

A microscopic model for resistance drift in amorphous Ge₂Sb₂Te₅

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ABSTRACT

A microscopic model for the resistance drift in the phase-change memory is proposed based on the first-principles results on the compressed amorphous Ge₂Sb₂Te₅. First, it is shown that the residual pressure in the phase-change memory cell can be significant due to the density change accompanying the phase transformation. Our previous first-principles calculations showed that the energy gap is reduced and the density of localized in-gap states increases as the cell is pressurized. This indicates that the compressed amorphous Ge₂Sb₂Te₅ is more conducting than those made under stress-free conditions. In addition, the crystallization dynamics was also accelerated under compressive stress. Based on these theoretical results, we propose a mechanism for the resistance drift in which the relaxation process in the amorphous Ge₂Sb₂Te₅ corresponds to the growth of the crystalline nuclei inside the amorphous matrix, thereby lowering the internal stress. Our model can consistently explain several experimental observations such as the dependence of the drift exponent on the amorphous size.

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1. Introduction

Chalcogenide-based materials have been widely used in optical storage devices because of the large reflectivity contrast between amorphous and crystalline phases. Recently, the application to the phase-change random access memory (PRAM) also attracts wide interests as PRAM is regarded as a promising next-generation non-volatile memory [1,2]. In PRAM, the information is stored as resistance states that are distinct in crystalline (semiconducting) and amorphous (insulating) phases.

Among the wide class of chalcogenide materials, Ge₂Sb₂Te₅ or GST, a representative compound in the GeTe–Sb₂Te₃ tie line, has been known to satisfy various technical conditions required in PRAM such as the rapid phase change and good stability of the amorphous phase. Three phases are known to be (locally) stable for GST: stable hexagonal phase, metastable cubic phase and amorphous phase [3]. In the application to optical and electric memories, the phase change between the metastable crystalline and amorphous states is employed since the phase change between the two phases can take place in nanoseconds.

The atomic densities in the three phases of GST are significantly different: 0.034, 0.033, and 0.031 atoms/Å³ for the hexagonal, cubic,

and amorphous phases [4]. The phase changing material in the PRAM cell is confined in a space with the volume corresponding to the crystalline density. The dimension of the PRAM cell is not allowed to change during the set and reset operations because hard materials such as TiN are enclosing the phase changing parts. This means that the phase transformation into the amorphous phase inevitably results in a significant stress building up inside the cell. The magnitude of the residual stress depends on the size of the programmable region. Experimentally, it has been suggested that the residual stress in PRAM cell can influence various physical properties of amorphous GST, most notably the resistance drift [5]. The resistance drift refers to the phenomena where the resistivity of amorphous GST (R) steadily increases over a stretched time (t) up to several months, in the form of $R \sim t^\nu$ (See Fig. 1). The resistance drift poses a serious obstacle against the multi-bit operation in which different resistivity levels are recorded in the amorphous GST. The multi-bit operation of PRAM is essential to compete with the current flash memories. In Ref. [5], it was found that the drift exponent ν depends on the size of the programmable region, hinting that the fundamental characteristics of the amorphous GST could be altered by the pressure within the PRAM cell. In addition, the drift exponents for GST nanowires show that the drift is extremely low when the surface of the nanowire is exposed and the almost stress-free condition is established [6]. In Ref. [7], we presented the first-principles results showing that the residual pressure significantly influences the electronic structures of amorphous

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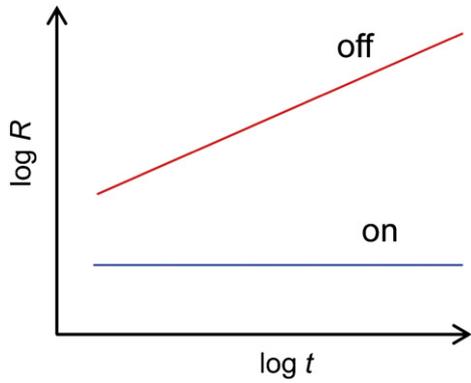


Fig. 1. Schematic diagram to describe a resistance drift phenomenon. (Jino Im et al.).

GST such as the energy gap. Based on these theoretical results, we are going to propose in this article a microscopic mechanism for the resistance drift that can provide consistent explanations on various experimental observations on the resistance drift.

2. Results and discussions

2.1. Analysis on the residual stress in the PRAM cell

We first demonstrate that the residual stress inside the PRAM cell can be significant due to the phase transformation. Fig. 2(a) shows a schematic structure of the PRAM cell. We assume that the

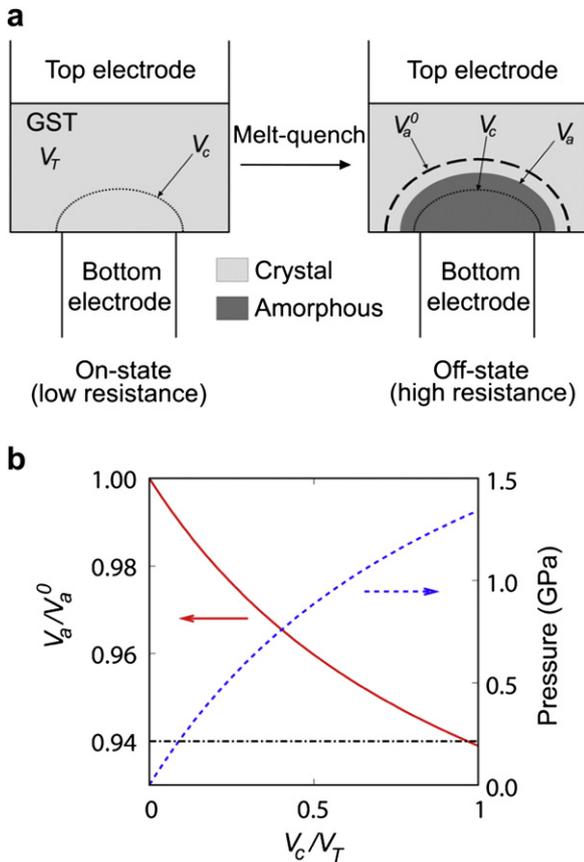


Fig. 2. (a) Schematics of the PRAM cell in on- or off-states. V_T is the total GST volume and V_c is the programmable region. On the right side, V_a^0 is the unstressed amorphous volume of GST in the programmable region while V_a is the actual volume in the PRAM cell due to the confinement. (b) The final volume of the programmable region and the residual pressure with respect to V_c/V_T . (Jino Im et al.).

phase change between the crystalline and amorphous phases occurs near the bottom electrode. Depending on the intensity and duration of the electric pulse, the volume of molten GST can be varied. Suppose that V_T is the total volume of GST, which is fixed throughout the melt-quench process. V_c is the volume of the crystalline part in the conducting on-state that is going to be amorphized in the insulating off-state. In the right-hand side of Fig. 2(a), V_a is the actual volume of this part in the off-state. V_a is smaller than V_a^0 which is the amorphous volume without any stress, i.e., $V_a^0 \sim 1.065V_c$. Assuming the hydrostatic pressure, the following relation is obtained under the equilibrium condition;

$$\frac{V_a}{V_a^0} = \frac{B_a(V_T - V_c) + B_c V_c}{B_c V_a^0 + B_a(V_T - V_c)}, \quad (1)$$

where B_a and B_c are the bulk moduli of amorphous and crystalline GST, respectively. Here we use the theoretical estimation of the bulk moduli, which are 22 and 40 GPa for B_a and B_c , respectively [8]. In Fig. 2(b), V_a/V_a^0 and the residual pressure in the cell is plotted as a function of the programmable region divided by the total volume (V_c/V_T). For example, if 20% of the total volume is amorphized ($V_c/V_T = 0.2$), the amorphous GST is compressed by 2% and the residual pressure is as high as 500 MPa. The confinement effect becomes more significant when the amorphous volume is increased. The pressure effect on the electrical properties of the amorphous GST has not been highlighted much despite its possible importance in PRAM operations.

2.2. Effects of pressure on the electronic structures of GST

The effect of pressure on the electronic structure of GST was studied in our previous molecular dynamics simulations at the first-principles level [7]. To recapitulate the main results, the residual pressure in the PRAM cell was mimicked by varying the simulation volume (V) with respect to the nominal amorphous volume V_a^0 such that $V/V_a^0 = 0.94, 0.97, 1.00, 1.03$ and 1.13 . The electronic density of states was closely examined and it was found that the energy gap was decreased and the number of in-gap states was increased with pressure. (See Table 1.) The gap change can be understood based on the band broadening effects; as the cell volume is reduced, the contacts between atoms increases. This results in a larger overlap between atomic orbitals and the widths of associated energy bands are increased because of the larger band dispersion. Both valence and conduction bands become broader but the distance between the band centers are more or less maintained because the interatomic distances do not change significantly. The combination of these two effects results in the band gap reduction. On the other hand, the increase of in-gap states with pressure can be explained as follows: with the compressed cell volume, the atoms are less mobile during the quenching process. This prevents each atom from developing stable chemical bonding, which would generate defect levels within the energy gap. The electronic transport in amorphous GST is well explained based on the Poole-Frenkel mechanism, where the charge carriers move between trap

Table 1

The volume dependence of the energy gap and the number of in-gap states. The data is extracted from the density of states fitted with a square-root form [7].

V/V_a^0	Energy gap (eV)	Number of in-gap states (states/unit cell)
0.94	0.16	0.44
0.97	0.24	0.42
1.00	0.30	0.20
1.03	0.36	0.26
1.13	0.48	0.07

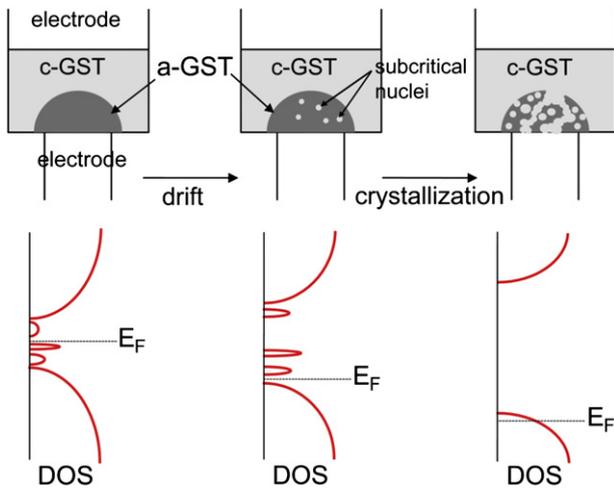


Fig. 3. Schematic diagram to depict resistance drift and crystallization processes. (Jino Im et al.).

levels by jumping into the conduction edge [9]. Therefore, both decreases in the energy gap and increases of in-gap states indicate that amorphous GST is more conductive when generated under compressive stress. In terms of atomic structures, it was found that the number of four-fold rings (N_{4r}), the basic building blocks of crystalline GST, increases with pressure. It was directly confirmed that the crystallization dynamics was accelerated in the compressed amorphous GST.

2.3. Relation to resistance drift

As was mentioned in the introduction, the amorphous phase in PRAM cells shows a resistance increase over stretched time scales with an exponent depending on the size of the programmable region. So far, the resistance drift has been explained by dilation effects [10] or structural relaxations [11] that may affect the transport behavior. Based on the present computational results, we propose a schematic but microscopic model for the resistance drift as depicted in Fig. 3. The left part of Fig. 3 denotes the initial state right after the melt-quench operation (reset). At this stage, significant stress should be built up within the PRAM cell due to the density difference between crystalline and amorphous phases. We assume that the compressive stress is released as subcritical crystalline nuclei are created and grow within amorphous GST (the middle part of Fig. 3). In Ref. [12], the population and evolution of this kind of subcritical nuclei were studied in terms of thermal history. From the discussions in the previous section, the stress relaxation results in the gap increase and the reduction of in-gap states in amorphous GST, both of which effectively suppresses the conductivity of amorphous GST. Since the crystalline nuclei are not percolated yet, the current still flows through the amorphous region and the overall resistance will increase. This corresponds to the resistance drift. Eventually the nuclei grow up to the critical size, and the device fails (the right part of Fig. 3).

While the above model rather simplifies the growth mechanism of the crystalline nuclei, it can account for several existing

experiments. First, the larger N_{4r} in the compressed cell should facilitate the creation of subcritical nuclei and its growth as it did for crystallization, and this can explain a larger drift exponent for the PRAM cell with a bigger portion of amorphous GST [5]. In addition, the microscopic process for the resistance drift is closely related to crystallization, and this is consistent with the analysis in Ref. [13] which showed that the activation energy for the slowest relaxation process in the resistance drift is similar to that for crystallization. Lastly, in an experiment carried out by some of the authors, the crystallization rate was found to increase after the resistance drift took place [14]. This is also understandable because the population of subcritical nuclei increases with the resistance drift, which significantly shortens the nucleation time for crystallization [12].

3. Conclusion

In conclusion, we have shown that the residual pressure in phase-change memory cell is significant due to the density change accompanying the phase transformation. As the cell is pressurized, it was found from the previous first-principles calculations that the energy gap is reduced and the density of localized in-gap states increases. This indicates that the pressurized amorphous GST is more conducting than those made under stress-free conditions. In addition, the crystallization dynamics was also accelerated under the compressive stress. Based on the previous simulation results, we proposed a mechanism for the resistance drift in which the relaxation process in the amorphous GST corresponds to the growth of the crystalline seed inside the amorphous GST, thereby lowering the internal stress. The current flowing through the amorphous GST is reduced due to the increased resistivity, which corresponds to the resistance drift. We have shown that the present microscopic model could consistently explain various experimental observations on the resistance drift.

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