First principles calculations for growth condition for CVD process of GeSbTe

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Introduction

In this paper, the condition of steady growth of GeSbTe (GST) crystal by chemical vapor deposition (CVD) process is investigated by first principles calculations.

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 computational approach together with the experiment. Many researches have reported that the deposited film composition and structure are significantly dependent on deposition temperature, pressure, precursors, substrates, and so on [1-3]. Accrdingly, gas-phase and/or surface reactions are expected to play important role for CVD process.

In our previous report, with assuming $\text{GeH}_3(\text{tBu})$, $\text{Sb}(\text{iPr})_3$, and $\text{Te}(\text{iPr})_2$ as precursors [3], gas-phase reactions between precursors and between a precursor and H₂ have been investigated in detail. Following the work, we consider two subject, the choice of substrate and reactions on GST surface. In the latter, we study surface reactions between GST surface and molecules produced by gas-phase reactions. We investigate the adsorption of these molecules on a pristine GST surface (particularly Te surface) of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. As the study of substrate, we carry out the geometric optimization calculation of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ on substrate and show the lattice mismatch, stabilization energy, and structures.

Calculation Method and Results

All the calculations are performed by using the VASP program package with the density functional theory method. In this program package, periodic boundary conditions are adopted and wave functions are expanded in plane wave functions.

First, we study the choice of substrate, where we consider W, TiN, Si, and SiO₂ as a substrate material. Geometric optimization calculations are carried out for these substrate and Ge₂Sb₂Te₅. As Ge₂Sb₂Te₅ structure, we consider the structures reported in Ref. [4] and all their periodic patterns. Our results are summarized in Table 1, and their optimized structures are shown in Fig. 1. The stabilization energy (ΔE) for SiO₂ is not shown, since these GST models have unacceptable structure for this supercell. For substrates with good lattice mismatch, W, TiN, and Si, the optimized structures are not disturbed around interface and surface. Small disorder of the structure for TiN with Ti surface is not serious. On the other hand, for substrate with relatively large lattice mismatch, SiO₂, the structure is significantly disturbed around surface or Te-Te interface. These results are somewhat consistent with the knowledge that the GST on SiO₂ has worse quality than that on TiN.

Next, we investigate surface reactions between a GST surface and molecules in gasphase. For this study, we use the GST surface model shown in Fig. 2. This model has Te pristine surface, since Te surface model is most stable, and six layers, which are a part of GST unit cell. As reactant, we consider what molecules exist in gas-phase. First of all, we

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assume $GeH_3(tBu)$, $Sb(iPr)_3$, and $Te(iPr)_2$ as precursors [3]. In addition, we consider that these precursors react with carrier gas H_2 . These reactions are studied in our report of the last year. As a result, we have shown that GeH_4 , $SbH(iPr)_2$, $SbH_2(iPr)$, SbH_3 , TeH(iPr), and TeH_2 are more stabilized after reactions. These molecules may be produced by gasphase reactions with hydrogen. We consider these molecules and precursors as reactant in this paper.

In Fig. 3, we show the optimized structures of Ge compounds on the GST surface model. The stabilization energies of $GeH_3(tBu)$ and GeH_4 are -0.020 and 0.041 eV, respectively. Hence, our result implies that $GeH_3(tBu)$ is not attached on this Te surface. On the other hand, GeH_4 is seen to be attached, and however the distance from the nearest Te atom is much longer (about twice) than the Ge-Te distance in the GST crystal. This is because hydrogen atoms prevent the Ge atom from bonding surface Te atoms directly. The optimized structures of Sb and Te compounds on the GST surface model are shown in Figs. 4 and 5. The stabilization energies of $Sb(iPr)_3$, $SbH(iPr)_2$, $SbH_2(iPr)$, and SbH_3 , are 1.489, 1.390, 1.425, and 1.447 eV, respectively. Surface of all structures of Sb compounds are disturbed significantly. The large stabilization energy is contributed dominantly from the surface reconstruction. The distance from the nearest Te atom is much longer than the Te-Sb distance in the GST crystal for all structures. The stabilization energies of $Te(iPr)_2$, TeH(iPr), and TeH_2 , are 0.013, 0.019, and 0.054 eV, respectively. The distance from the nearest Te atom is longer than the Te-Te distance in the GST crystal for TeH(iPr), while the distances for $Te(iPr)_2$ and TeH_2 are almost the same length as the Te-Te distance in the GST crystal. Our results imply that the adsorption of Ge compounds on Te surface is more difficult than Te compounds. Hence, we consider that Ge flow rate is a key ingredient of CVD process. The adsorption of Sb compounds is seen to disturb Te surface. For further understanding of CVD process, we should consider other phenomena, the adsorption of dimer and decomposed molecules, hydrogen covered GST surface, hydrogen elimination reaction on surface, and so on.

Conclusion

We have investigated the CVD condition of steady growth of GST crystal by first principles calculations. The choice of substrates has been studied in terms of the optimized structure and lattice mismatch. Our results have shown that SiO_2 substrate are worse than other substrates. We have also studied surface reactions between molecules in gasphase and Te atoms on GST surface. Ge compounds have less activity due to their steric effect, while Te compounds have good reactivity for Te surfaces.

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Table 1: Comparison of substrates. *TiN is matched for $TiN:Ge_2Sb_2Te_5=3:2$.

Substrate	Lattice mismatch	$\Delta E \ (eV)$	Atom (Interface)	Atom (Surface)
W	-0.04	-11.31	Ge	Te
TiN (Ti)	-0.05*	-16.85	Te	Sb
TiN(N)	-0.05*	-6.53	Ge	Te
Si	0.11	-4.78	Sb	Te
SiO_2 (Si)	-0.14	-	Te	Te
SiO_2 (O)	-0.14	-	Ge	Te



Figure 1: The optimized structures of GST on substrate. From left to right, results for W, TiN(Ti), TiN(N), Si, $SiO_2(Si)$, and $SiO_2(O)$ are shown.



Figure 2: The GST surface model



Figure 3: The optimized structures of (a) GeH₃(tBu) and (b) GeH₄ on the GST surface model.



Figure 4: The optimized structure of Sb compoites on the GST surface model. Compounds are (a) Sb(iPr)₃, (b) SbH(iPr)₂, (c) SbH₂(iPr), and (d) SbH₃.



Figure 5: The optimized structure of Te compoites on the GST surface model. Compounds are (a) $Te(iPr)_2$, (b) TeH(iPr), and (c) TeH_2 .