

Mechanism Investigation of Temperature Dependent Growth and Etching Process of GeCl₄ on SiGe Surface: *ab-initio* Study

Ji Young Park

CSE Team,

Data & Information Technology Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

jy.qc37.park@samsung.com

Gyeom Kim

Foundry Process Development Team,

Semiconductor R&D Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

g93.kim@samsung.com

Jin Bum Kim

Foundry Process Development Team,

Semiconductor R&D Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

bumii.kim@samsung.com

Sang-Moon Lee

Foundry Process Development Team,

Semiconductor R&D Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

bryan.lee@samsung.com

Sae-jin Kim

CSE Team,

Data & Information Technology Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

saejin.kim@samsung.com

Hyungssoo Ko

CSE Team,

Data & Information Technology Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

hyungssoo.ko@samsung.com

Seungmin Lee

CSE Team,

Data & Information Technology Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

sm101.lee@samsung.com

Seung Hun Lee

Foundry Process Development Team,

Semiconductor R&D Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

hun0301.lee@samsung.com

Inkook Jang

CSE Team,

Data & Information Technology Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

inkook.jang@samsung.com

Dae Sin Kim

CSE Team,

Data & Information Technology Center

Smaung Electronics Co., Ltd.

Hwasung-si, Gyeonggi-do, Korea

daesin.kim@samsung.com

Abstract—Herein, we unveil the deposition and etch mechanism of GeCl₄ on the SiGe surface. At the high temperature, GeCl₄ is dissociated to GeCl₂ and then worked as a deposition source. Thus, the rate determinant step of surface growth is GeCl₄ dissociation, and a novel precursor that quickly dissociates to GeCl₂ will be a proper precursor target to Ge growth at the low-temperature process. Otherwise, at the low temperature, GeCl₄ works as an etching gas by reacts with surface Ge/Si atoms and forms Ge₂H_nCl_{6-n} or GeSiH_nCl_{6-n} (n=2,3) molecules. From the etch mechanism analysis, the first activation energy of Ge desorption is lower, 65.8 (kcal/mol), than GeCl₄ dissociation (101 kcal/mol), but the etched surface has higher energy, -6.7 (kcal/mol), than the Ge doped, -19.2 (kcal/mol). This energy profile successfully explains the experimental observation, deposition at high temperature, etch at low temperatures. Additionally, we figured out that the GeCl₃ intermediate shows the most tightly bind to surface atoms.

Keywords—*Ab-initio, Surface Reaction, Precursor, Etch, Deposition*

I. INTRODUCTION

As the semiconductor becomes smaller and more complicated, process temperature becomes various for the targeted process [1, 2]. Particularly, precursor deposition and etch rate sensitively change within the wide range of the temperature. Because of molecular adsorption and desorption reaction are thermochemical reactions, external condition, like as temperature, is essential to overcome the activation

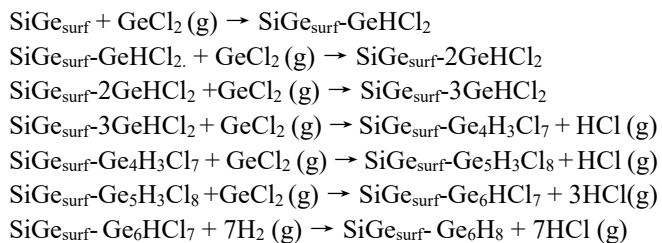
energy of the step. To investigate proper depo/etch gas material for various temperature regions, we could figure out that GeCl₄ works as a deposition source and an etch source in different temperature region [3-7]. Although it shows temperature dependent behavior, the detailed adsorption/desorption process is still under a veil, making it hard to design novel depo/etch gas. By understanding the exact reaction mechanism of GeCl₄ on the SiGe surface, we can understand the origin of this curious behavior of GeCl₄. And even more, we can design a novel Ge precursor which works at low temperature. Herein we provide the detailed reaction mechanism of the growth and etch process to unveil the temperature-dependent deposition properties and suggest the direction of the novel Ge precursor design.

II. RESULTS AND DISCUSSION

A. GeCl₄ at the high temperature

The activation energy for GeCl₄ dissociation to GeCl₂ + Cl₂ is obtained as 101 (kcal/mol) by *ab-initio* calculations and which supports the information that GeCl₄ spontaneously dissociates at the high temperature [8]. With the high-temperature assumption, we obtained the reaction energy profile of GeCl₂ on the SiGe surface until half-layer deposition. Interestingly, only 46.4 (kcal/mol) activation energy is required for GeCl₂ adsorption on the SiGe surface, which is much less than activation energy of GeCl₄

adsorption (62.5kcal/mol) and GeCl_4 dissociation (101 kcal/mol). Followed by the first adsorption, the stepwise energy of GeCl_2 attachment on the surface is obtained as -7.8, -14.3, -1.0, -5.5, 3.4, 38.2, -19.2 (kcal/mol). This energy profile suggests that just after overcoming the activation energy barrier of dissociation, adsorption on the SiGe surface spontaneously processes under the same condition. This analysis implies that control the dissociation energy barrier to generating GeCl_2 molecules is important to control the growth rate.



When the GeCl_2 adsorbs on the SiGe surface, a terminal hydrogen atom is spilled over to a GeCl_2 molecule and generates GeHCl_2 add on to SiGe surface. As the number of attached GeHCl_3 increases, each GeHCl_3 molecule reacts with a nearby GeHCl_3 molecule and produces a new Ge-Ge bond and HCl byproduct.

B. GeCl_4 at the low temperature

At the low temperature, it is observed that GeCl_4 etches the SiGe surface instead of deposition [3, 4]. Therefore, to verify the etch mechanism of GeCl_4 , we compared the activation energy of Ge desorption and Si desorption reaction. Ge desorption activation energy, $E_a = 1.211$ (eV) is lower than Si desorption, $E_a = 2.108$ (eV). So, we can guess that step by step Ge half-layer etching process will start from Ge desorption and which is shown in Fig. 1.

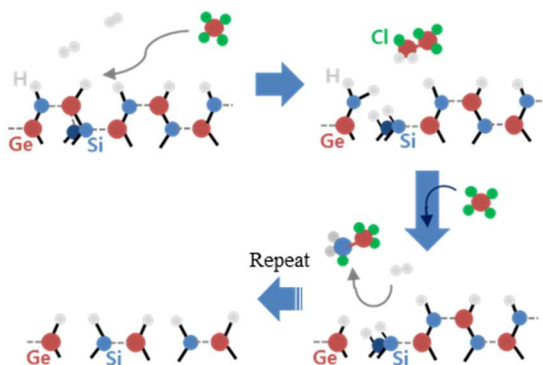


Fig. 1. The illustration of first two steps of SiGe etch

Different from deposition, which proceeds with GeCl_2 molecule, etch process directly react with GeCl_4 molecule. By generating relatively stable $\text{Ge}_2\text{H}_n\text{Cl}_{6-n}$ or $\text{SiGeH}_m\text{Cl}_{6-m}$ ($n=1,2$ and $m=2,3$) molecule with surface Ge or Si atom, GeCl_4 etches surface layer. With only 65.8 (kcal/mol), the first Ge dissociates its bond in the SiGe surface, which is much lower than adsorption activation energy, 101 (kcal/mol). This low activation energy means that dissociation can proceed under a lower temperature than the

growth temperature.

Among the various paths, the most reliable and low-lying path is below mechanism.

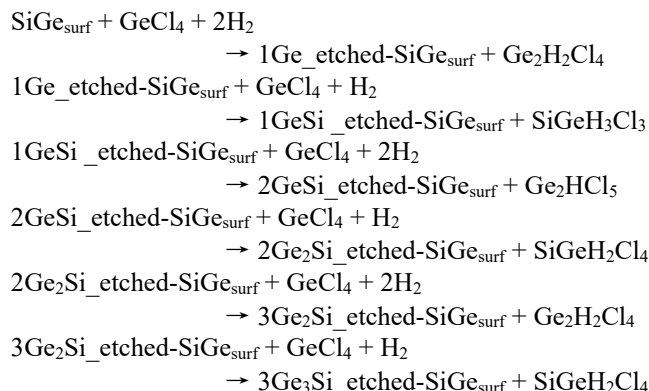


Fig. 2 shows the detailed reaction path of the first etch step. Just after GeCl_4 precursor adsorbed on one of Ge site on SiGe cluster, it reacts with H_2 molecule in the reaction system or HCl molecule from the byproduct of terminal H and GeCl_4 molecule. Both of the gases can dissociate the Ge-Si bond and generates a new Ge-H/Ge-Cl and Si-H/Si-Cl bond. The activation energy for each dissociation is 54.0 (kcal/mol) for H_2 insertion and 78.2 (kcal/mol) for HCl insertion. All three Ge-Si bonds become Ge-H or Ge-Cl bonds by repeating this step, and the surface Ge atom is etched and flows away. Same reaction proceeds to GeCl_4 attached surface Si atom. After all of the Si/Ge atoms in the remaining surface layer are

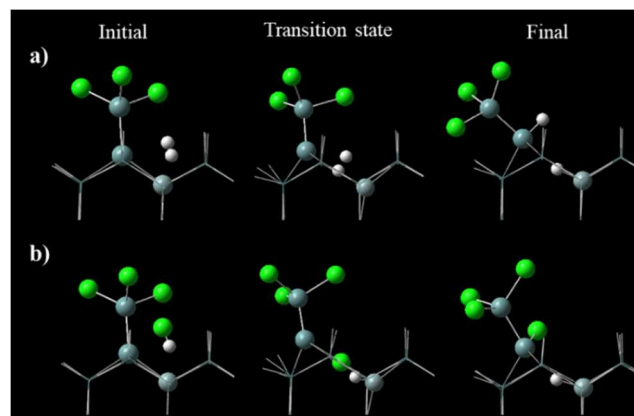


Fig. 2. Transition state structure of H_2/HCl insertion between surface SiGe and adsorbed $\text{Ge}_2\text{H}_2\text{Cl}_4$.

dissociated, one layer etches at the end.

Next, we focused on the energy difference between the growth paths and the etch paths. Compared with growth, etch's transition state energy is lower, 101 (kcal/mol) for growth versus 65.8 (kcal/mol) for etch, while the energy of the final product is higher, -19.2 (kcal/mol) for growth versus -6.7 (kcal/mol) for etch. Based on the thermal equilibrium, most of the reactions follow the path which has lower reaction barrier at the low temperature because reaction cannot overcome the reaction barrier of growth path.

While at a higher temperature, molecules have enough

energy even higher than the reaction barrier of the growth path. Then the stability of the final structure determines the excellent product. For example, the etch reaction has lower reaction barrier but its final structure energy is higher than growth. Therefore the etched product can undergo reverse reaction and back to the start point easier than growth. Otherwise, since one molecule adsorbed on the surface, it is rarely back to the dissociated-start point. Therefore, etch is preferred at the lower temperature and growth is preferred at the high temperature because of the equilibrium difference in two different temperature, for this kinds of energy profiles. This analysis explains why GeCl_4 works as an etchant at a lower temperature while working as a deposition source at a high temperature.

C. Novel Precursor Design I - Deposition

As shown in **section A**, surface growth is based on the GeCl_2 molecule and which means how much the dissociation energy is lower from stable precursor is the key factor in designing a new Ge deposition precursor. In the **Fig. 3** and **Table 1**, we compared the $\text{GeH}_n\text{Cl}_{4-n}$ ($n=0-4$) dissociation energy in gas phase. As the bond dissociation energy between each atom is various, H-H (436), H-Cl (428), Cl-Cl (243), Ge-H (288), and Ge-Cl (349) (kJ/mol), transition state energy also varies on each difference molecule.

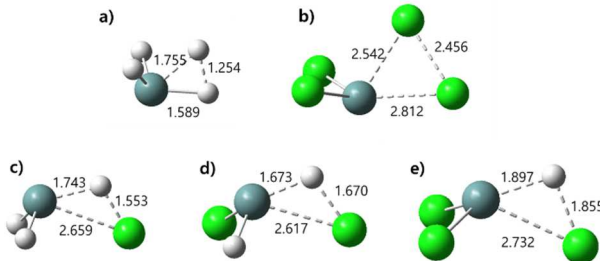


Fig. 3. Optimized transition state structure of a) GeH_4 , b) GeCl_4 , c) GeH_3Cl , d) GeH_2Cl_2 , and e) GeHCl_3 . Units in Å.

Table 1. Transition state energy of the dissociation of GeH_4 , GeH_3Cl , GeH_2Cl_2 , GeHCl_3 , and GeCl_4 into GeH_2 , GeHCl , and GeCl_2

| structure | Reaction | Ea (kcal/mol) |
|-----------|--|---------------|
| b) | $\text{GeCl}_4 \rightarrow \text{GeCl}_2 + \text{Cl}_2$ | 101.00 |
| e) | $\text{GeHCl}_3 \rightarrow \text{GeCl}_2 + \text{HCl}$ | 49.30 |
| | $\text{GeHCl}_3 \rightarrow \text{GeHCl} + \text{Cl}_2$ | 99.23 |
| d) | $\text{GeH}_2\text{Cl}_2 \rightarrow \text{GeHCl} + \text{HCl}$ | 52.82 |
| | $\text{GeH}_2\text{Cl}_2 \rightarrow \text{GeCl}_2 + \text{H}_2$ | 66.83 |
| c) | $\text{GeH}_3\text{Cl} \rightarrow \text{GeH}_2 + \text{HCl}$ | 57.54 |
| | $\text{GeH}_3\text{Cl} \rightarrow \text{GeHCl} + \text{H}_2$ | 57.86 |
| a) | $\text{GeH}_4 \rightarrow \text{GeH}_2 + \text{H}_2$ | 53.95 |

Among all the dissociable fragments, $\text{GeHCl}_3 \rightarrow \text{GeCl}_2 + \text{HCl}$ has the lowest activation barrier. Therefore, by using GeHCl_3 , GeCl_2 is more easily obtained than GeCl_4 . Moreover, not only GeHCl_3 but also all other molecules showed lower activation barriers than GeCl_4 and generated GeCl_2 , GeHCl , or GeH_2 .

D. Novel Precursor Design II -Etch

It is necessary to break the bond between nearby Ge/Si atoms while keeping the new bond between surface Ge/Si and

adsorbed GeCl_3 molecule for dissociation as $\text{Ge}_2\text{H}_n\text{Cl}_{6-n}$ and $\text{Ge}_2\text{H}_n\text{Cl}_{6-n}$ or $\text{SiGeH}_m\text{Cl}_{6-m}$ ($n=1,2$ and $m=2,3$) to desorbed surface Ge/Si atoms. In **Fig. 4a**, red arrow shows the new Ge-Ge bond between surface Ge atom and adsorbed GeCl_3 molecule. As far as stronger bond forms between the Ge-Ge maintains the bond during the bond breaking with a nearby

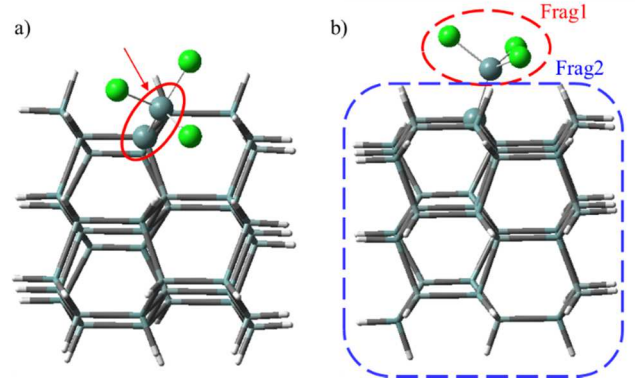


Fig. 4. a) Top view and b) side view of cluster adsorption model. To verify the interaction between Ge-Ge (red circle in a)), system is separated as Frag1 (Red dashed) and Frag2 (blue dashed).

atom. To verify the effect of chloride in the precursor, we divided the system into Frag 1 and Frag 2, shown in **Fig. 4b**.

By changing the precursors, we performed energy decomposition analysis (EDA) calculation and compared each precursor's frozen density, polarization, and charge transfer effect. We decomposed the interaction between Frag1 and Frag2 into frozen density, polarization, and charge transfer terms. As shown in **Table 2**, polarization and charge transfer are relatively small at the symmetric molecule (GeH_3 and GeCl_3), but the dispersion penalty is also small. Therefore, to sum up all the correlation term effects between two fragments, we can conclude that the interaction between surface Ge and GeCl_3 molecule is the strongest among four target precursors.

Table 2. Binding energy of $\text{GeCl}_n\text{H}_{3-n}$ precursors and surface Ge and orbital overlap occupancy between precursor adsorbed Ge and nearby Si.

| precursor | FRZ | POL | CT | Total |
|-------------------------|---------|----------|----------|----------------|
| GeH_3 | 486.615 | -442.282 | -95.128 | -50.794 |
| GeH_2Cl | 745.483 | -634.306 | -151.111 | -39.933 |
| GeHCl_2 | 713.832 | -621.077 | -135.657 | -42.903 |
| GeCl_3 | 245.724 | -249.606 | -66.480 | -70.362 |

III. COMPUTATIONAL DETAIL

The surface growing string method (sGSM) [9, 10] is used to verifying the transition state of the molecular reaction mechanism on the surface. For this study, the double-ended sGSM, user-defined initial and final structure using, is used with 11 node calculation. VASP package [11, 12] is used to run sGSM module and to optimize crystal structures. Perdew-Burke-Ernzerhof (PBE) [13] functional is used with $2 \times 2 \times 1$ Monkhorst-Pack k -point mesh. Pre-optimized surface structure of 50:50 SiGe (111) surface is obtained from the Materials Project database [14], and passivation H atoms are

included. The mid-layer of surfaces is fixed to reduce calculation cost, and all H atoms are relaxed. Gaussian 16 A.02 package [15] is used to describe detailed etch and adsorption structures. SiGe(111) surface is compactly modeled to Si₂₀Ge₁₉H₄₁ cluster. SiGe cluster is optimized with AM1 [16], semi-empirical method, and then Si and Ge atoms are fixed (drawn as a tube in **Fig. 4**) except all hydrogens and the adsorption target Ge atom and the connected Si atom (drawn as a ball and stick model in **Fig. 4**). Dissociation of a bond between Si-Ge by H₂ is described by QST2 model [17] with AM1 method. The optimized structure of GeH_nCl_{4-n} (n=0-4) on the SiGe surface is obtained by the same level, AM1, in the same program package. The transition state of Gas-phase dissociation of GeH_nCl_{4-n} (n=0-4) molecules are calculated by QST2 method using b3lyp functional [18] with 6-31G* level of basis set [19] in Gaussian 16 package.

Using the previously optimized Ge source adsorbed on the SiGe cluster model, energy decomposition analysis (EDA) [20] is performed in QChem 5.1 package [21]. To include the van der Waals interaction into EDA analysis, we used a wb97xd method [22] with a 6-31G* basis set for H, Si, and Cl atoms. For Ge, the Stuttgart-Bonn relativistic large core (SRLC) effective core potential (ECP) [23] is used with a related basis set. By EDA analysis, the binding energy is decomposed into:

$$\Delta E = \Delta E_{FRZ} + \Delta E_{POL} + \Delta E_{CT} \quad (1)$$

Herein, ΔE_{FRZ} is electrostatic interactions caused by geometrical complexity, ΔE_{POL} is polarization interaction caused by the distorting of the charge distributions of monomer, and ΔE_{CT} is the charge transfer energy of occupied molecule orbital of one fragment to the virtual orbital of another fragment.

IV. CONCLUSION

Temperature-dependent deposition and etch source property of GeCl₄ is theoretically investigated. Based on the activation energy difference, we could successfully explain why the GeCl₄ works as a deposition source at the high temperature while the same molecule works as an etchant at the low temperature on the SiGe (111) surface. For atomic layer deposition on SiGe, GeCl₄ dissociation to GeCl₂ at the gas phase is necessary. Just after the GeCl₂ formed, it spontaneously adsorbed on the SiGe surface until one layer filled with new Ge atoms. The reaction rate determining step of this process is that gas phase dissociation of GeCl₄ → GeCl₂ + Cl₂ requires 101 (kcal/mol), higher than 1000 (°C).

To etch the SiGe surface, GeCl₄ works as an etchant without the formulation change. When the GeCl₄ molecule is adsorbed to surface Ge/Si atom, abundant H₂ in the reaction system dissociates the bond between Ge/Si and neighbor atoms. As a result, GeCl₄ etches SiGe surface as Ge₂H₂Cl₄ or GeSiH₂Cl₄ molecules. H₂ induced bond dissociation requires only 54.0 (kcal/mol) and is much lower than growth process

activation energy. Therefore, the deposition proceeds with higher activation energy, 101 (kcal/mol), and a more stable final product, -19.6 (kcal/mol), and etch process is proceeding with lower activation energy, 65.8 (kcal/mol), and the less stable final product, -9.6 (kcal/mol). Based on the thermodynamic equilibrium of the reaction, deposition proceeds at a higher temperature, while etching proceeds at a lower temperature.

We can expand our study into designing a better Ge-based precursor to deposition and etch. As we mentioned above, lower the GeH_nCl_{4-n} → GeH_mCl_{2-m} (n = 0-4 and m= 0,1,2) dissociation energy barrier, reaction barrier of rate determining step is lowered and overall reaction will be proceed faster. Otherwise, to enforce the etch property, GeH_nCl_{4-n} sources should be more tightly bound to surface atoms and remained their bond during the H₂ induced dissociation with neighboring atoms. GeCl₃ shows the tightest bond in our calculation, and GeH₃, GeH₂Cl, and GeHCl₂ follow behind the GeCl₃. This result implies that until now, GeCl₄ might be the best etchant. As shown in EDA analysis, we could conclude that symmetric molecule shows better etchant performance than asymmetric molecules.

We have presented here, for the first time to our knowledge, a theoretical analysis for the temperature-dependent deposition/etch property. We could design and suggest novel deposition/etch sources for low-temperature processes based on this analysis. Our calculation successfully supports the experimental observation and can be applied to any surface-precursor interaction system. Also, in the computational view, we could check the GSM method's potential to describe the stepwise surface-precursor reaction and this is the first paper to see the stepwise reaction using the GSM method.

REFERENCES

- [1] K. Mrihiro, "Research and Development History of Three-Dimensional Integration Technology". Three-Dimensional Integration of Semiconductors: Processing, Materials, and Applications. Springer. pp. 15–8. (2015)
- [2] V. Subramaniana "Multiple gate field-effect transistors for future CMOS technologies" IETE Technical Review. **27**, 446–454 (2010).
- [3] K. J. Miller and M. J. Grieco, "A Study of HCl-H₂ and GeCl₄-H₂ Etching of Germanium Substrates for Epitaxial Deposition" J. Electrochem. Soc., **111**, 1099 (1964)
- [4] H. Ishii and Y. Takahashi, "Growth and Etching of Germanium Films by Chemical Vapor Deposition in a GeCl₄-H₂ Gas System" J. Electrochem. Soc.: Solid-state science and technology, **135**, 1539 (1988)
- [5] J.-S. Park, M. Curtin, C. Major, S. Bengtson, M. Carroll, and A. Lochtefeld, "Reduced-Pressure chemical Vapor Deposition of Epitaxial Ge Films on Si(001) Substrates Using GeCl₄" Electrochemical and Solid-State Letters, **10**, H313 (2007)
- [6] M. Bauer and S. G. Thomas, "Low temperature catalyst enhanced etch process with high etch rate selectivity for amorphous silicon based alloys over single-crystalline silicon based alloys" Thin Solid Films, **520**, 3139 (2012)
- [7] Z. Zhang, Y. Huang, G. Tetiker, S. Sriraman, A. Paterson, R. Faller, "Computational Modelling of Atomic Layer Etching of Chlorinated Germanium Surfaces by Argon" Phys. Chem. Chem. Phys., **21**, 5898 (2019)
- [8] R. Becerra and R. Walsh "Thermochemistry of germanium and organogermanium compounds" Phys. Chem. Chem. Phys., **21**, 988 (2019)

- [9] P. M. Zimmerman, "Growing string method with interpolation and optimization in internal coordinates: Method and examples" *Journal of Chemical Physics*, **138**, 184102 (2013)
- [10] P. M. Zimmerman, "Reliable Transition State Searches Integrated with the Growing String Method" *Journal of Chemical Theory and Computation*, **9**, 3043-3050 (2013)
- [11] G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set" *Phys. Rev. B* **54**, 11169 (1996).
- [12] G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method", *Phys. Rev.* **59**, 1758 (1999).
- [13] J. P. Perdew, K. Burke, M. Ernzerhof, "Generalized gradient approximation made simple" *Phys. Rev. Lett.*, **77**, 3865-3868 (1996)
- [14] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, "The Materials Project: A materials genome approach to accelerating materials innovation" *APL Materials*, **1**, 011002 (2013)
- [15] M. J. Frisch et al., *Gaussian 16*, Revision A.01, Gaussian, Inc., Wallingford CT (2016)
- [16] E. Anders, R. Koch, and P. Freunsch, "Optimization and application of lithium parameters for PM3" *J. Comp. Chem.*, **14**, 1301-1312 (1993)
- [17] C. Peng and H. B. Schlegel, "Combining Synchronous Transit and Quasi-Newton Methods for Finding Transition States" *Israel J. Chem.*, **33**, 449-454 (1993).
- [18] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, "Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields" *J. Phys. Chem.* **98**, 11623-11627 (1994).
- [19] R. Ditchfield, W. J. Hehre, J. A. Pople, "Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules" *J. Chem. Phys.* **54**, 724-728 (1971).
- [20] R. J. Azar, P. R. Horn, E. J. Sundstrom, and M. Head-Gordon. "Polarization contributions to intermolecular interactions revisited with fragment electric-field response functions" *J. Chem. Phys.*, 138084102 (2013).
- [21] Y. Shao et al., "Advances in molecular quantum chemistry contained in the Q-Chem 4 program package" *Mol. Phys.* **113**, 184-215 (2015)
- [22] J.-D. Chai and M. Head-Gordon, "Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections" *Phys. Chem. Chem. Phys.*, **10**, 6615-6620 (2008).
- [23] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, "Ab initio energy-adjusted pseudopotentials for elements of groups 13-17" *Mol. Phys.* **80**, 1431 (1993).