{(OH)}. Its adsorption energy of 1.16 eV was higher than that of 1.00 eV on the half H- and half OH-terminated Si (001) surface, due to additional attractive interactions between -CH_{3(TMA)}`s and H_{(OH)}`s. H_{(OH)}`s near the adsorbed TMA were attracted towards -CH_{3(TMA)}`s, as shown in the red box. Due to the attractive interactions between -CH_{3(TMA)} and H_{(OH)}, Al-C bonds of the adsorbed TMA were weakened, indicated by an increased bond length of 1.90 Å. When one -CH_{3(TMA)} reacted with H_{(OH)} to produce CH_{4} at a distance of 2.59 Å between a C atom of -CH_{3(TMA)} and H_{(OH)} for bond breaking, Al_{DMA group} bonded to the exposed O atom with an Al-O bond length of 1.71 Å and a reaction energy barrier of 0.50 eV. In the transition state, the Al atom of the broken DMA group moved to the exposed O atom for bond breaking at a distance of 1.87 Å, and H_{(OH)} moved to the broken –CH_{3(TMA)} for bond making. The lower reaction energy barrier (0.50 eV) than that on the half H- and half OH-terminated Si (001) surface (0.62 eV) was due to the weakened Al-C bonds of the adsorbed TMA for bond breaking and the shorter distances of C_{(TMA)}-H_{(OH)} from 2.64 to 2.59 Å, and Al_{(TMA)}-O_{(OH)} from 2.06 to 2.05 Å for bond making.

Fig. 5(a) shows the adsorption energy of TMA and its reaction energy barrier on the fully OH-terminated α-SiO_{2} (001) surface with the surface –OH density of 9.2/nm^{2}. Al_{(TMA)} was located on O_{(OH)} on the surface at a distance of 2.07 Å due to lone pair electrons of O_{(OH)}. Its adsorption energy of 0.99 eV was lower than that of 1.16 eV on the fully OH-terminated Si (001) surface, due to hydrogen bonds between the –OHs themselves on the fully OH-terminated α-SiO_{2} (001) surface, as shown in the red box. The Al-C bonds of the adsorbed TMA were strengthened, because the attractive interaction between O_{(OH)} and the adsorbed TMA were weakened. The Al–C bond lengths and the distance between O_{(OH)} and TMA decreased to 1.98 and increased to 2.07 Å, respectively, as shown in the red box. When one –CH_{3(TMA)} reacted with H_{(OH)} to produce CH_{4} at a distance of 2.87 Å between the C atom of –CH_{3(TMA)} and H_{(OH)} for bond making, Al_{DMA group} bonded to the exposed O atom with an Al–O bond length of 1.72 Å and a reaction energy barrier of 0.73 eV. In the transition state, the Al atom of the broken DMA group moved to the exposed O atom for bond making at a distance of 1.90 Å, and H_{(OH)} moved to the broken –CH_{3(TMA)} for bond making. The higher reaction energy barrier (0.73 eV) than that on the fully OH-terminated Si (001) surface (0.50 eV) was due to the longer distances of C_{(TMA)}-H_{(OH)} and Al_{(TMA)}-O_{(OH)} for bond making. Fig. 5(b) shows adsorption energies of TMA and its energy barriers on the surface as a function of the surface –OH density. Adsorption energy of TMA increased to 1.16 eV and its reaction energy barriers decreased to 0.50 eV until the surface –OH density of 6.8/nm^{2}. However, those trends were reversed at the high surface –OH density of 9.2/nm^{2} due to the hydrogen bonds between –OH’s themselves on the surface.

4. Conclusions

The adsorption energy of TMA and its reaction energy barrier with varying surface –OH density were calculated to understand the effect of the surface –OH density on TMA reaction for initial ALD using DFT. When the surface –OH density of the Si (001) surface increased from 0 to 6.8/nm^{2}, the adsorption energy increased while its reaction energy barrier decreased, due to increased attractive interaction between –CH_{3(TMA)} and H_{(OH)}. When the surface –OH density was further increased using the fully OH-terminated α-SiO_{2} (001) surface (9.2/nm^{2}), the trends were reversed, due to the hydrogen bonds among –OH’s themselves. The energy barrier for TMA reaction was strongly affected by the distance between C_{(TMA)} and H_{(OH)} for bond making and the Al–C bond length of TMA for bond breaking.

Acknowledgements

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2011-0002549), and partially by the Education and Research Promotion Program of Korea University of Technology and Education (KUT).

References