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Ge$_2$Sb$_2$Te$_5$, an extensively studied narrow band gap semiconductors for phase-change memories, always displays *p*-type conductivity. However, the defect physics and origin of the *p*-type conductivity are not yet clear. We have studied various types of defects in layered *n*GeTe·*m*Sb$_2$Te$_3$ (GST) using *ab initio* calculations. The results show that the formation energies of V$_{Ge}$ are always the lowest followed by Sb$_{Te}$ in the studied GST. The majority defects are V$_{Ge}$ and Sb$_{Te}$, which results in the *p*-type conductivity of GST. Although Ge$_2$Sb$_2$Te$_5$ always has *p*-type character, one can make both *p* and *n* type GeSb$_2$Te$_4$ and GeSb$_4$Te$_7$ by tuning the atomic chemical environments.

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Point defects, such as vacancies, antisite and interstitial atoms, play an important role in the electrical properties of semiconductors. For example, the native defects of Zn_i and V_O in ZnO are the origin of its *n*-type conductivity and the difficulty of making it *p*-type for this technologically important semiconductor.[1] In contrast to ZnO, all the reported work on layered nGeTe$\cdot m$Sb$_2$Te$_3$ (GST) reveals *p*-type conductivity.[2-4] These chalcogenide semiconductors, such as Ge$_2$Sb$_2$Te$_5$ (n=2, m=1) and GeSb$_2$Te$_4$ (n=1, m=1), are technologically important recording materials for optical data storage and nonvolatile electronic memories or phase-change random access memories.[5,6] Even though experimental measurements have shown *p*-type conductivity in the amorphous, rock-salt and hexagonal or trigonal states of GST chalcogenides,[6] the defect physics and origin of *p*-type conductivity have been neglected for quite a long time whereas a significant attention has been focused on the structure and reversible phase-change mechanism in the phase-change community.[5,6] However, understanding of the defects and *p*-type conductivity in GST is important for tuning the performance in the memories. On the other hand, stable GST chalcogenides that crystallize in a hexagonal or trigonal structure have been investigated to be promising candidate materials even for thermoelectric applications.[2] For thermoelectric applications, it is important to unravel the origin of *p*-type conductivity and defect physics in order to make both *p* and *n* type conductivity be achieved in the same material. By the above motivations, in this work, we have performed extensive *ab initio* calculations and made an analysis to unravel the defect physics and origin of *p*-type conductivity in GST semiconductors.

As far as we know, the origin of *p*-type conductivity in amorphous chalcogenides was

attributed to the role of lone-pair electrons and charged defects based on the analysis of a valence-alternation-pairs model by Kolobov.[7] For crystalline GST, Ge or Sb vacancies have been suggested as the main reason of p-type conductivity in hexagonal GST225.[6] It is known that V_{Ge} and Sb_{Te} are the most readily formed defects in GeTe and Sb_2Te_3,[8,9] respectively. Therefore, it is natural to apply the defect physics in GeTe and Sb_2Te_3 to the GST pseudobinaries. We may also immediately suggest that the majority defect in GST will be V_{Ge} as $n > m$ (e.g. $Ge_2Sb_2Te_5$) and will be Sb_{Te} as $n < m$ (e.g. $GeSb_4Te_7$, n=1, m=2). In other words, the concentration of V_{Ge} decreases and that of Sb_{Te} increases as the ratio of n / m decreases. However, the above assumption is not completely true based on our present results. Below we will provide a fundamental understanding on the defects and origin of p-type conductivity in layered GST semiconductors.

Our *ab initio* calculations were performed based on the density functional theory as implemented in the VASP code.[10] We used projector-augmented-wave pseudopotentials (PAW) within the generalized gradient approximation (GGA) adopting the Perdew-Burke-Ernzerhof (PBE) exchange correlations.[11,12] An energy cutoff of 218.73 eV and Monkhorst-Pack grids of $2 \times 2 \times 1$ for k-points sampling were used. We used $Ge_2Sb_2Te_5$ (GST225), $GeSb_4Te_7$ (GST147) and $GeSb_2Te_4$ (GST124) to study the point defects in GST, where the former two compounds have a space group of $P\,\overline{3}m1$ and GST124 has a $R\,\overline{3}m$ symmetry.[13] We choose the lowest energy configurations which has building stackings of /Te/Ge/Te/Sb/Te/Te/Sb/ for the three compounds.[14,15] Supercells containing 81-, 84-, and 108-atoms were used for GST225, GST124 and GST147, respectively. The crystal structures were fully optimized in terms of volume and internal

atomic coordinates.

The formation energy of a neutral defect is calculated as follows:[16]

$$\Delta H_f = \Delta E(d) + n_{Ge}\mu_{Ge} + n_{Sb}\ \mu_{Sb} + n_{Te}\mu_{Te} \tag{1}$$

where

$$\Delta E(d) = E(d) - E(stoi.) + n_{Ge}\mu_{Ge}^{solid} + n_{Sb}\mu_{Sb}^{solid} + n_{Te}\mu_{Te}^{solid} \tag{2}$$

$E(d)$ and $E(stoi.)$ are the total energies of the GST supercells with and without the defect, respectively. μ_{Ge}^{solid}, μ_{Sb}^{solid} and μ_{Te}^{solid} are the total energies of ground solid states Ge (diamond cubic), Sb (trigonal) and Te (trigonal), respectively. n_i are the number of atoms transferred from the supercell to the reservoir in order to create defects. μ_{Ge}, μ_{Sb} and μ_{Te} represent the atomic chemical potential of germanium, antimony and tellurium corresponding to the energy variation of an atom to or from a chemical reservoir, which is not necessary in solid ground states. To maintain the accuracy by error cancellation, $E(d)$ and $E(stoi.)$ are calculated with the same k points, cutoff energy, and supercell size.

Table I lists the formation energy of isolated neutral point defects for layered GST compounds. Herein Sb_{Te1} represents the Sb anti-atom being in the Te layer that locates between Te and Sb layers, while Sb_{Te2} represents the Sb anti-atom being in the Te layer that locates between Ge and Sb layers. For V_{Te1}, the missing Te atom locates between Ge and Sb layers, while that locates between Sb and Te layers for V_{Te2}. Some interesting conclusions can be obtained from Table I: (1) The formation energy of one V_{Ge} is always lower than that of one Sb_{Te} and the formation energy generally follows the sequence of $Te_{Sb} > Sb_{Te2} > Sb_{Te1} > V_{Ge}$, suggesting that neutral germanium vacancies are more likely to form than antisite atoms in layered GST; (2) All the calculated formation energies for

various types of defects in GST225 are the lowest among the three investigated compounds; (3) Antisite atom Sb_{Te} is more likely to form in the Te layers where weak Te-Te bond exists; (4) Forming one V_{Sb} is much easier in GST225 and the formation of V_{Sb} is unlikely in GST124 and GST147. We have also calculated the formation energy for defect pairs, for example, the formation energies of $V_{Ge}+Sb_{Te1}$ are 0.810 and 0.811 eV in GST225 for the cases of the two defects being close and far, respectively. The calculated value are very close to that of $H_f(V_{Ge}) + H_f(Sb_{Te1})$ that is 0.852 eV.

Based on the defect formation energies in Table I, the equilibrium defect concentrations were estimated by the formalism as follows:[17]

$$[D] = N_{sites} \exp\left(-\frac{H_f}{K_B T}\right) \qquad (3)$$

Where $[D]$ is the defect concentration, N_{sites} is the number of sites per unit volume of GST where point defects may be present, H_f is the formation energy, K_B and T are Boltzmann constant and temperature.

Fig. 1 (a) to (c) show the concentration of some selected point defects which are more likely to form in GST. It is interesting to note that in the three compounds, the V_{Ge} concentration is always the highest, followed by that of Sb_{Te1}, suggesting that the majority charge carrier in GST are holes, consequently result in the observed p-type conductivity. The defect concentrations of Te_{Sb} and Sb_{Te2} are several orders lower than that of V_{Ge} and Sb_{Te1}. The values of defect concentration at various temperatures can be read from Fig. 1. For example, if materials were synthesized at 1000 K which is slightly above the melting temperature, the V_{Ge} concentrations in GST225, GST124 and GST147 would be 1.23×10^{20} cm^{-3}, 5.44×10^{18} cm^{-3} and 3.63×10^{18} cm^{-3}, respectively, while the Sb_{Te1} concentrations

would be 3.65×10^{19} cm^{-3}, 4.72×10^{18} cm^{-3} and 4.00×10^{18} cm^{-3}, respectively. The calculated

hole concentration in GST225 is in good agreement with that of the reported value of

$\sim3\times10^{20}$ cm^{-3}.[6] It is also interesting to note that the concentration of V_{Ge} and Sb_{Te1} in

GST225 are several orders higher than that in GST124 and GST147, with the latter two

compounds have similar defect concentrations.

Further analysis shows that atomic chemical potentials drastically affect the defect

formation energies in GST. As we know, among the three elements in GST, tellurium has

the highest volatility and Ge is nonvolatile material. Therefore, experimentally it is most

likely to have a Te deficient chemical enviroment and followed by a Sb deficient

enviroment if we start from the nominal compositions to synthesize GST. A literature

survey reveals that most of the experimental works only showed the nominal composition,

however, a stoichiometric compound was hardly obtained as shown by the composition

analysis. For example, in the work by Lyeo et al,[18] the composition for GST225 is

Ge:Sb:Te=22.5:23.3:54.2 that may be rewritten as Ge:Sb:Te($+Sb_{Te}$)=22.5:22.5:55,

suggesting the existance of Sb_{Te}. In contrast, another recent work showed a composition of

Ge:Sb:Te=2.02:1.88:5.13 that may be rewritten as Ge:Sb(Te_{Sb}):Te=2.02:2.01:5.00,[19] which

suggests the existance of Te_{Sb}. Therefore, in the present work, we considered the Sb or Te

deficient condition. The defect formation energies with various atomic chemical potentials

are estimated by the following restrictions for $\{\mu_{Ge}, \mu_{Sb}, \mu_{Te}\}$:

$$n_{Ge}\mu_{Ge} + n_{Sb}\mu_{Sb} + n_{Te}\mu_{Te} = \Delta H_f(Ge_{n_{Ge}}Sb_{n_{Sb}}Te_{n_{Te}}) \qquad (1)$$

is required to maintain a stable nGeTe·mSb$_2$Te$_3$;

$$\mu_{Ge} + \mu_{Te} \leq \Delta H_f(GeTe) \ , \ \ 2\mu_{Sb} + 3\mu_{Te} \leq \Delta H_f(Sb_2Te_3) \qquad (2)$$

is required to prevent the formation of binaries. $\mu_{Ge} \leq 0$, $\mu_{Sb} \leq 0$, $\mu_{Te} \leq 0$ are also needed to prevent the precipitation of solid elemental Ge, Sb and Te. Where our calculated $\Delta H_f(Ge_2Sb_2Te_5) = -1.881eV$, $\Delta H_f(GeSb_2Te_4) = -1.564eV$, $\Delta H_f(GeSb_4Te_7) = -2.464eV$, ΔH_f (rock-salt GeTe) = -0.364eV, ΔH_f (rhombohedral Sb_2Te_3) = -1.222eV.

As Te is deficient, the atomic chemical potentials are estimated to be -0.376, -0.391, -0.352 eV for μ_{Te} in GST225, GST124 and GST147, respectively, which correspondingly produce the formation energies of Sb_{Te1} to be 0.126, 0.258 and 0.324 eV, respectively. In this case, the Sb_{Te1} concentrations are calculated to be 1.66×10^{21} cm^{-3}, 4.40×10^{20} cm^{-3} and 2.38×10^{20} cm^{-3} with a synthesis temperature 1000K in GST225, GST124 and GST147, respectively. Consequently, Sb_{Te1} is the predominated defect at a Te deficient environment, which results in the p-type conductivity. Moreover, as seen in Fig. 1 (d) which shows the Sb_{Te} concentration as a function of temperature with Te deficiency, the Sb_{Te} concentration in GST225 is the highest among the three investigated compounds. This is in contrast to the above assumption of the Sb_{Te} concentration increasing as the increase of Sb_2Te_3 building block in GST.

At the condition of Sb deficiency, the estimated atomic chemical potential μ_{Sb} = -0.941, -0.782, -0.616 eV for GST225, GST124 and GST147, respectively. As a result, the formation energies for Te_{Sb} are -0.003, 0.011 and 0.317 eV in GST225, GST124 and GST147, respectively, which will respectively produce Te_{Sb} concentrations of 7.43×10^{21} cm^{-3}, 7.74×10^{21} cm^{-3} and 2.58×10^{20} cm^{-3} with synthesized temperature of 1000K. However, this does not imply that electrons will be the majority charge carrier as the V_{Sb} concentration will also increase drastically with Sb deficiency. For example in GST225,

with Sb deficiency the formation energy of one V_{Sb} will be -0.143 that indicates the spontaneous formation of antimony vacancies. In this case, the V_{Sb} concentration is 1.35 $\times 10^{22}$ cm^{-3} at 1000 K, which is much higher than that of Te$_{Sb}$. Together with the large V_{Ge} concentration, the majority charger carrier in GST225 is still holes and the conductivity remains a *p*-type character. While in GST124 and GST147, the V_{Sb} concentrations are 1.35×10^{18} and 1.01×10^{18} cm^{-3}, respectively, which are the same order as that of V_{Ge} but are 3 and 2 orders lower than the Te$_{Sb}$ concentration, respectively. Therefore, it is likely Te$_{Sb}$ is the majority defect and *n*-type conductivity can be achieved in GST124 and GST147. It is clear that GST225 always has *p*-type conductivity, while it is possible to make both *p* and *n* type conductivity in GST124 and GST147. This is good for thermoelectric applications as both *p* and *n* type conduction can be achieved in one type of material. The present results show a picture of multi-carriers of both holes and electrons in GST, where the majority charge carrier can be tuned by varying synthesis chemical environment except GST225 which always exhibit *p*-type behavior.

Fig. 2 shows the total density of states for GST225 of ideal and defect states. It is seen that the Fermi level of ideal GST225 locates between the conduction band and valence band, while for the defective compounds, the Fermi level locates within a small tail of valence band states for V_{Ge} and Sb$_{Te}$ containing-system which results from V_{Ge} and Sb$_{Te}$. For Te$_{Sb}$ antisite defetive GST225, the Fermi level locates within a small tail of conduction band states which comes from Te$_{Sb}$. Furthermore, even though with present DFT calcuations, one can not obtain accurate band gap, a trend obtained from Fig. 2 is that the band gap narrows with the presence of point defects.

Analyses on the electron localization function (ELF) reveals that the introduction of defects results in slight changes just around the defects. Fig. 3 (a) and (b) shows the ELF projected on the (110) plane for V_{Ge} and Sb_{Te} containing GST225, respectively. As seen in Fig. 3 (a), non-bonded electrons at Te1 and Te2 facing the Ge vacancy position are clearly seen and the Te2-Sb covalent bond as well as weak Te3-Te4 bond turns to stronger. With the presence of Sb_{Te} as shown in Fig. 3 (b), the Sb2-Sb_{Te1} covalent bond and stronger Sb_{Te1}-Te2 bond turns to stronger. Nevertheless, the introduction of vacancies and antisite defects only results in slight changes in the chemical bonding around the defects. Moreover, slight change in *a* lattice parameters but obvious decrease in *c* lattice parameters are found by the presence of vacancies and antisite defects, which will be present in an extensive paper in the future.

In summary, the majority defects in GST are V_{Ge} and Sb_{Te} which results in the *p*-type conductivity. The defects formation energies of various types are the lowest in GST225, and hence the highest defect concentrations. Furthermore, GST225 are always *p*-type semiconductors at the condition of various atomic chemical potentials, while it is possible to make both *p* and *n* type conductivity in GST124 and GST147 by tuning the synthesis environments. Finally, the introduction of defects only changes the chemical bonding character just around the defect in the building chains.

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Figure captions

FIG. 1 (Color online) The concentration of various types of defects as a function of synthesis temperature for (a) $Ge_2Sb_2Te_5$, (b) $GeSb_2Te_4$, (c) $GeSb_4Te_7$ and (d) the Te deficient condition

FIG. 2 The calculated total density of states for (a) stoichiometry $Ge_2Sb_2Te_5$, defective $Ge_2Sb_2Te_5$ containing (b) Te_{Sb}, (c) V_{Ge} and (d) Sb_{Te1}.

FIG. 3 (color online) The ELF projected on the (110) planes for defective $Ge_2Sb_2Te_5$ containing (a) V_{Ge} and (b) Sb_{Te1}, where the scale is from 0 (blue) to 1 (red) and the interval is 0.14.

Table captions

Table I. Formation energies of isolated neutral point defects (in eV) in layered GST compounds.

Table I.

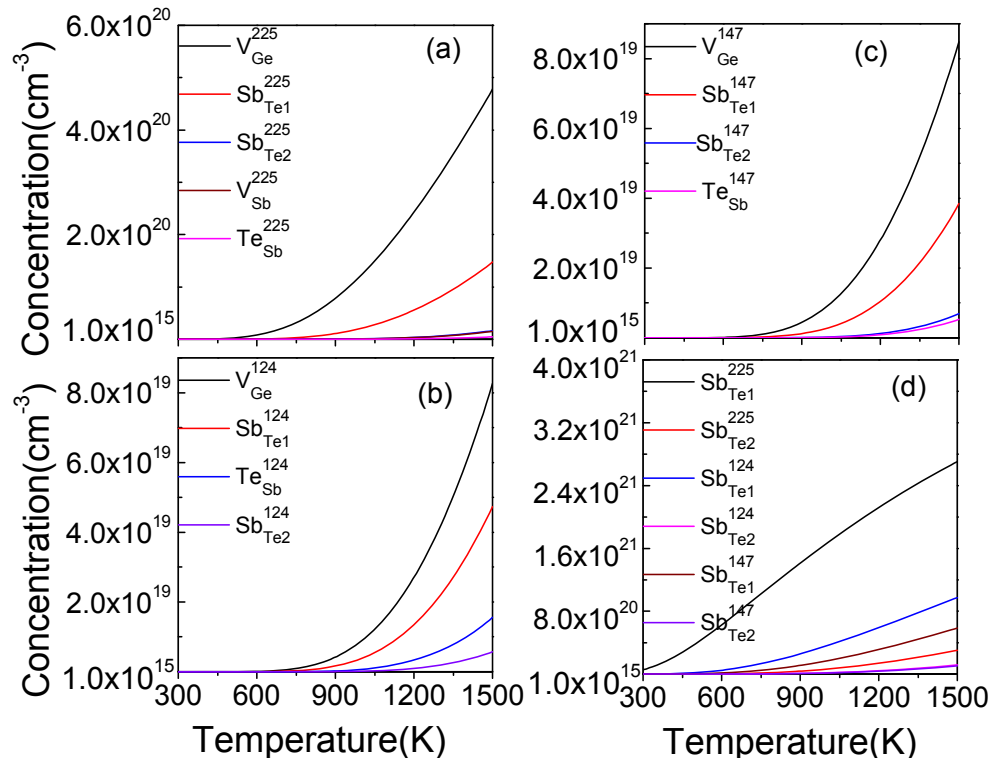|	Antisite			Vacancy			
	Sb_{Te1}	Sb_{Te2}	Te_{Sb}	V_{Ge}	V_{Sb}	V_{Te1}	V_{Te2}
GST225	0.502	0.785	0.938	0.350	0.798	1.705	1.503
GST124	0.649	0.922	0.793	0.577	1.539	—	—
GST147	0.676	0.898	0.936	0.565	1.411	—	—

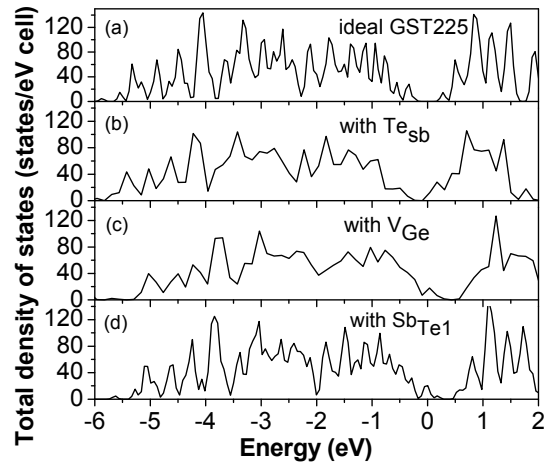Fig. 2 of Sun et al submitted to PRB with a manuscript No. LW12097BR

Fig. 3 of Sun et al submitted to PRB with a manuscript No. LW12097BR