Adsorption Reactions of Trimethylgallium and Arsine on H/Si(100)-2x1 Surface

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The adsorptions of trimethygallium (TMG) and arsine (AsH_3) on H/Si(100)-2x1 surface were theoretically investigated. In the case of TMG adsorption, methane loss reaction, surface methylation, hydrogen loss reaction and ring closing reaction channels were found. The mechanism of AsH_3 adsorption on the surface was also identified. Among these, the methane loss reaction depositing $-Ga(CH_3)_2$ was found to be the major channel due to its low barrier height and the large exothermicity. The surface methylation reaction is the second most favorable channel. In contrast, arsine turned out to be less reactive on the surface, implying that Arsine surface reaction would be the rate limiting step in the overall ALD process.

Key Words: Silicon surface, ALD process, Trimethylgallium, Arsine, Mechanism

Introduction

Atomic layer deposition (ALD) is a film deposition technique that is based on the sequential use of self-terminating gas-solid reactions.[1] It is usually adopted when precise control of thickness and conformal structure are required[2,3,4] The GaAs thin film on Si substrates has attracted much attention for the opto-electronic applications.[5,6,7] While GaAs film has high electron mobility and wide bandgap, silicon substrate has large area, less brittle property, and high thermal conductivity.[8] The epitaxial growth of GaAs film on Si substrate is recognized as a way to combine the best characteristics of both materials.

Arsine is the most commonly used as source for the growth of GaAs on Si. Kipp *et al.*[9] studied the adsorption and the decomposition of arsine molecule on bare Si(001)-2x1 surface by AES, LEED, XPS and STM techniques. They reported that, (i) below 100 °C the arsine dissociatively adsorbs with the arsenic saturation coverage of 20%; (ii) between 100 °C and 400 °C the saturation coverage is 25% with the formation of As–As dimers; (iii) above 400 °C the hydrogen starts to desorbs; (iv) all hydrogen is desorbed resulting in nearly 100% As coverage at 575 °C and (v) near 650 °C the As desorption rate becomes significant. Miotto *et al.*,[10] McDonell *et al.*,[11] and Northrup[12] theoretically showed that the AsH_3 molecule adsorbs molecularly on the electrophilic surface Si atom and then dissociates into AsH_2 and H.

Among various precursors, $GaMe_3$ (TMG) is the prominent precursor used in molecular beam epitaxy (MBE),[13,14] vapor phase epitaxy (VPE),[15] liquid phase epitaxy (LPE),[16] ion beam epitaxy,[17] pulse laser deposition (PLD)[18,19] and metal-organic chemical vapor deposition (MOCVD).[20] Cadwell and Masel[21] studied the adsorption and decomposition of TMG on clean Si(100) with temperature desorption spectroscopy (TDS) and Auger electron spectroscopy (AES). They reported that TDS experiment produces methane (370 K, 500 K), hydrogen (800 K), and atomic gallium (970 K) at low coverage. At high coverage some additional products like ethylene (570 K, 740 K), dimethylgallium (350 - 550 K), monomethylgallium, and methyl species (770 K) were also produced. However, the atomistic details of such surface decomposition reactions are not available.

In order to obtain better understanding on the growth mechanisms of GaAs film, the mechanistic aspects of individual surface chemical reactions of Ga and As precursors are critical.[22] In this letter, the initial surface reactions of $GaMe_3$ (TMG) and AsH_3 precursors on H/Si(100)-2x1 surface were theoretically investigated in order to obtain the detailed potential energy surfaces. As compared to bare and OH terminated silicon surfaces, the frequently used H-passivated Si(100)-2x1 surface provides chemically less reactive environments.

Computational Details

Electronic structure calculations based on second order Moller-Plesset Perturbation theory (MP2) were performed on the QM part of our cluster models. Only singlet spin state was considered in this letter. All calculations reported here were performed with the GAMESS[23] (general atomic and molecular electronic structure system) electronic structure program. All-electron 6-31(d)[24] basis set was used throughout this work. Minimum energy reaction paths were determined by first optimizing the geometries of the minimum and the transition states. The Hessian matrix (matrix of energy second derivatives) was computed and diagonalized for all stationery points to characterize them. Intrinsic reaction coordinate (IRC) calculations, using the Gonzalez-Schlegel second order method,[25] were conducted to verify that each saddle point connects minima of interest.

In order to take into account of the surface size effects, a hybrid quantum mechanics/molecular mechanics (QM/MM) method called SIMOMM was adopted.[26] The chemically inactive region of the system is calculated by computationally inexpensive force field methods, while the chemically active part is treated by quantum mechanics. In this work, the QM/MM models were designed such that $AsSi_9H_{17}$ and $GaC_3Si_9H_{23}$ quantum regions are embedded in $AsSi_{48}H_{45}$ and $GaC_3Si_{48}H_{51}$

clusters for arsine and $GaMe_3$ studies, respectively. These two models have one and three surface dimer(s) in the QM and MM regions, respectively. MM3[27] parameters were used for the molecular mechanics part of the computations. All of the computations were done without imposing symmetry unless otherwise specified.

Results and Discussion

AsH_3 precursor on H/Si(100)-2x1. The detailed reaction pathway of AsH_3 adsorptions on H/Si(100)-2x1 surface is presented in Figure 1. The initial approach of the AsH_3 molecule to the surface forms a reactant like intermediate **I1** with the exothermic enthalpy of 9.4 kcal/mol. The transition state **TS1**, where the As1 is making a bond with the Si7, and the H5 is migrating from Si7 to H3, connects the initial intermediate **I1** and another intermediate **I2** with the overall barrier height of 52.2 kcal/mol. The resulted intermediate **I2** and the final product **P1** are more stable than the reactant **R1** by 22.6 and 21.1 kcal/mol, respectively. Mechanistically, AsH_3 on bare Si(100)-2x1 surface dissociatively adsorbs on surface. However, AsH_3 on H-terminated Si(100)-2x1 produces hydrogen molecule. The corresponding adsorption energy of AsH_3 on bare Si(100)-2x1 surface is 13.0 kcal/mol exothermic by passing the barrier height of 9.0 kcal/mol.[16] The higher reaction barrier on H-terminated surface is expected due to the surface Si-H, which must be broken in the course of adsorptions. Although the H-passivated silicon surface reduces the kinetic reactivity quite significantly as compared to the bare Si(100)-2x1 surface, interestingly it produces thermodynamically more stable product. In short, the overall reaction is thermodynamically favorable. However the large reaction barrier due to the H-passivated surface makes this channel kinetically less accessible.

TMG precursor on H/Si(100)-2x1. According to our calculations, four reaction pathways were found in the initial adsorptions of the *tri*-methylgallium (TMG) on the H/Si (100)-2x1 surface, which are discussed in order. Note that the asterisks indicate the surface species.

Methane loss reaction: Si–H* + TMG → Si–$Ga(CH_3)_2$* + CH_4. Methane loss channel yields a surface Si–Ga bond and a methane molecule. The detailed reaction pathway is presented in Figure 2. The initial TMG approach to the surface forms a reactant like complex **I3** by releasing the exothermic energy of 12.7 kcal/mol. As compared to the previous As1–H5 interaction (see **I1**), the Ga–H interaction is stronger by 3.3 kcal/mol. The distance of Ga1–H7 is calculated to be 2.175 Å, which is 0.324 Å shorter than that of As–H. The transition state **TS2** connects the initial complex **I3** and the second complex **I4** with the overall barrier height of 15.6 kcal/mol, which is found to be 8.4 and 12.5 kcal/mol lower than the corresponding values of DMAI (Dimethylaluminum Isopropoxide)[28] and TMA (trimethylaluminum)[29] adsorptions, respectively. Therefore, the methane releasing from Ga precursor is easier than

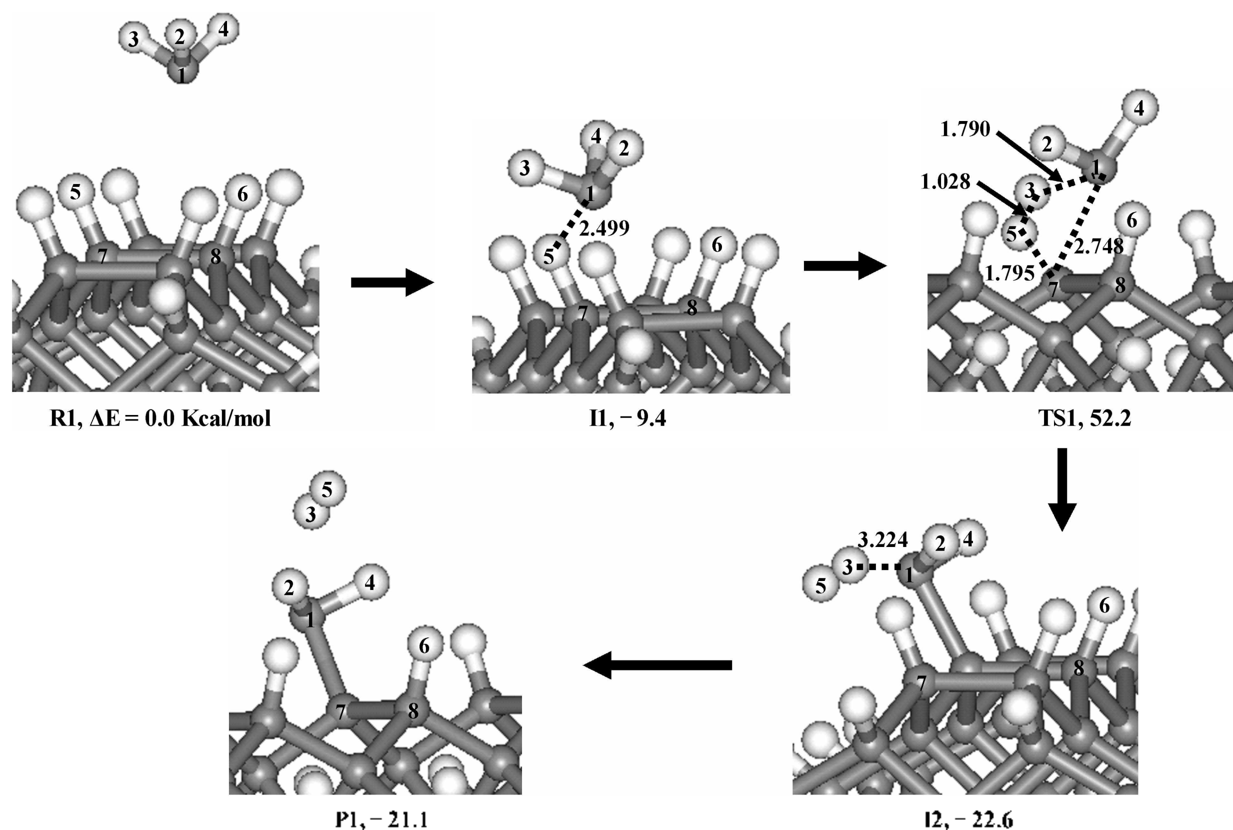

Figure 1. Stationary points along the initial arsine adsorption on H/Si(100)-2x1 surface as calculated with SIMOMM:MP2/6-31G(d). The bond distances are in Angstrom and the energies are in kcal/mol.

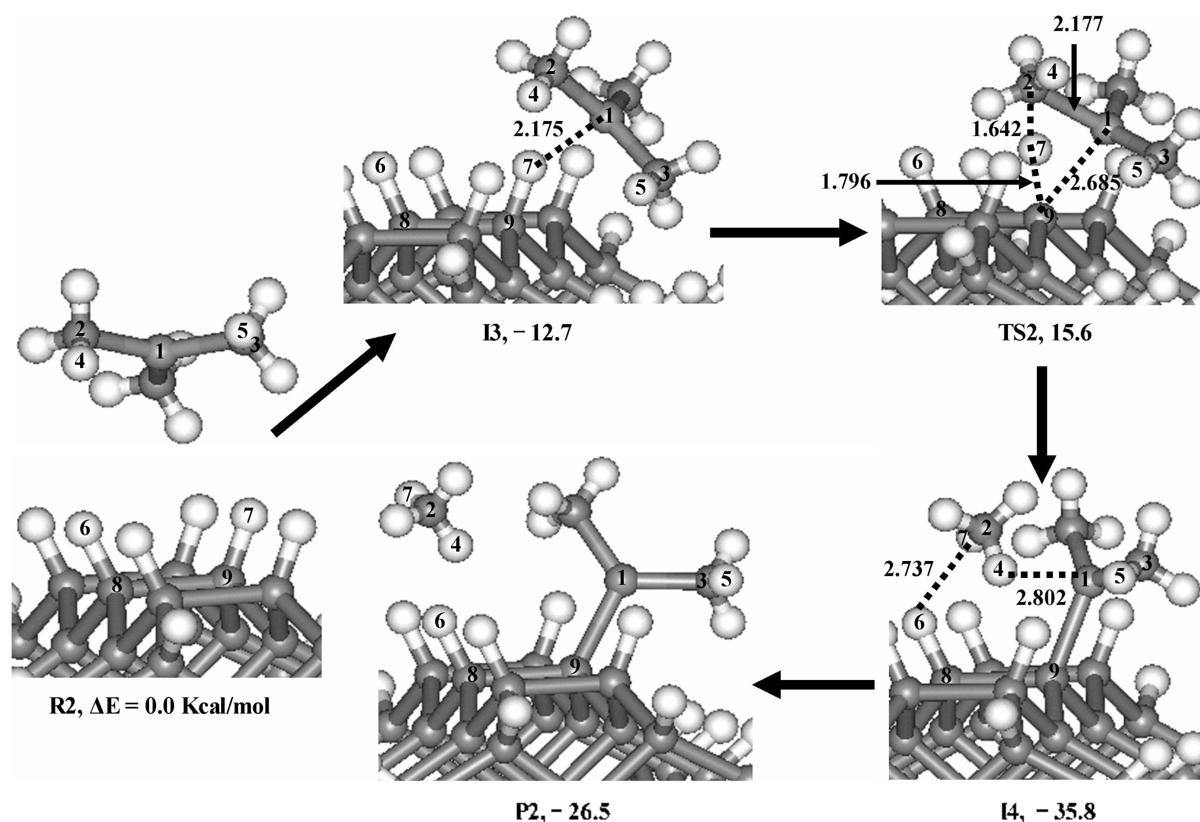

Figure 2. Stationary points along the methane loss reaction of TMG on H/Si(100)-2x1 surface as calculated with SIMOMM:MP2/6-31G(d). The bond distances are in Angstrom and the energies are in kcal/mol.

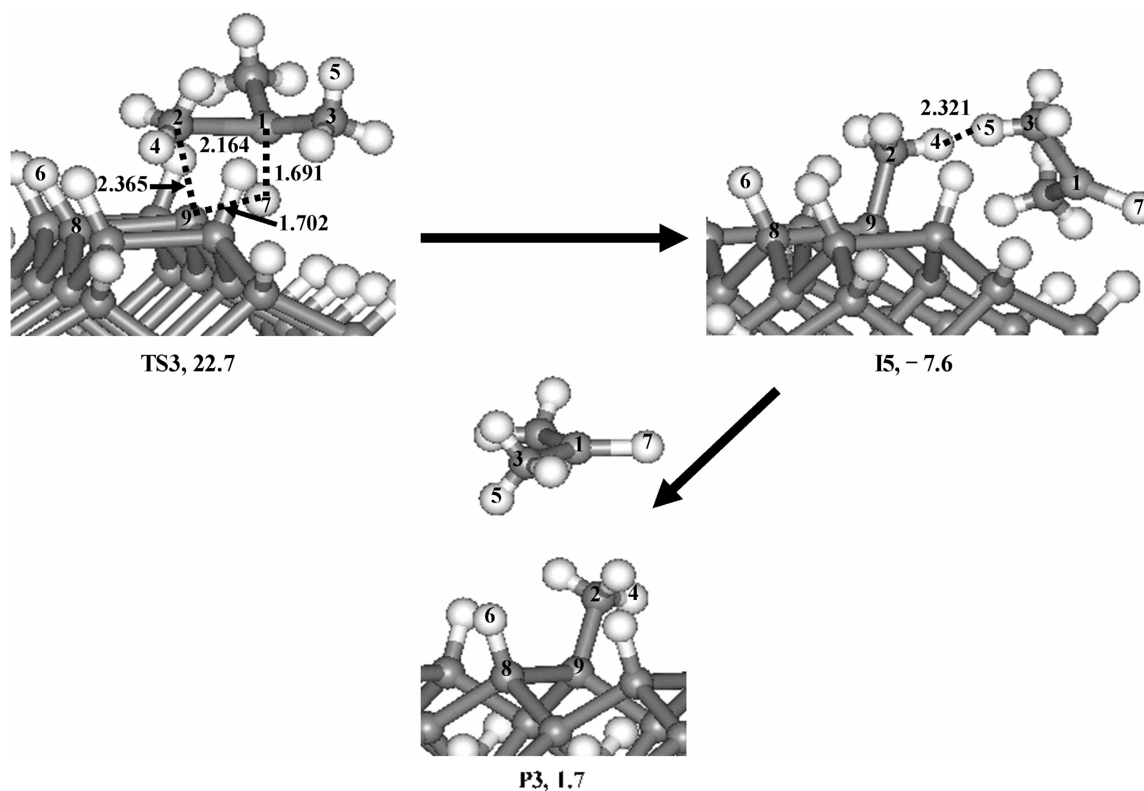

Figure 3. Stationary points along the methylation of TMG on H/Si(100)-2x1 surface as calculated with SIMOMM:MP2/6-31G(d). The bond distances are in Angstrom and the energies are in kcal/mol.

those from Al precursors. In addition to this, the methane loss channel is kinetically also more favorable than the AsH_3 adsorption reaction of the previous section. The electron rich methyl substituent of TMG can stabilize the transition state more than the hydrogens of Arsine. The **I4** is an intermediate where the leaving methane is trapped due to the interaction between the surface Ga1 and H4. The complete methane desorption is accomplished with the endothermic energy of 9.3 kcal/mol from the intermediate **I4**, indicating that the methane is strongly trapped. The overall reaction is exothermic by 26.5 kcal/mol. A direct comparison with experiment[21] is not possible, since earlier experiment was done on bare silicon surface. However, our predicted low reaction barrier of methane loss channel is consistent with experiment[21] in which methane is produced at 370 K and 500 K.

Surface methylation: Si–H* + TMG → Si–CH_3* + $HGa(CH_3)_2$. The surface methylation forms a surface Si–C bond. The starting point of this channel is the intermediate **I3**. The initial TMG approach to the surface as shown in the transition state **TS3**, transfers a methyl group to the surface and at the same time abstracts the H7 making a four-membered transition state. (see Figure 3) As a result of this concerted conformation, the **TS3** connects the **I3** and another intermediate **I5** with the barrier height of 22.7 kcal/mol, which is 7.1 kcal/mol higher than that of the methane loss reaction. The lower reaction barrier of methane loss channel can be attributed to the more strong Ga–Si interaction as compared to the C–Si interaction in the transition state, which would more stabilize **TS2**. Furthermore, the overall reaction is endothermic by 1.7 kcal/mol. Therefore, the surface methylation is both thermodynamically and kinetically less favorable than the methane loss reaction. However, this reaction barrier is still lower than that of Arsine adsorption channel, indicating that methylation can also easily occur. In fact, experiment showed that dimethylgallium which may be the product of surface methylation is produced at 350 - 550 K[21], which is consistent with our conclusions.

Hydrogen loss reaction: Si–H* + TMG → Si–CH_2–$Ga(CH_3)_2$* + H_2. Like the surface methylation, the hydrogen loss reaction yields a surface Si–C bond (Figure 4). Again the starting point of this channel is the intermediate **I3**. The transition state **TS4** connects the **I3** and the product complex **I6** with the barrier height of 102.5 kcal/mol, which is 10.2 kcal/mol higher than the relevant barrier of TMA adsorption. In the transition state **TS4**, C2 of TMG is making a bond with the surface Si9 and is releasing H4. Even though the overall reaction enthalpy is calculated to be 10.2 kcal/mol exothermic, it is predicted that the large barrier prohibits this channel from being activated under normal condition. Experiment[21] done on bare silicon surface also showed that hydrogen is observed at higher temperature than the other products.

Ring closing reaction/Second methane loss reaction: The most stable surface product **P2** can further undergo a ring closing reaction as shown in Figure 5. In order to study this

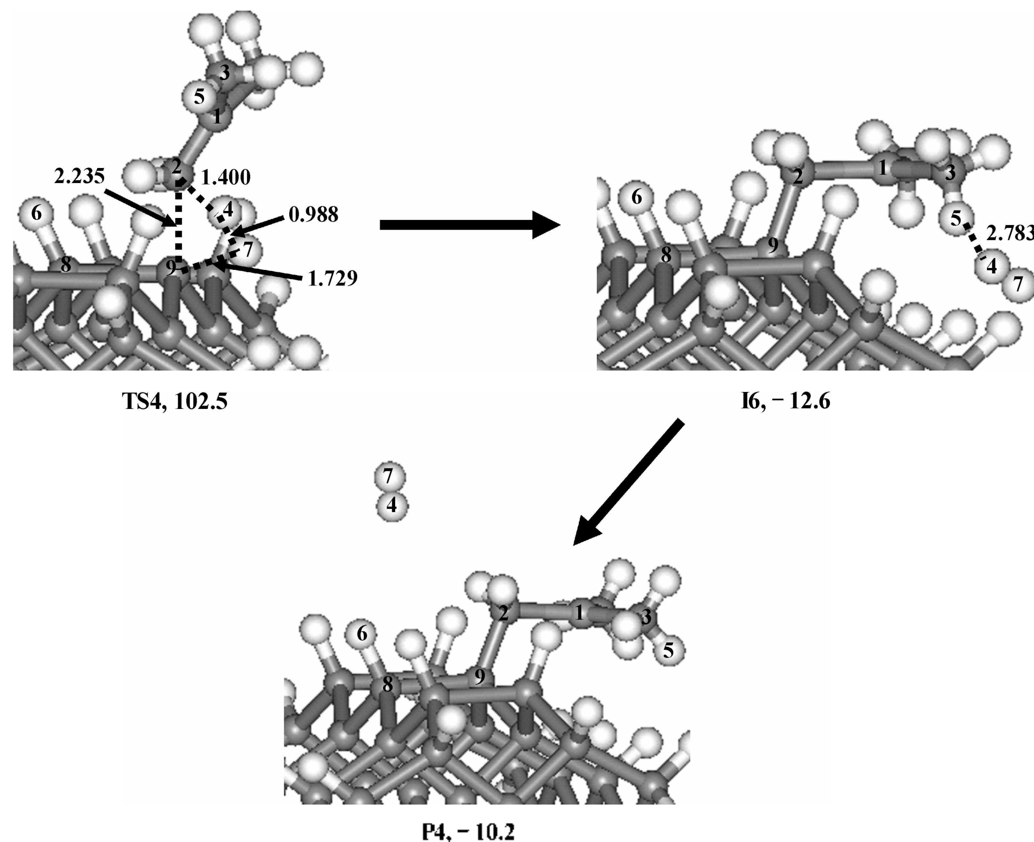

Figure 4. Stationary points along the hydrogen loss reaction of TMG on H/Si(100)-2x1 surface as calculated with SIMOMM:MP2/6-31G(d). The bond distances are in Angstrom and the energies are in kcal/mol.

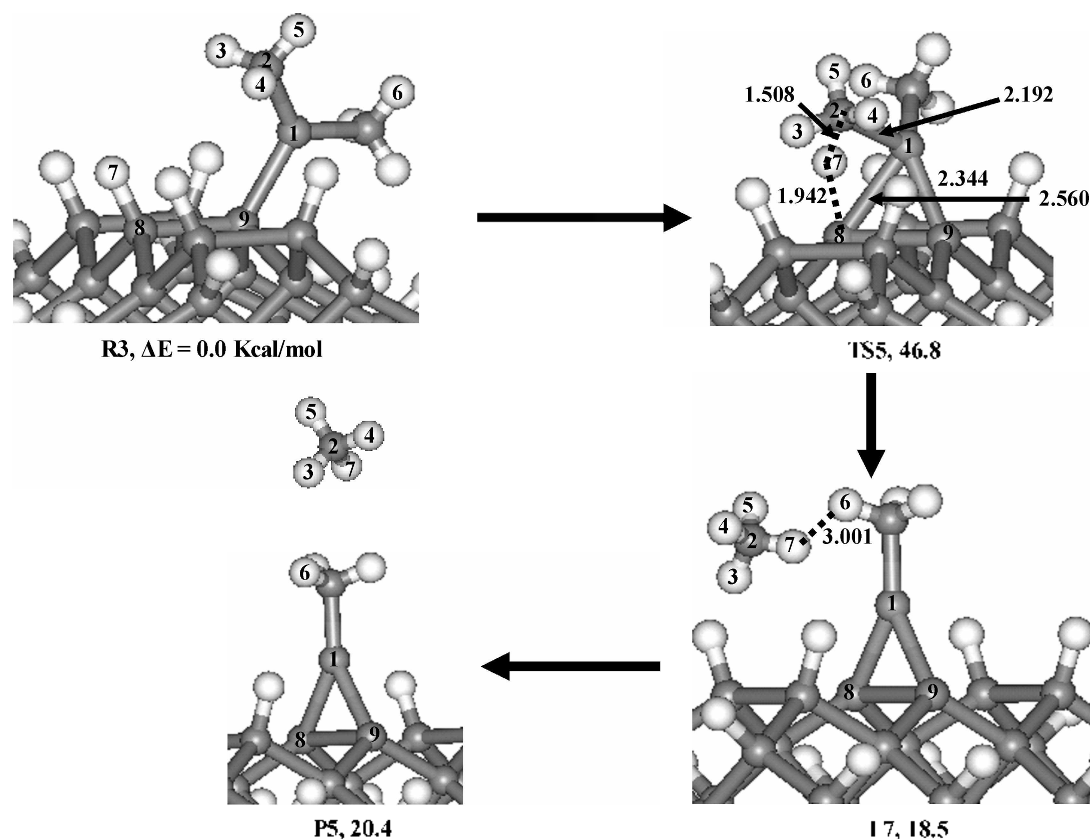

Figure 5. Stationary points along the ring closing reaction of TMG on H/Si(100)-2x1 surface as calculated with SIMOMM:MP2/6-31G(d). The bond distances are in Angstrom and the energies are in kcal/mol.

part of potential energy surface, a new reactant **R3**, which is the **P2** without CH_4 is considered. All the relative energies are calculated with respect to the **R3**. The ring closing transition state **TS5** connects the **R3** and the product complex **I7**. During the reaction, Ga1 interacts with Si8 while C2 abstracts H7 from the surface with the energy barrier of 46.8 kcal/mol. The H7 of leaving CH_4 is making a weak interaction with H6 in **I7**. The weakly bound CH_4 desorbs yielding the final product **P5** with the dissociation energy of 1.9 kcal/mol. The barrier height of the presently discussed channel is not as prohibitively large as the hydrogen loss reaction. Further experimental studies are expected for the existence of this product.

Conclusions

The surface reaction pathways of trimethylgallium (TMG) and Arsine (AsH_3) on H/Si(100)-2x1 surface were theoretically investigated. A large reaction barrier was found in the case of AsH_3 adsorption. Therefore, it would the rate limiting reaction of the overall ALD process. Four reaction channels were found in the TMG adsorption, which are the methane loss reaction, the methylation, the hydrogen loss reaction and the ring closing reaction channels. Among these, the methane loss reaction is predicted to be the major channel due to the low barrier height and large exothermicity. The surface methylation channel is thermodynamically the second most accessible channel. Even though hydrogen loss reaction gives a kinetically stable product than the surface methylation reaction, a large barrier height prohibits this channel from being activated under normal conditions. It is shown that from the product of the most probable methane loss reaction, a subsequent ring closing reaction would be possible. Our theoretical predictions are consistent with experiments done on bare silicon surface.

In summary, the methane loss reaction and the surface methylation by TMG are the two most probable surface reactions in the TMG adsorption on H-terminated surface. And it is predicted that the arsine adsorption is the rate limiting step in the overall ALD process.

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