Quantum chemical calculation for CVD process of GeSbTe

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1 Introduction

It has been long known that the ab initio calculation of electronic structure of atomic and molecular system based on quantum chemistry can be a powerful tool to analyze details of chemical reactions. In this paper, we apply the quantum chemical calculation to chemical vapor deposition (CVD) process of GeSbTe (GST) alloys which is used for phase change memory (PCM).

PCM is one of the most promising candidates for the next-generation memory device and GST is widely used as the PCM material. So far, GST thin fils are deposited by physical vapor deposition such as sputtering and pulsed laser deposition. However, CVD has many advantages and considered to be necessary for future PCM applications. The CVD process for GST is relatively new field of research and there remains much things which are not known. Therefore, to establish more efficient CVD process, it would be useful to investigate the details of the process by using quantum chemical calculation together with the experiment.

In this paper, we assume $GeH_3(tBu)$, $Sb(iPr)_3$ and $Te(iPr)_2$ as precursors [1] and study gas phase reactions among them (and carrier gas H_2) by quantum chemical calculation.

2 Calculation Method and Results

All the calculations are performed by the DFT (density functional theory) method with the B3LYP functional [3]. The Gaussian 09 package [2] is used for the calculations. The D95(d,p) basis set [4] is used for the H atoms, the 6-31G(d) basis set is used for the C atoms and the LanL2DZ effective core potential [5] is used for the Ge, Sb and Te atoms.

First of all, we show the optimized structures of the precursors in Fig. 1. We then investigate how these structures decompose by itself or by reacting with the carrier gas, the H_2 molecules. As for the Ge precursor, we can imagine the following reaction paths: (i-1) $GeH_3(tBu) \rightarrow GeH_3 + C_4H_9$, (i-2) $GeH_3(tBu) + H_2 \rightarrow GeH_4 + C_4H_{10}$ and (i-3) $GeH_3(tBu) \rightarrow GeH_2 + C_4H_{10}$. The reaction (i-1) proceeds without energy barrier and is endothermic by 2.456 eV. The reaction (i-2) is exothermic by 0.561 eV with the energy barrier of 3.534 eV. The reaction (i-3) is endothermic by 1.121 eV with the energy barrier of 2.392 eV. These paths are summarized in Fig. 2. As for the Sb precursor, we first consider the reactions that the isopropyl groups are removed by reacting with H_2, namely (ii-2) $Sb(iPr)_3 + H_2 \rightarrow SbH(iPr)_2 + C_3H_8$ and (ii-2) $SbH(iPr)_2 + H_2 \rightarrow SbH_2(iPr) + C_3H_8$. They are endothermic by 0.643 eV and 0.577 eV with the barriers of 1.858 eV and 1.968 eV respectively. Then, the $SbH_2(iPr)$ molecule may decompose by the following reactions: (ii-3) $SbH_2(iPr) \rightarrow SbH_2 + C_3H_7$ and (ii-4) $SbH_2(iPr) \rightarrow SbH + C_3H_8$. The reaction (ii-3) proceeds without the barrier and is endothermic by 1.787 eV. The reaction (ii-4) is endothermic by 1.544 eV with the barrier of 1.817 eV. We also investigate the decomposition into radicals: (ii-5) $Sb(iPr)_3 \rightarrow Sb(iPr)_2 + C_3H_7$ and (ii-6) $SbH(iPr)_2 \rightarrow SbH(iPr) + C_3H_7$. The energy needed for these reactions are 1.797 eV and 1.821 eV respectively which are somewhat smaller than the barriers for the reactions (ii-1) and (ii-2). As for the Te precursor, we show the results for the reactions as regards TeH(iPr): (iii-1) $TeH(iPr) + H_2 \rightarrow TeH_2 + C_3H_8$, (iii-2) $TeH(iPr) \rightarrow TeH + C_3H_7$ and (iii-3) $TeH(iPr) \rightarrow Te + C_3H_8$. The reaction (iii-1) is exothermic by 0.592 eV with the energy barrier of 4.025 eV. The energy needed for the decomposition processes (iii-2) and (iii-3) are much lower with 1.931 eV and 1.966 eV respectively.

We next examine the optimized structures and stabilization energy of possible dimers formed from the molecules which are derived from the precursors through the reactions such as described above. The structures of dimers which are derived from pairs of Ge precursors are shown in Fig. 3. Those from Sb pairs are shown in Fig. 4 and Te pairs in Fig. 5. The dimers which stem from different kinds of precursors are shown in Figs. 6, 7 and 8, respectively for combinations of Ge-Sb, Ge-Te and Sb-Te. Let us focus on the Ge-Ge dimers and discuss their stabilization energy. The stabilization energy for the reactions $2GeH_2(tBu) \rightarrow (GeH_2(tBu))_2$ is 2.593 eV, $GeH_3 + GeH_2(tBu) \rightarrow GeH_3GeH_2(tBu)$ is 2.596 eV and $2GeH_3 \rightarrow (GeH_3)_2$ is 2.584 eV. Remind that the energy needed for the reaction (i-1) is 2.456 eV which is smaller than the stabilization energy of the dimer formation. This implies that GeH_3 tends to form the dimers rather than goes back to the original precursor.

3 Conclusion

We have applied quantum chemical calculation to the possible reactions of the precursors for the CVD process of GST alloys. Some likely reaction pathways are suggested regarding decomposition of the precursors and dimer formations from them. The whole picture of the process would be revealed by more computational investigation and comparison of the results with experimental data.

Acknowledgment

This research work is supported by the national project “Green Nanoelectronics”.

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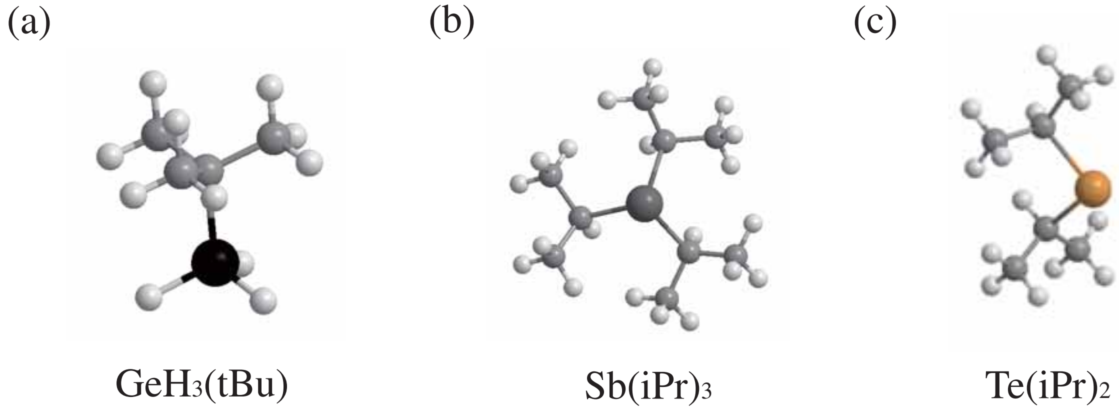


Figure 1: The optimized structures of (a) Ge precursor: GeH_3(tBu), (b) Sb precursor: $Sb(iPr)_3$ and (c) Te precursor: $Te(iPr)_2$.

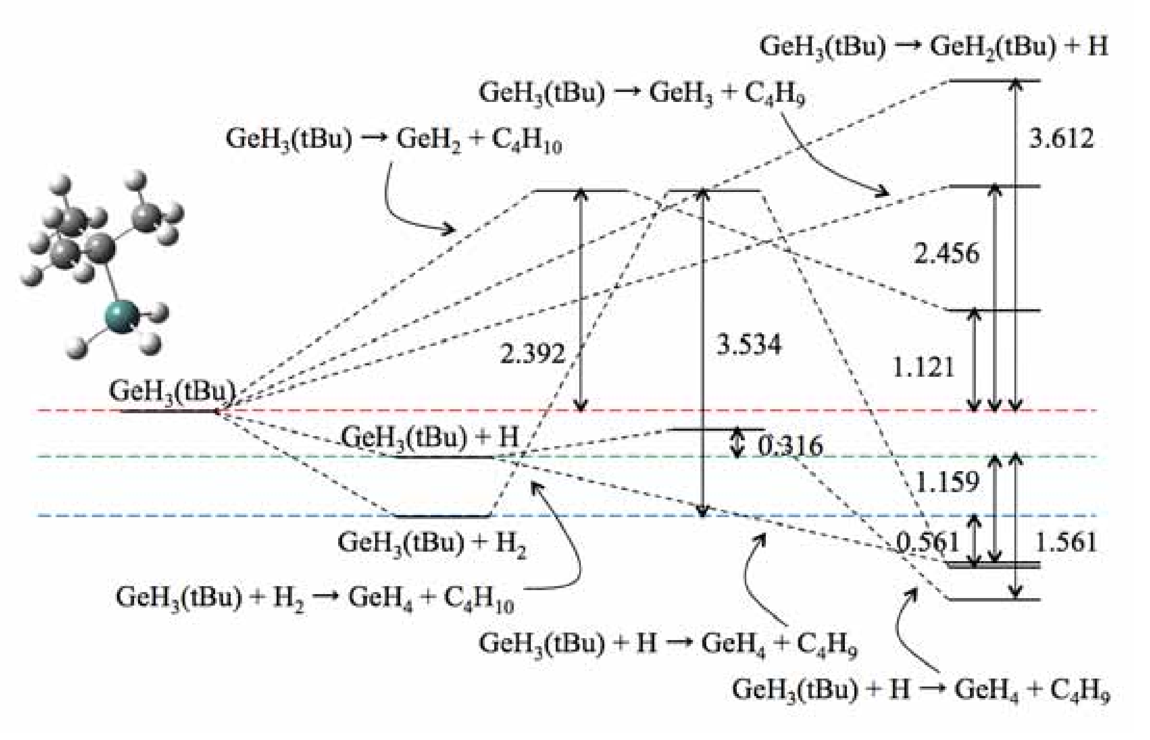
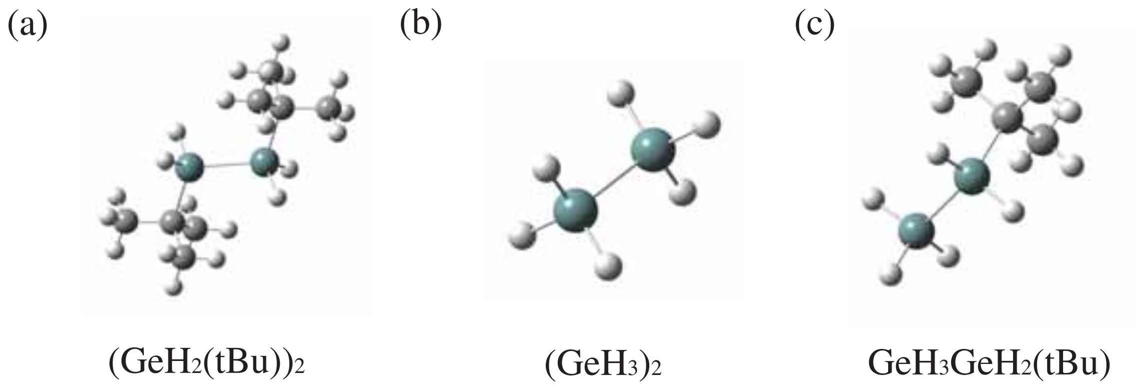
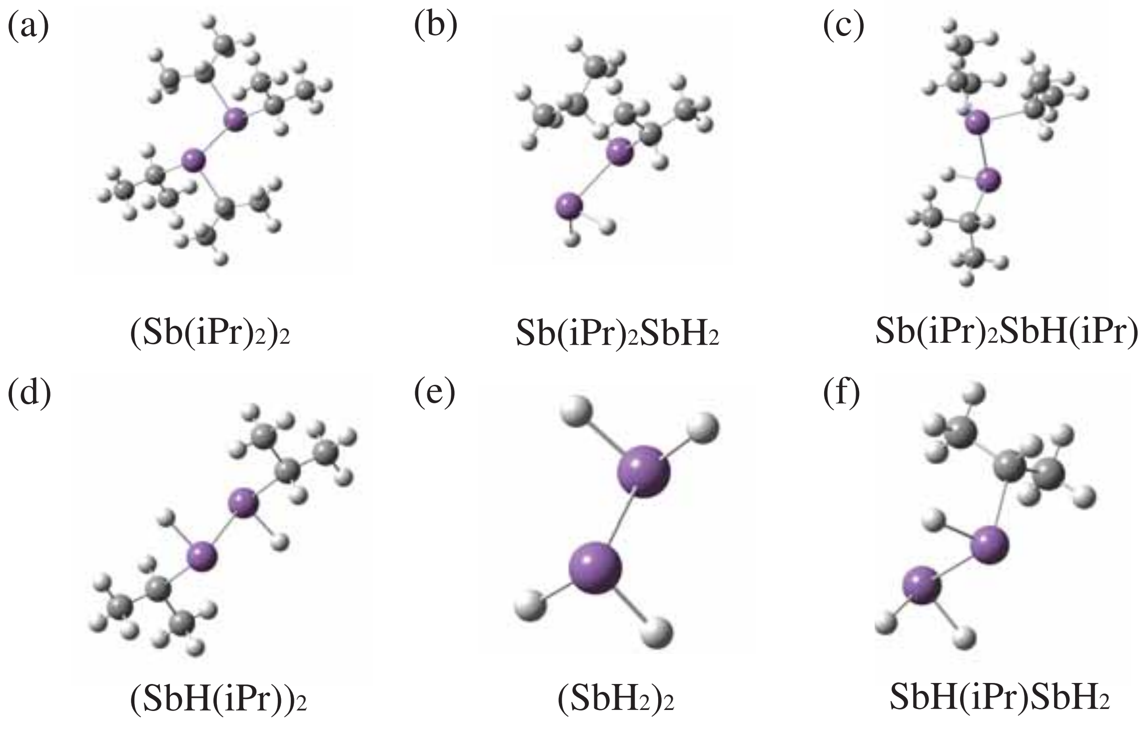


Figure 2: The possible reaction pathways as regards Ge precursor GeH_3(tBu). The energy is expressed in units of eV.



(a) $(GeH_2(tBu))_2$ (b) $(GeH_3)_2$ (c) $GeH_3GeH_2(tBu)$

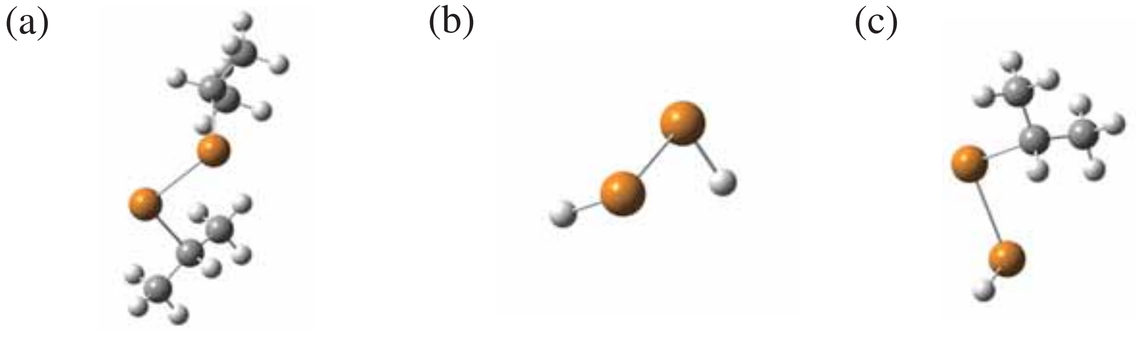
Figure 3: The optimized structures for Ge-Ge dimers.



(a) $(Sb(iPr)_2)_2$ (b) $Sb(iPr)_2SbH_2$ (c) $Sb(iPr)_2SbH(iPr)$

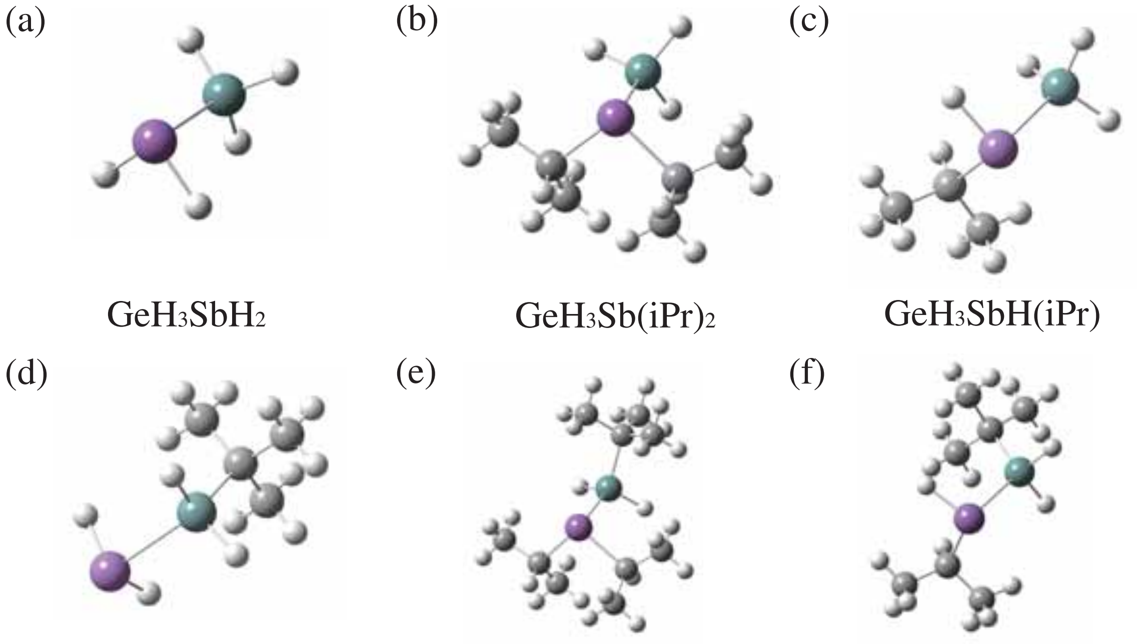
(d) $(SbH(iPr))_2$ (e) $(SbH_2)_2$ (f) $SbH(iPr)SbH_2$

Figure 4: The optimized structures for Sb-Sb dimers.



(a) $(Te(iPr))_2$ (b) $(TeH)_2$ (c) $Te(iPr)TeH$

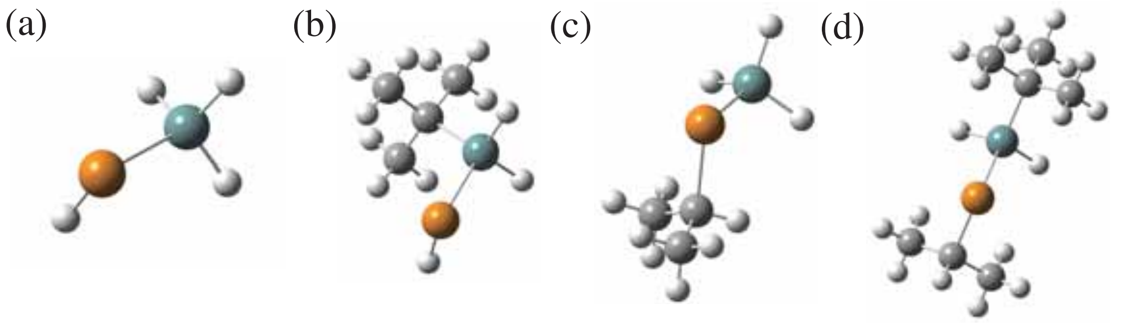
Figure 5: The optimized structures for Te-Te dimers.



(a) GeH_3SbH_2 (b) $GeH_3Sb(iPr)_2$ (c) $GeH_3SbH(iPr)$

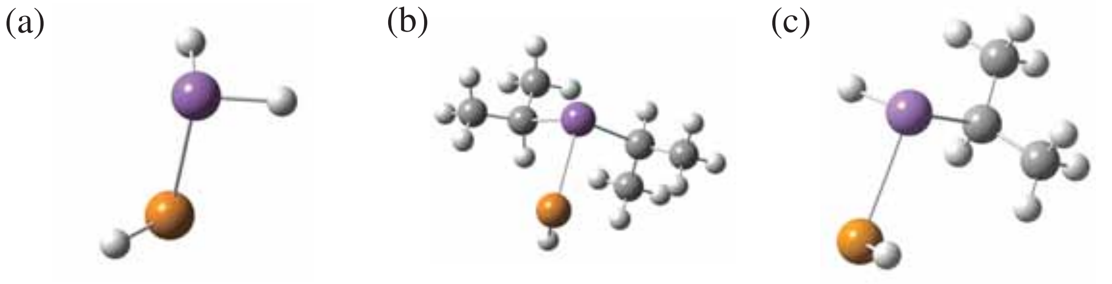
(d) $GeH_2(tBu)SbH_2$ (e) $GeH_2(tBu)Sb(iPr)_2$ (f) $GeH_2(tBu)SbH(iPr)$

Figure 6: The optimized structures for Ge-Sb dimers.



GeH_3TeH $GeH_2(tBu)TeH$ $GeH_3Te(iPr)$ $GeH_2(tBu)Te(iPr)$

Figure 7: The optimized structures for Ge-Te dimers.



SbH_2TeH $Sb(iPr)_2TeH$ $SbH(iPr)TeH$

$SbH_2Te(iPr)$ $Sb(iPr)_2Te(iPr)$ $SbH(iPr)Te(iPr)$

Figure 8: The optimized structures for Sb-Te dimers.