A-8-02

Origin of the difference between high resistive and low resistive structures for interfacial phase change memories based on $GeTe/Sb_2Te_3$ superlattice

H. Shirakawa[1*], M. Araidai[1,2], and K. Shiraishi[1,2]
[1]Graduate School of Engineering, Nagoya University, [2]Institute of Materials and Systems for Sustainability, Nagoya University
([*]E-mail:shirakawa@fluid.cse.nagoya-u.ac.jp)

Abstract

We have succeeded in making an atomic structure consistent with the experimental EDX maps of iPCRAM based on $GeTe/Sb_2Te_3$ superlattice. We have revealed that the bandgap closes when the Ge atoms in the GeTe layer are crystallized. On the other hand, the bandgap is opened when the Ge atoms are disordered in the electrode direction. Furthermore, it has been also revealed that the distribution of Ge atoms in the horizontal direction (the perpendicular direction to the electrode direction) does not strongly rely on whether the bandgap is opened or not. In other words, the resistance change mechanism of iPCRAM is attributed whether Ge atoms are disordered in the electrode direction or not.

Introduction

A new type of phase change RAM based on a $GeTe/Sb_2Te_3$ superlattice, known as an interfacial phase change RAM (iPCRAM), for use as a high-speed, low power non-volatile memory has been examined [1]. The high and low resistance states (HRS/LRS) of an iPCRAM can be switched by the movement of Ge atoms in the GeTe layer (Fig.1 (b)), and HRS and LRS structures remain perfect crystalline structure [2]. In addition, J. Kalikka et al., has reported that only the GeTe layers melt to the amorphous structure and the Sb_2Te_3 layers remain crystalline structure during heating when the GeTe/ Sb_2Te_3 is expanded by equivalent biaxial strain in the horizontal direction (the perpendicular direction to the electrode direction) [3]. The last SSDM, we also have reported that $GeTe/Sb_2Te_3$ with amorphous GeTe layer does not have bandgap, leading to it is LRS [4]. However, all structures in the previous work are not consistent with the experimental image. Fig. 2 is the EDX maps of iPCRAM based on $GeTe/Sb_2Te_3$ superlattice on HRS [5]. Te and Sb atoms are crystallized, while only Ge atoms are disordered as show in Fig 2. The GeTe layer of conventional theoretical models is crystalline or amorphous structure. The experimental image and the conventional theoretical models are different in that only Ge atoms are disordered in the GeTe layer. In this study, we aim to make a theoretical model consistent with the experiment of the EDX maps.

Simulation model and method

The atomic and electrical structures were obtained using VASP, which is based on density functional theory with the generalized gradient approximation [6]. We employed Perdew-Burke-Enzerhof exchange correlations [7] with dispersion corrections (DFT-D2 methods of Grimme) [8] in order to describe the Van der Waals (vdW) interactions originating from the Te-Te vdW gaps in the $GeTe/Sb_2Te_3$ superlattice. The core-valence interactions were represented by projected-augmented-wave potentials [9]. We employed a 3×3×1 stoichiometric $GeTe/Sb_2Te_3$ superlattice shown in Fig.3 (a) based on Tominaga's HRS model as an initial structure [2]. In the case of Kalikka *et al.,* and our first principles molecular dynamics (MD) calculation of last year, it seems that crystallization does not occur because the annealing and the cooling time was very short. Therefore, in this study, we cooled slowly during MD calculations. Specifically, the temperature history is following steps. Step 1: heating from 0 to 2500 K at 10 ps, Step 2: heating at 2500 K for 10 ps, Step 3: rapid cooling from 2500 K to 1000 K at 10 ps, Step 4: gradually cooling down from 1000 K to 0 K at 180 ps. The last SSDM, we have reported that Ge atoms cohere in the central region of the GeTe layer by heating, while the Ge atoms move from central region to the interface between GeTe and Sb_2Te_3 layer by heating and hole injection. Therefore, we have executed first principles MD calculation with a neutral and positively charge state in order to obtain the different Ge atoms distribution. Finally, all structures are optimized in the neutral charge state.

HRS and LRS structures of a $GeTe/Sb_2Te_3$ superlattice iPCRAM obtained by first principles molecular dynamics

Fig.3 (b) and (c) shows the obtained structures and its density of states by first principles MD calculation with neutral and positively charge state, respectively. We have found that the GeTe layer are crystallized by slow cooling. Although the crystal structure of the GeTe layer is similar to the initial structure, several Ge atoms and Te atoms are exchanged with each other as shown in Fig.3 (b). This structure has more electronic states in the Fermi energy than in the initial structure. In other words, the structure of Fig.3 (b) is LRS. Furthermore, Fig.3 (c) shows that only Ge atoms are disordered, while Te and Sb atoms are crystallized by holes injected first principles MD calculation. For the structure of Fig. 3 (c), the Te layer of GeTe keeps the same triangular lattice as the initial structure. We also have found that most of the Ge atoms are located in the center of the triangular lattice of Te atoms as well as the initial structures. The different point between the initial structure and the structure of Fig. 3(c) is whether Ge atoms are only disordered in the electrode direction or not. This structure is consistent with the EDX maps of HRS. In fact, the structure of Fig. 3 (c) has a bandgap, leading to HRS.

How to obtain HRS structure with bandgap

As the above results, it is expected that the bandgap will be opened by disordering Ge atoms in the electrode direction keeping the triangular lattice of Te atoms. Next, we randomly put Ge atoms in the upper, middle and bottom layers while keeping the triangular lattice of the Te atoms (Fig 4 (a)). The distribution of Ge atoms in the electrode direction was prepared 6 cases shown in Fig. 4 (b). In each case, we also calculated 10 structures with different distributions of Ge atoms in the horizontal direction. For the case 5 and the case 6, GeTe layer is perfectly crystallized as shown in Fig. 6. All structure was optimized with neutral charge state. Fig 5 shows the averaged bandgap values for the each case. As shown in Fig. 5, we can see that the bandgap is opened when Ge atoms were put in the three layers. In addition, the distribution of Ge atom in the horizontal direction (the perpendicular direction to the electrode direction) does not strongly rely on whether the bandgap is opened or not. On the other hand, we have found that if GeTe layer are perfectly crystalized, the bandgap is closed. Thus, the bandgap of GeTe/ Sb_2Te_3 superlattice is attributed whether Ge atoms are disordered in the electrode direction or not.

Summary

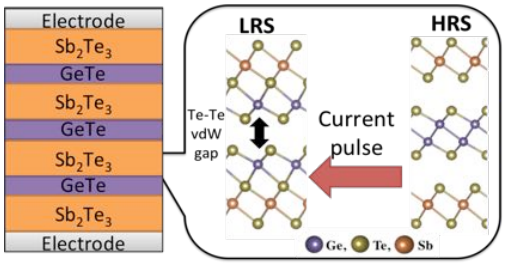
We clarified that the conditions which the bandgap of the GeTe/ Sb_2Te_3 superlattice is opened by first principles calculations. The bandgap is closed when the Ge atoms in GeTe layer are crystallized without disordering in the electrode direction. As a result, the GeTe/ Sb_2Te_3 superlattice with crystalline GeTe layer becomes LRS. On the other hand, the bandgap is opened when Ge atoms are disordered in the electrode direction and distributed in the all range of GeTe layer. In other words, GeTe/ Sb_2Te_3 superlattice becomes LRS by disordering of Ge atoms in the electrode direction. This characteristic is opposite to Ge deficient Ge_xTe_{1-x}/Sb_2Te_3 superlattice reported in last SSDM [4].

Acknowledgement

This work was based on results obtained from "Project to develop cross-sectoral technologies for IoT promotion" commissioned by the New Energy and Industrial Technology Development Organization (NEDO) and supported by CREST, JST.

References

[1] M.Tai *et al*. VLSI 2015. [2] J. Tominaga *et al*., Jpn. J. Appl. Phys. **48**, 03A058, (2009). [3] J. Kalikka *et al*., nature comm. **7** 11983 (2016). [4] H. Shirakawa *et al*., SSDM, (2016). [5] T. Ohyanagi and N. Takaura AIP advances, **10,** 1063, (2016). [6] G. Kresse *et al*. Phys. Rev. B 47, 558, 1993. [7]J. P. Perdew *et al*., Phys. Rev. Lett. **77**, 3865 (1996). [8] S. Grimme, J. Comp. Chem. **27**, 1787 (2006). [9] P. E. Bloöchl, Phys. Rev. B **50**, 17953 (1994).



(a) (b)

Fig. 1 (a) Schematic illustration of iPCRAMs. (b) Conventional HRS and LRS models of iPCRAMs.

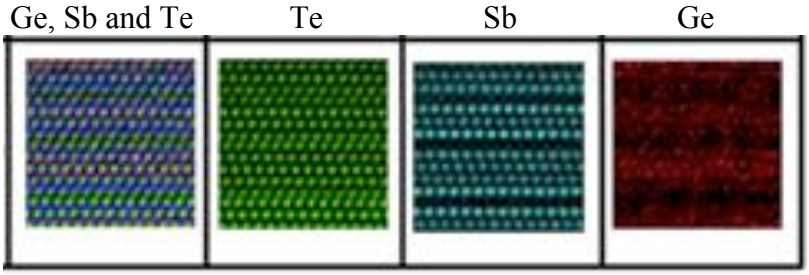


Fig. 2 EDX maps of $GeTe/Sb_2Te_3$ superlattice on HRS. Gree, light blue, and red shows Te, Sb, and Ge atoms, respectively. Te and Sb atoms remain crystalline structure, while only Ge atoms are disordered. This figure is reprinted from Fig.1 of Ref.5.

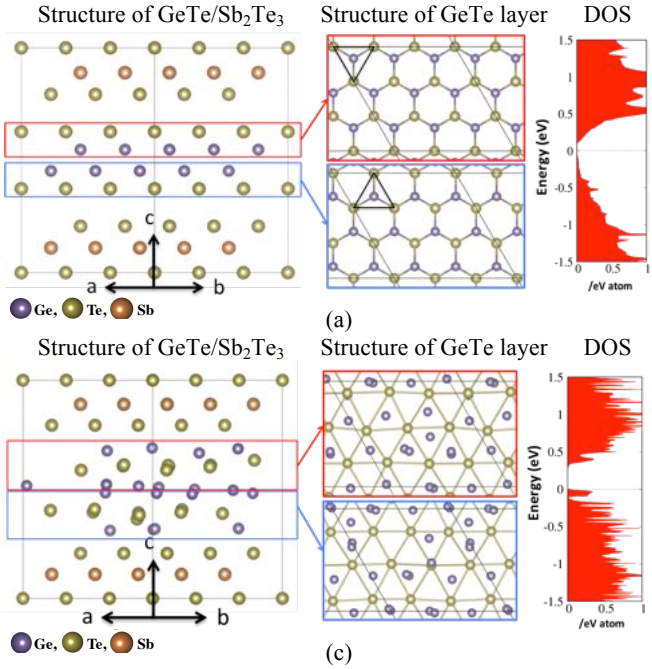
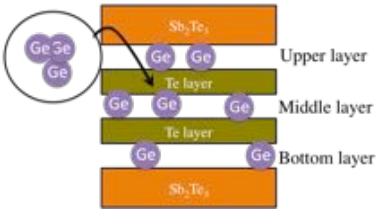


Fig. 3 Atomic structures and density of states. (a) Initial structure. (b) One of obtained by first-principles MD calculation with the neutral charge state. (c) One of obtained by first- principles MD calculation with the positive charge state. Purple, orange and yellow balls are Ge, Sb and Te atoms. Te layers remain a triangular lattice and most of the Ge atoms are located in the center of the triangular lattice in the all structures. The structure with disordering Ge atoms to the electrode direction is consistent with the EDX maps of HRS, which has a bandgap.



(a)

Ge distribution on the direction of electrode

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Ge atoms in upper layer	4	5	6	7	9	9
Ge atoms in middle layer	10	8	6	4	9	0
Ge atoms in bottomlayer	4	5	6	7	0	9
The number of calculated structures	10	10	10	10	1	1

(b)

Fig. 4 (a) Schematic illustration of putting Ge atoms while keeping the triangular lattice of the Te atoms. (b) The Ge distribution in the direction of the electrode when randomly putting Ge atoms in the upper, middle and bottom layers. GeTe layer becomes a stoichiometric one by putting 18 Ge atoms.

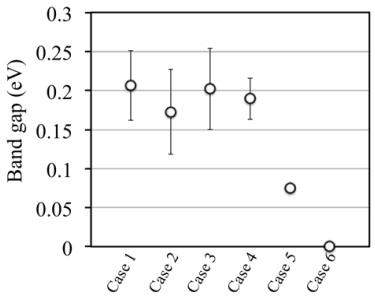


Fig. 5 The bandgap values for each case shown in Fig.4 (b). The error bars show a standard deviation.

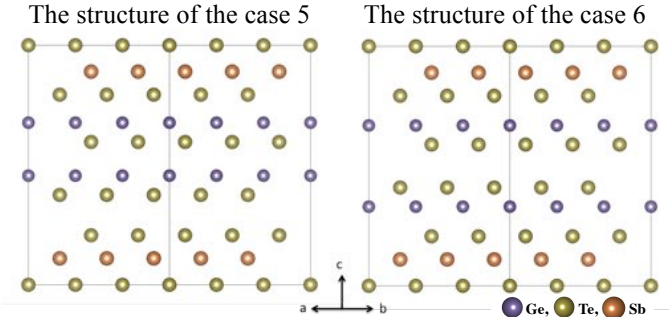


Fig. 6 The structures of the case 5 and the case 6 shown in Fig 4 (b). Purple, orange and yellow balls are Ge, Sb and Te atoms. For the structure of the case 5, the bandgap is 0.075 eV. The structure of the case 6 does not have bandgap.

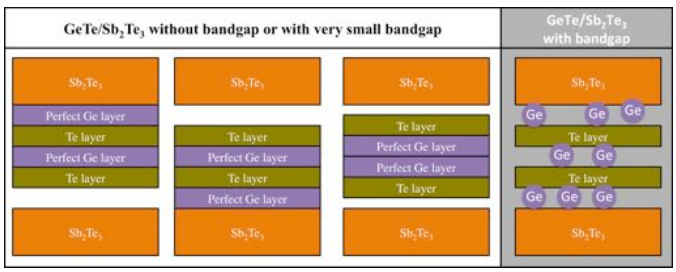


Fig. 7 Schematic illustration of classification for $GeTe/Sb_2Te_3$ superlattice. If Ge atoms are disordered in the electrode direction and distributed in the all range of GeTe layer, the bandgap is opened.