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Stable nitride complex and molecular nitrogen in N doped amorphous Ge$_2$Sb$_2$Te$_5$

Zhimei Sun,$^{1,a}$ Jian Zhou,$^1$ Hyun-Joon Shin,$^2$ Andreas Blomqvist,$^3$ and Rajeev Ahuja$^3$

$^1$Department of Materials Science and Engineering, Xiamen University, Xiamen 361005, China
$^2$Pohang Accelerator Laboratory, Pohang University of Science and Technology, Pohang 790784, South Korea
$^3$Department of Physics and Materials Science, Uppsala University, 75121 Uppsala, Sweden

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Nitrogen doping is identified to be a sufficient way to reduce the power consumption of Ge$_2$Sb$_2$Te$_5$, a phase-change material for data storage. On the basis of ab initio molecular dynamics simulations, we show that the doped N in amorphous Ge$_2$Sb$_2$Te$_5$ coexist as Ge(N, Te)N complex and N$_2$, and high density of the film produces more N$_2$. Furthermore, both Ge(N, Te)N complex and N$_2$ are stable upon annealing at 600 K. © 2008 American Institute of Physics. [DOI: 10.1063/1.3052046]

Phase-change random access memory (PRAM) using Ge$_2$Sb$_2$Te$_5$ (GST) as record medium is considered as a very promising candidate for the next generation memory device. To compete with other memory types, such as flash memory, it is required to reduce the power consumption of GST. Nitrogen doping is identified to be a sufficient way. In nitrogen-doped amorphous GST (a-NGST), N was reported to have the form of GeN$_x$ and N$_2$. For practical applications, the stability of GeN$_x$ and N$_2$ is critical because poor stability will induce performance degradation. In addition, density of the film should have a profound influence on the configuration of doped N. In this work, we studied these two issues by ab initio molecular dynamics simulations. Our results show that the doped N coexist as Ge(N, Te)N complex and N$_2$ and high density produces more N$_2$. Furthermore, both Ge(N, Te)N complex and N$_2$ are stable upon annealing at 600 K.

The present ab initio molecular dynamics simulations were carried out using the Vienna ab initio simulation package. The calculation parameters can be found in our previous work. Supercells containing 24 Ge, 24 Sb, 60 Te, and 12 N atoms are constructed from cubic GST based on the (111) plane along the [111] direction. The 10% N doped GST is close to the experimental work. NGST is simulated at the densities of amorphous ($\rho_L=5.7$ g/cm$^3$, referred to as La-NGST) and the cubic ($\rho_H=6.37$ g/cm$^3$, referred to as Ha-NGST) phases. The supercells were melted and thermalized at 5000 K for 3 ps to completely eliminate the effect of their original structures, where the temperature was controlled using the algorithm of Nosé. The liquids were then quenched down to 300 K by a continuous quenching of 333 K ps$^{-1}$ and followed by a rethermalizing process of 3 ps at 300 K. The anneal process is that the amorphous structures obtained at 300 K were reheated to 600 K and thermalized at this temperature for 30 ps.

The coexistence of N$_2$ and Ge(N, Te)N complex in a-NGST can be characterized by pair distribution functions (PDFs) around N, as shown in Fig. 1. The formation of N$_2$ is shown by the first sharp peak at ~1.1 Å of the N–N pair function, which is comparable to the N–N bond length of N$_2$. Furthermore, the N$_2$ content in Ha-NGST is higher than that in La-NGST, as demonstrated by the larger area under the first peak of the N–N pair for the former phase. The existence of N–Ge and N–Sb bonds in both a-NGST is exhibited by the first peaks of the N–Sb and N–Ge PDFs, where the peak positions of 2.1 and 1.9 Å correspond to the average bond lengths of N–Sb and N–Ge, respectively. It is noted that the N–Te PDF shows a first peak for La-NGST but not for Ha-NGST, which illustrates that the N–Te bonds exist in La-NGST but not in Ha-NGST. The average N–Te bond length is 2.1 Å, which is close to that of N–Sb bonds. It is known that the covalent radii for N, Ge, Sb, and Te are 0.71, 1.20, 1.39, and 1.38 Å, respectively, by which we obtain that the covalent bond lengths for N–Ge, N–Sb, and N–Te are 1.91, 2.10, and 2.09 Å, respectively. Compared with the corresponding calculated average bond lengths in a-NGST above, we may conclude that the nitride complexes in a-NGST are covalently bonded. However, in contrast to the present results, only the existence of N–Ge was reported in the previous experimental work. This is because the experimental accuracy in the previous reports is not enough to vividly show the existence of the bonding configurations of N–Sb and N–Te, which is partly due to the lower relative concentration expected by the modeling.

Figure 1 lists the partial and total coordination numbers (Z) for N calculated by integrating the first peaks of PDFs. As seen from Table I, the major contribution to Z of N is the N–Ge bond ($Z_{N-Ge}=0.84$ and 1.41) for Ha-NGST and

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$^a$Author to whom correspondence should be addressed. Electronic addresses: zmsun@xmu.edu.cn and zhmsun2@yahoo.com.
La-NGST, respectively), suggesting that the N–Ge bond dominates. The second most important contribution is the N–N bond for Ha-NGST, which is the least important contribution for La-NGST. The total Z for Ha-NGST (Z = 1.84) is smaller than that of La-NGST (Z = 2.58), partly due to more N atoms existing in a molecular form in the former phase. The present result indicates that high density will induce the formation of more N2 in a-NGST.

The effect of N on the local structure of GST can be analyzed by the (first-neighbor) bond angle distributions (BADs). For around Ge, Sb, and Te, sharp peaks centering at ~90° are observed in the BAD in Fig. 2, which reminisce the octahedral geometry of rocksalt structured GST, while the small broad peaks at ~170° indicate a distorted octahedrally coordinated a-NGST, which is quite similar to amorphous GST and GeSb2Te4.6,10,11 This indicates that N doping has minor effects on the basic local atomic structure of GST. Compared to undoped amorphous GeSb2Te5 and GeSb2Te4.6,10,11 there are more peaks centering at ~30°, ~60°, and ~120° in the angle distributions of a-NGST, which is due to the formation of nitride complex. Peaks at ~60° and ~120° mean triangular rings and threefold coordinations for Ge, Sb, and Te in a-NGST, respectively. Density also shows significant effects on the BAD around Sb, Te, and Ge, as seen in the angle distribution of La-NGST, in which there are peaks centering at ~120°, which are not observed in the BAD of Ha-NGST. For around N, a sharp peak at ~120° is observed for both a-NGST phases, which indicates that threefold coordinated N dominates in a-NGST. This is obvious by analyzing the distribution of coordination numbers for individual elements in a-NGST, which is shown in Figs. 3(a) and 3(b) for La-NGST and Ha-NGST, respectively. As seen in Fig. 3, fivefold and sixfold coordinations predominate for Ge, Sb, and Te atoms in both a-NGST phases. Compared with a-GST, Te is overcoordinated in a-NGST. As for N, it is seen that roughly 33% and 67% N exist as N2 in La-NGST and Ha-NGST, respectively, which is demonstrated by the onefold coordinated N. The remaining N is mainly threefold coordinated by Ge, Sb, and Te atoms, except for a small amount of twofold coordinated N. Further analysis shows that both threefold and twofold coordinated N forming Ge(Sb, Te)N complexes have a nearest neighbor bond angle of ~120°. This can be understood by analyzing the valence electrons of the constituent elements. The three equivalent 2p\textsuperscript{1} orbitals of N assuming planar orientation with bond angles of 120° could form σ bonds with Ge 4p, Sb 5p, and Te 5p orbitals by p–p orbital overlap.

A closer study on the snapshot structures of a-NGST shows that among the Ge(Sb, Te)N complex, the N–Ge bond has the highest tendency to form, followed by the N–Sb bond and then the N–Te bond. This trend can be understood by comparing the electronegativity difference between the constituent elements. The Pauling electronegativities for N, Ge, Sb, and Te are 3.04, 2.01, 2.05, and 2.1, respectively. Obviously the largest difference is between N and Ge, followed by between N and Sb, and then between N and Te. Therefore the N–Ge bond is the easiest to form, followed by the N–Sb bond, and the N–Te bond is the last preference to form among them. Furthermore, with increasing density, the N–Te bond is not energetically preferred at 300 K.

Finally we performed an annealing process of a-NGST to investigate the stability of the Ge(Sb, Te)N complex and N2 within the amorphous structures. Some changes are observed in the configuration of the nitride complex after being annealed at 600 K for 30 ps, while the change in N2 is not observed. As seen in Table I, for La-NGST, the number of

<table>
<thead>
<tr>
<th>Around N</th>
<th>With Ge</th>
<th>With Sb</th>
<th>With Te</th>
<th>With N</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>p0: Amor.</td>
<td>0.84</td>
<td>0.33</td>
<td>0</td>
<td>0.67</td>
<td>1.84</td>
</tr>
<tr>
<td>Anne.</td>
<td>0.50</td>
<td>0.33</td>
<td>0.25</td>
<td>0.67</td>
<td>1.75</td>
</tr>
<tr>
<td>p0: Amor.</td>
<td>1.41</td>
<td>0.43</td>
<td>0.41</td>
<td>0.33</td>
<td>2.58</td>
</tr>
<tr>
<td>Anne.</td>
<td>1.77</td>
<td>0.44</td>
<td>0.24</td>
<td>0.33</td>
<td>2.78</td>
</tr>
</tbody>
</table>

FIG. 3. (Color online) Distribution of coordination numbers for individual atoms in (a) La-NGST and (b) Ha-NGST at 300 K.
the N–Ge bond ($Z_{N-Ge}=1.77$) increases slightly and that of the N–Te bond ($Z_{N-Te}=0.24$) decreases slightly after annealing, while the number of the N–Sb and N–N bonds are generally unchanged. Consequently, the total coordination numbers increase slightly. For $Ha$-NGST, the number of the N–Ge bond ($Z_{N-Ge}=0.50$) decreases slightly in contrast to $La$-NGST, while that of the N–Sb and N–N bonds is unchanged, which is similar to $La$-NGST (Table I). In addition, the N–Te bond ($Z_{N-Te}=0.25$) is also present after annealing. Further analysis of the results in Table I shows that there might be saturation of Sb and Te atoms bonded to N in $a$-NGST of both densities at certain temperatures.

In summary, through the $ab$ $initio$ molecular dynamics study, we have shown that both Ge(Sb, Te)N complex and N$_2$ coexist in $a$-NGST, while no significant effect of N on the local atomic structure of $a$-NGST is observed. High density of $a$-NGST will induce more N$_2$ rather than nitride complex. Furthermore, those N$_2$ in the interstitial position of $a$-NGST are very stable after being annealed at 600 K for 30 ps, while some nitride complexes slightly change their configurations. In addition, saturation of N–Sb and N–Te bonds in $a$-NGST is expected during annealing. Based on the present results, high quality NGST films will work well in the PRAM devices.

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