

Full Length Article

Surface reaction of silicon chlorides during atomic layer deposition of silicon nitride

Luchana L. Yusup^a, Jae-Min Park^a, Tirta R. Mayangsari^a, Young-Kyun Kwon^{b,*}, Won-Jun Lee^{a,*}^a Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 05006, Korea^b Department of Physics and Research Institute for Basic Sciences, Kyung Hee University, Seoul 02447, Korea

ARTICLE INFO

Article history:

Received 31 October 2016

Received in revised form 4 June 2017

Accepted 5 June 2017

Available online 7 June 2017

Keywords:

Density functional theory (DFT)

Atomic layer deposition (ALD)

Silicon nitride

Silicon chlorides

Surface reaction

ABSTRACT

The reaction of precursor with surface active site is the critical step in atomic layer deposition (ALD) process. We performed the density functional theory calculation with DFT-D correction to study the surface reaction of different silicon chloride precursors during the first half cycle of ALD process. SiCl₄, SiH₂Cl₂, Si₂Cl₆ and Si₃Cl₈ were considered as the silicon precursors, and an NH/SiNH₂*-terminated silicon nitride surface was constructed to model the thermal ALD processes using NH₃ as well as the PEALD processes using NH₃ plasma. The total energies of the system were calculated for the geometry-optimized structures of physisorption, chemisorption, and transition state. The order of silicon precursors in energy barrier, from lowest to highest, is Si₃Cl₈ (0.92 eV), Si₂Cl₆ (3.22 eV), SiH₂Cl₂ (3.93 eV) and SiCl₄ (4.49 eV). Silicon precursor with lower energy barrier in DFT calculation showed lower saturation dose in literature for both thermal and plasma-enhanced ALD of silicon nitride. Therefore, DFT calculation is a promising tool in predicting the reactivity of precursor during ALD process.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Silicon nitride is one of the most popular dielectric materials in semiconductor manufacturing process due to its unique properties, such as high etching selectivity against silicon oxide, superior diffusion barrier against copper or alkali ions, high charge trap density, and high dielectric constant. Major application of silicon nitride includes the sidewall spacer of CMOS device [1] and the charge trap layer in three-dimensional NAND flash device [2]. Silicon nitride thin films have been produced by low-pressure or plasma-enhanced chemical vapor deposition (CVD) techniques, and recently atomic layer deposition (ALD) technique was introduced for better step coverage and better film quality at lower temperatures. Silicon chloride precursors, such as SiCl₄ [3], SiH₂Cl₂ [4,5] and Si₂Cl₆ [6], were used as the silicon precursors with ammonia or hydrazine [8] as reactants in the thermal ALD of silicon nitride at 450 °C or higher temperatures. Plasma-enhanced ALD (PEALD) process is gaining attention due to lower deposition temperature and lower saturation dose as compared with thermal ALD.

PEALD of silicon nitride using silicon chloride precursors, such as SiH₂Cl₂ [7] and Si₂Cl₆ [8], with NH₃ plasma were reported at lower deposition temperatures below 400 °C. The high reactivity of plasma species can give opportunity to use various precursors in deposition process, and the PEALD using aminosilane precursors, such as trisilylamine (TSA) [9], bis(tert-butylamino)silane (BTBAS) [10,11] and tris(dimethylamino)silane (TDMAS) [12], were also reported. Experimental and theoretical studies comparing nitriding agents showed that N₂ plasma gives the highest growth rate in PEALD using BTBAS, and N₂/H₂ or NH₃ plasma produces hydrogen-terminated silicon nitride surface which hinders the reaction of aminosilane precursor with the surface [13].

Only few theoretical study described the effect of silicon precursors in thermal ALD or PEALD of silicon nitride. In our previous work [14], we reported the effect of different surface active sites of silicon nitride on the reactivity of silicon chloride precursors, SiCl₄ and Si₂Cl₆. Density functional theory (DFT) calculation showed that the reaction of silicon chlorides on NH/SiNH₂*-terminated surface were plausible due to exothermic energy of chemisorption reaction. We also found out that different precursors can give different reactivity towards the surface.

Therefore, in the present work we focuses on comparison of the reactivity of different silicon chloride precursors. ALD processes of silicon nitride using silicon chloride precursors are popular

* Corresponding authors.

E-mail addresses: ykkwon@khu.ac.kr (Y.-K. Kwon), wjlee@sejong.ac.kr (W.-J. Lee).

Table 1
Bond lengths and bond angles of the optimized silicon chlorides.

Precursors	Bond Length (Å)	Bond Angle (°)		
SiCl ₄ *	Si–Cl	2.042	Cl–Si–Cl	109.5
SiCl ₄	Si–Cl	2.044	Cl–Si–Cl	109.5
SiH ₂ Cl ₂	Si–Cl	2.059	Cl–Si–Cl	111.0
	Si–H	1.478	H–Si–H	113.0
Si ₂ Cl ₆	Si–Cl	2.053	Cl–Si–Cl	109.8
	Si–Si	2.335	Cl–Si–Si	109.1
Si ₃ Cl ₈	Si–Cl (terminal)	2.054	Cl–Si–Cl (terminal)	109.8
	Si–Cl (mid)	2.062	Cl–Si–Cl (mid)	111.1
	Si–Si	2.345	Cl–Si–Si	109.6
			Si–Si–Si	113.6

*Without DFT-D correction.

especially in memory device manufacturing due to its superior film quality as compared with the ALD using aminosilane precursors. Chemisorptions of SiCl₄, SiH₂Cl₂, Si₂Cl₆ and Si₃Cl₈ molecules on NH/SiNH₂*-terminated surface were comparatively studied to model the thermal ALD process using NH₃ and the PEALD process using NH₃ plasma. The total energies of the system were calculated for the geometry-optimized structures of physisorption, chemisorption, and transition state. The order of silicon precursors in energy barrier was determined, and was compared with ALD experiments in literature.

2. Calculation details

First principle density functional theory calculations were performed using Material Studio 7.0 with Dmol³ package (BIOVIA, USA) [15,16]. All of the optimized structures and energies were obtained by the Perdew-Burke-Ernzerhof (PBE) scheme [17] in the generalized gradient approximation (GGA) for exchange correlation functional, with the double numerical polarization (DNP) as a basis set [18–20]. Octupole scheme for multipolar expansion with scalar relativistic effect were included for more precise results, because the octupole scheme gave a good convergence of energy for the calculation of system that involved a lone pairs of electron [21]. Smearing of 9×10^4 Ha and dipole slab correction in the orbital occupancy scheme were applied. We used a customized quality of convergence tolerance without symmetry constraint until the total energy change was converged to 10^6 Ha and all the atomic forces became smaller than 2×10^4 Ha Å⁻¹. We also compared the calculation results with and without dispersion corrections using DFT-D (Grimme) [22] method in order to observe the influence of the non-covalent forces. Since the non-covalent forces such as van der Waals force or hydrogen bonding can be accounted properly by high quantum-chemical wave function such as Quantum Monte Carlo, the semi-empirical approaches such as DFT-D correction give the best compromise in the standard DFT dispersion terms [23].

We constructed the geometry-optimized NH/SiNH₂*-terminated silicon nitride surface using the method described in our previous study [14] with an addition of DFT-D correction, except in Fig. 1(a) which is produced without DFT-D correction. We also optimized structures of silicon chloride molecules using DFT-D correction. The optimized bond lengths and bond angles of silicon chloride molecules of the present work are summarized in Table 1.

The “unbound” state was constructed by placing the geometry-optimized precursor molecule above the geometry-optimized surface with a distance of >10 Å. To model the physisorption process, the precursor was placed 4 Å above the surface in several positions, then geometry optimization was performed for searching the lowest total energy of physisorption [24–26]. The structure with the lowest total energy value is called as “initial” structure. Based on the initial structure, we considered several possible

chemisorption reactions, then optimized the geometry for searching the lowest total energy of chemisorption. The structure with the lowest total energy value is called as “final” structure.

Finally, the transition state (TS) search was performed [27–29] in order to obtain the energy barrier between the physisorption (initial structure) and the chemisorption (final structure). The TS search task was performed based on the linear synchronous transit (LST), followed by repeated conjugate gradient minimization and quadratic synchronous transit (QST) maximizations approach.

3. Results and discussion

3.1. SiCl₄ precursor

Fig. 1 shows the total energies of the unbound, initial, TS and final structures for the reaction of SiCl₄ on an NH/SiNH₂-terminated surface without [14] and with the DFT-D correction scheme. The initial structure shows the physisorption of a SiCl₄ molecule on the surface. The energy of physisorption is -0.05 eV without DFT-D correction or -0.34 eV with DFT-D correction, which shows that the physisorption process is exothermic. The distance between the Si atom in the precursor and the N atom of the surface is 4.38 Å without DFT-D correction or 3.93 Å with DFT-D correction. The TS structure shows the dissociation of a Cl atom from the precursor and the dissociation of an H atom from the surface to produce HCl. When DFT-D correction is included, the precursor is closer to the surface, reducing the distance between the Si atom of SiCl₄ and the N atom of the surface from 3.16 Å to 2.82 Å. The energy barrier of 4.89 eV or 4.49 eV was generated by TS search, which corresponds to the dissociation energy of Cl₃Si–Cl (4.77 eV) [30] or N–H (~ 3.5 eV) [31]. In the final structure, the SiCl₄ molecule chemisorbs on the surface by forming an Si–N bond and an HCl molecule as the byproduct. Energy of chemisorption is -1.11 eV or -1.78 eV depending on the presence of the DFT-D correction, which shows the process is exothermic.

The DFT-D correction did not affect the reaction mechanism, and the initial, TS and final structures with DFT-D correction in Fig. 1(b) look similar with the structures without the correction in Fig. 1(a). However, the reaction between the precursor and the silicon nitride surface became stronger with DFT-D correction. The energies of initial, TS and final structures are lowered and the distance between the precursor and the surface was reduced by the correction. Since the silicon nitride surface of the present study is NH/SiNH₂*-terminated and fully covered by hydrogen atoms, the non-covalent force between H and Cl would be important. We have confirmed that the reaction mechanism for other silicon chlorides is the same regardless of the DFT-D calibration. This paper reports the calculation results with the correction.

3.2. SiH₂Cl₂ precursor

We compared SiH₂Cl₂ with SiCl₄ to investigate the effect of hydrogen atoms in SiH₂Cl₂. The total energies of the unbound, initial, TS and final structures for the reaction of SiH₂Cl₂ on NH/SiNH₂*-terminated silicon nitride surface are shown in Fig. 2. The physisorption structure shows the energy of -0.135 eV and the distance between the Si atom in the precursor and the N atom of the surface is 3.66 Å. The TS structure shows that an H atom from the surface and an H atom from the precursor are dissociated to form H₂, unlike the case of SiCl₄. The distance between the Si atom of SiH₂Cl₂ and the N atom of the surface is reduced to 2.47 Å, and the energy barrier of 3.93 eV was obtained by TS search. Lower dissociation energy of Si–H bond ($3-3.3$ eV) [31–34] as compared with Si–Cl bond ($3.9-4.8$ eV) [31–34] correspond to the lower energy barrier in the SiH₂Cl₂ case. In the final structure, the chemisorption gives

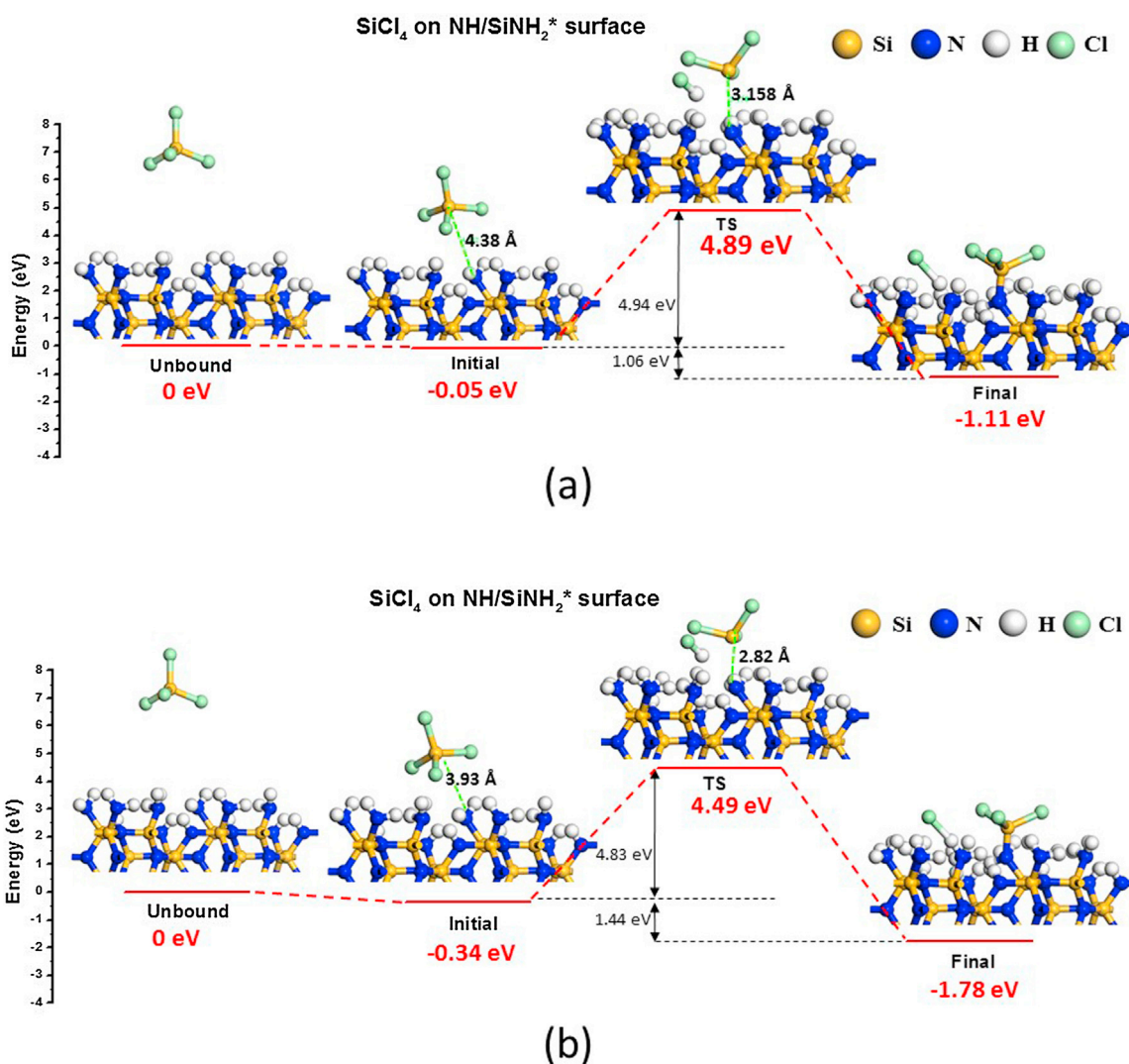


Fig. 1. The total energies of the unbound, initial, TS and final structures for reaction of SiCl₄ on an NH/SiNH₂-terminated surface (a) without DFT-D correction and (b) with DFT-D correction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

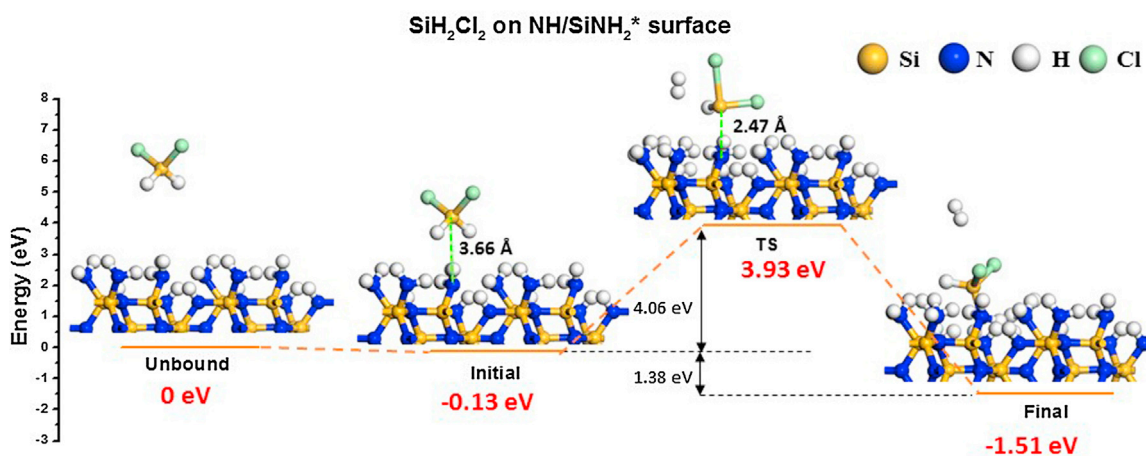


Fig. 2. The total energies of the unbound, initial, TS and final structures for the reaction of SiH₂Cl₂ on NH/SiNH₂*-terminated silicon nitride surface.

energy of reaction of -1.51 eV with the formation an Si–N bond on the surface and an H₂ molecule as byproduct instead of HCl. The energy of chemisorption is higher than the SiCl₄ case probably

due to hydrogen repulsion force between the H atom of $-\text{SiHCl}_2^*$ surface group and H atoms of the surface.

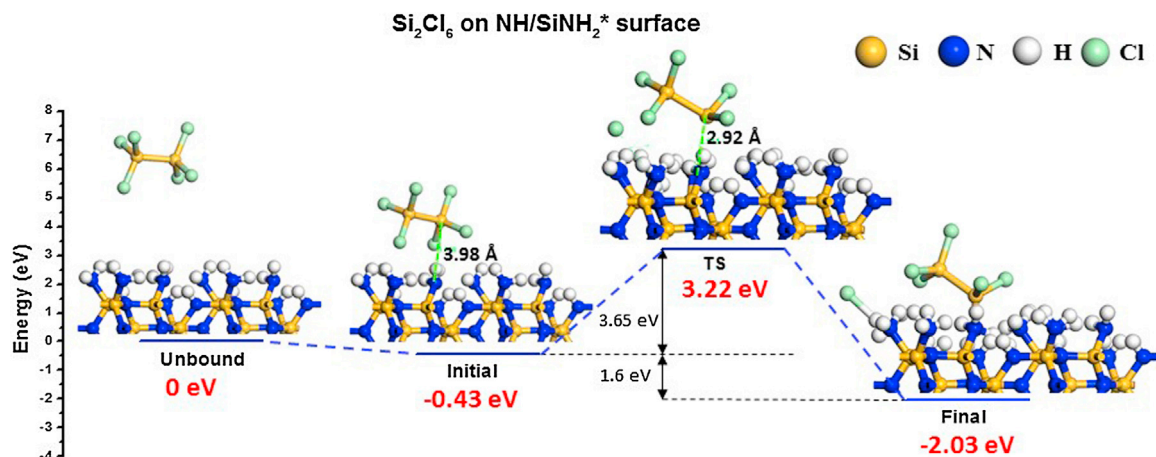


Fig. 3. The total energies of the unbound, initial, TS and final structures for the reaction of Si_2Cl_6 on NH/SiNH_2^* -terminated silicon nitride surface.

3.3. Si_2Cl_6 precursor

We compared Si_2Cl_6 with SiCl_4 to compare a disilane-type precursor with a monosilane-type precursor. The total energies of the unbound, initial, TS and final structures for the reaction of Si_2Cl_6 on NH/SiNH_2^* -terminated silicon nitride surface are shown in Fig. 3. For physisorption, the distance between the Si atom in the precursor and the N atom of the surface is 3.98 Å, and the physisorption energy is -0.43 eV which is lower than the SiCl_4 case. The TS structure shows that there is no dissociation of an H atom from the surface and the Cl atom dissociated from the precursor attached on a surface H atom. The energy barrier is 3.22 eV which is lower than those of the SiCl_4 and SiH_2Cl_2 cases. The distance between the Si atom in the precursor and the N atom of the surface is 2.92 Å, which is significantly lower than those of the SiCl_4 and SiH_2Cl_2 cases. In the final structure, the energy of chemisorption reaction is -2.03 eV which is also lower than those of the SiCl_4 and SiH_2Cl_2 cases probably due to the interaction between $-\text{SiCl}_3^*$ surface group and H atoms of the surface.

3.4. Si_3Cl_8 precursor

We considered Si_3Cl_8 after Si_2Cl_6 , because increasing the number of silicon was effective to increase the reactivity of silicon precursor. Fig. 4 shows the total energies of the unbound, initial, TS and final structures for the reaction of Si_3Cl_8 on NH/SiNH_2^* -terminated silicon nitride surface. Physisorption structure shows the distance between the Si atom in the precursor and the N atom of the surface of 4.26 Å and the energy of physisorption of -1.47 eV, which is very exothermic as compared with other precursors. The transition state search yielded an energy barrier of 0.92 eV, which is the lowest energy barrier in this study. Si atom from Si_3Cl_8 already formed a new Si–N bond with surface to produce an HCl molecule in TS structure. The final structure shows the chemisorption of Si_3Cl_8 with two Si–N bonds and the production of an additional HCl molecule as a byproduct. The total energy of chemisorption is -3.30 eV, showing that the Si_3Cl_8 is the most reactive precursor among precursors of this study. Two Si–N bonds on chemisorption structure are responsible for the lowest energy of chemisorption observed, by stabilizing the final structure.

3.5. Comparison with experimental results

In the ALD process, the chemisorption of silicon precursor on the surface is very important in determining the growth rate. The kinetics of the chemisorption depends on the energy barrier between

physisorption and chemisorption states. In this study, the order of silicon precursors in energy barrier, from lowest to highest, is Si_3Cl_8 (0.92 eV), Si_2Cl_6 (3.22 eV), SiH_2Cl_2 (3.93 eV) and SiCl_4 (4.49 eV). Thermal ALD of silicon nitride has been reported by using NH_3 as the reactant, and the saturation doses were 2×10^{10} L ($1 \text{ L} = 10^{-6}$ Torr s) for SiCl_4 [3], 6×10^9 L for SiH_2Cl_2 [4,5], and 2×10^8 L for Si_2Cl_6 [6]. This agrees well with the order in energy barrier calculated by DFT in this study, and only a very small portion of precursor molecules would have energies sufficient to overcome the high energy barriers. The PEALD of silicon nitride has been also reported by using SiH_2Cl_2 [6,27] or Si_2Cl_6 [7] with NH_3 plasma, and the saturation doses of SiH_2Cl_2 and Si_2Cl_6 were reported to be 5.4×10^6 and 8×10^5 L, respectively. Higher saturation dose of SiH_2Cl_2 is also in a good agreement with higher energy barrier of SiH_2Cl_2 in this study.

DFT calculation also can explain higher concentration of hydrogen impurity of thermal ALD using SiH_2Cl_2 as compared with the ALD using SiCl_4 [28]. The surface group generated by chemisorption of SiH_2Cl_2 is $-\text{SiHCl}_2$ in Fig. 2, whereas $-\text{SiCl}_3$ is formed by the chemisorption of SiCl_4 , as predicted in ref [28]. In the next step of ALD process, NH_3 molecules react with the surface group of $-\text{SiCl}$ to form $-\text{SiNH}_2$, but would not react with $-\text{SiH}$ to leave H atoms in the growing film.

4. Conclusion

We studied the reactions of different silicon chlorides with NH/SiNH_2^* -terminated silicon nitride surface using DFT calculation. We included the DFT-D correction to consider the non-covalent interaction between precursor and hydrogen-saturated surface, and the correction generated lower total energy values of the system. SiCl_4 showed the highest energy barrier for the chemisorption among silicon chlorides of this study, because Cl and H atoms should be dissociated from SiCl_4 and the surface. Lower energy barrier of SiH_2Cl_2 corresponds to the lower dissociation energy of Si–H as compared with Si–Cl. Si_2Cl_6 also showed lower energy barrier probably because of the absence of H atom dissociated from the surface and the lower bond dissociation energy of Si–Cl in Si_2Cl_6 as compared with Si–Cl in SiCl_4 . The lowest energy barrier was obtained for Si_3Cl_8 , corresponding to Si–N bond in TS structure. The trend in calculation results is in a good agreement with experimental results in literature. Silicon precursor with lower energy barrier in DFT calculation showed lower saturation dose for both thermal ALD and PEALD of silicon nitride. Therefore, DFT calculation is a promising tool in predicting the reactivity of precursor during ALD process.

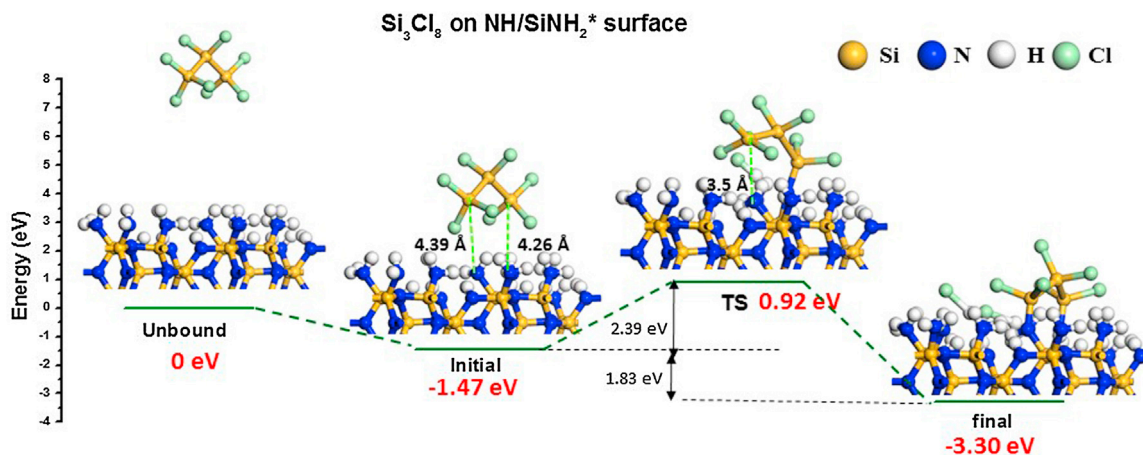


Fig. 4. The total energies of the unbound, initial, TS and final structures for the reaction of Si_3Cl_8 on NH/SiNH_2^* -terminated silicon nitride surface.

Acknowledgment

This work was supported by Industrial Strategic Technology Development Program (Project No. 10041792) funded by MOTIE (Ministry of Trade, Industry and Energy). We also would like to acknowledge financial support from the Future Semiconductor Device Technology Development Program (Project No. 10045360) funded by MOTIE (Ministry of Trade, Industry and Energy) and KSRC (Korea Semiconductor Research Consortium).

References

- [1] K.J. Yang, T.J. King, C. Hu, S. Levy, H.N. Al-Shareef, *Solid. State. Electron.* 47 (2003) 149–153.
- [2] J.-M. Park, S.J. Jang, L.L. Yusup, W.-J. Lee, S.-I. Lee, *ACS Appl. Mater. Interfaces* 8 (2016) 20865–20871.
- [3] J.W. Klaus, A.W. Ott, A.C. Dillon, S.M. George, *Surf. Sci.* 418 (1998) L14–L19.
- [4] W. Lee, J. Lee, C.O. Park, Y. Lee, S.-J. Shin, S.-K. Rha, *Korean J. Mater. Res.* 45 (2004) 1352–1355.
- [5] W. Lee, U. Kim, C.-H. Han, M.-H. Chun, S.-K. Rha, Y. Lee, *J. Korean Phys. Soc.* 47 (2005) 598–602.
- [6] K. Park, W.-D. Yun, B.-J. Choi, H.-D. Kim, W.-J. Lee, S.-K. Rha, et al., *Thin Solid Films* 517 (2009) 3975–3978.
- [7] H. Goto, K. Shibahara, S. Yokoyama, *Appl. Phys. Lett.* 68 (1996) 3257–3259.
- [8] R.A. Ovanesyan, D.M. Hausmann, S. Agarwal, *ACS Appl. Mater. Interfaces* 7 (2015) 10806–10813.
- [9] W. Jang, H. Jeon, C. Kang, H. Song, J. Park, H. Kim, et al., *Phys. Status Solidi.* 211 (2014) 2166–2171.
- [10] H.C.M. Knoops, E.M.J. Braeken, K. De Peuter, S.E. Potts, S. Haukka, *Appl. Mater. Interfaces* 7 (2015) 1–2.
- [11] R.H.E.C. Bosch, L.E. Cornelissen, H.C.M. Knoops, W.M.M. Kessels, *Chem. Mater.* 28 (2016) 5864–5871.
- [12] Y. Kim, J. Provine, S.P. Walch, J. Park, W. Phuthong, A.L. Dadlani, et al., *ACS Appl. Mater. Interfaces* 8 (2016) 17599–17605.
- [13] C.K. Ande, H.C.M. Knoops, K. de Peuter, M. van Drunen, S.D. Elliott, W.M.M. Kessels, *J. Phys. Chem. C* 6 (2015) 3610–3614.
- [14] L.L. Yusup, J.-M. Park, Y.-H. Noh, S.-J. Kim, W.-J. Lee, S. Park, et al., *RSC Adv.* 6 (2016) 68515–68524.
- [15] B. Delley, *J. Chem. Phys.* 92 (1990) 508–517.
- [16] B. Delley, *J. Chem. Phys.* 113 (2000) 7756–7764.
- [17] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865–3868.
- [18] J. Baker, A. Kessi, B. Delley, *J. Chem. Phys.* 105 (1996) 192–212.
- [19] J. Andzelm, R.D. King-Smith, G. Fitzgerald, *Chem. Phys. Lett.* 335 (2001) 321–326.
- [20] J. Melorose, R. Perroy, S. Careas, *Phys. Rev. B* 45 (1992) 13709–13712.
- [21] A. Klamt, *COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*, Elsevier, 2005, pp. 27.
- [22] S. Grimme, *J. Comput. Chem.* 27 (2006) 1787–1799.
- [23] E.R. McNellis, J. Meyer, K. Reuter, *Phys. Rev. B* 80 (2009) 205414.
- [24] K. Young-Kyun, *J. Korean Phys. Soc.* 57 (2010) 778–786.
- [25] G. Kim, S.H. Kang, C.Y. Lim, Y.K. Kwon, *Chem. Phys. Lett.* 545 (2012) 83–87.
- [26] H.J. Lee, G. Kim, Y.K. Kwon, *Chem. Phys. Lett.* 580 (2013) 57–61.
- [27] C.J. Cerjan, *J. Chem. Phys.* 75 (1981) 2800–2806.
- [28] J. Baker, *J. Comput. Chem.* 7 (1986) 385–395.
- [29] N. Govind, M. Petersen, G. Fitzgerald, D. King-Smith, J. Andzelm, *Comput. Mater. Sci.* 28 (2003) 250–258.
- [30] R. Walsh, *Bond Dissociation Energies in Organosilicon Compounds*, 2017 (accessed May 2015) <http://www.gelest.com/goods/pdf/library/10bonddiss.pdf>.
- [31] Y. Luo, J. Kerr, *Bond dissociation energies*, in: *CRC Handb Chem. Phys.*, 2007, pp. 65–98.
- [32] B.D. Darwent, *Bond Dissociation Energies in Simple Molecules*, *Natl. Stand. Ref. Data Syst. Natl. Bur. Stand.* (1970) 1–58.
- [33] T.L. Cottrell, *The Strengths of Chemical Bonds*, 2nd ed., Butterworths, London, 1958.
- [34] S.W. Benson, *J. Chem. Educ.* 42 (1965) 502–518.