Thermomechanical properties and mechanical stresses of Ge$_2$Sb$_2$Te$_5$ films in phase-change random access memory

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**Abstract**

The biaxial modulus and the coefficient of thermal expansion (CTE) of Ge$_2$Sb$_2$Te$_5$ (GST) films with the thickness of 300 nm were characterized using the substrate curvature method on two different substrates. The elastic modulus of the GST films was also separately determined using nanoindentation. Measured biaxial modulus and CTE from substrate curvature method were $29.5 \pm 1.87$ GPa and $(13.3 \pm 1.39) \times 10^{-6}$ K$^{-1}$ for the amorphous state and $36.8 \pm 1.54$ GPa and $(17.4 \pm 1.21) \times 10^{-6}$ K$^{-1}$ for the crystalline state. The elastic moduli determined using nanoindentation for the amorphous and crystalline states were $33.9 \pm 0.67$ GPa and $58.7 \pm 0.48$ GPa, respectively. Based on the results of the thermomechanical properties, the stresses in the phase-change random access memory (PRAM) structures were calculated using finite element analysis (FEA) considering the thermal and the phase-change stress. The FEA simulations showed that the thermal stress is higher in magnitude than the phase-change stress in a PRAM structure, but the gradient of the phase-change stress is higher than the gradient of the thermal stress.

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1. Introduction

The phase-change random access memory (PRAM) is expected to be one of the most promising candidates for the next-generation nonvolatile electrical memory due to high scalability, high density, high endurance, fast operation speed and low power consumption [1]. In the PRAM device, the rapid and reversible transformation between an amorphous and a crystalline state without phase separation is employed to write and erase information [1,2]. Recrystallization without phase separation is necessary to avoid long range atomic motion leading to a single stable structure. For the Ge$_x$Sb$_y$Te$_z$ system, several different alloys have been found to be suitable: Ge$_x$Sb$_{1-x}$Te$_z$, Ge$_x$Sb$_{1-x}$Te$_z$, and Ge$_x$Sb$_{1-x}$Te$_z$ [3]. Among these alloys, Ge$_2$Sb$_2$Te$_5$ (GST) is most widely used as the phase-change material for PRAM. However, stress in thin GST films is an important factor for practical applications of PRAM devices.

There are two contributing terms to the stress in GST films and PRAM devices according to their origins: the thermal stress originating from the mismatch in the coefficient of thermal expansion (CTE) of a film and the surrounding materials and the phase-change stress induced by the change in the density [4] due to phase transition from the amorphous to the crystalline phase. For instance, elevated temperatures during deposition will result in an introduction of thermal stresses in the film, when it is cooled to room temperature. The phase-change stress can arise due to the difference in densities of the crystalline and the amorphous states of GST when crystallization or amorphization occurs. Since the density of the crystalline state is higher than that of the amorphous state, amorphization should result in a compressive stress in the GST film because of the volume strain from the difference of the density [5]. When the PRAM device is under operation, the CTE differences will induce large thermal stresses and volume changes will induce large intrinsic stresses. Because this can cause mechanical failure, making a major reliability concern for PRAM devices, research on the mechanical behavior of GST thin films is necessary, but only a few studies has been reported [4,6,7].

Therefore, to evaluate the mechanical reliability, the stress behavior and thermomechanical properties of the GST were determined for thin films using the wafer curvature method and nanoindentation. Also, based on the measured values of material properties, stress simulations were carried out for the PRAM device structure using finite element analysis (FEA). Especially, the volume-averaged stress and the gradient of the hydrostatic stresses were evaluated.

2. Experimental details

GST films with the thickness of 300 nm were deposited by direct current magnetron sputtering of Ge$_2$Sb$_2$Te$_5$ target in a vacuum pressure...
at room temperature. The background pressure was below 10⁻³ Pa and the sputtering power used was 300 W. GST films are amorphous in the as-deposited state. In order to characterize the mechanical properties, the GST films were prepared on both a 490 µm Si substrate with (100) orientation and a 500 µm Corning 7740 glass substrate. The mechanical stress changes in the Ge₂Sb₂Te₅ film on the Si and glass were evaluated by measuring the change in the radius of curvature of the film–substrate system as temperature changes using the substrate curvature method (k-Space Multi-beam Optical Sensor System). The change in the radius of curvature of the film was measured by averaging the changes in the spaces between separated multi-beams on a square-shaped sample, 2.5 cm each side. Stress change was calculated from measured curvature change using Stoney’s equation [8]. The Stoney’s equation is given by

\[ \sigma = \frac{E_s t_f^2}{6(1-\nu_s) t_m} \Delta \kappa \]

where \(\kappa\), \(E_s\), and \(\nu_s\) are the curvature, elastic modulus and Poisson’s ratio of the substrate, respectively, and \(t_s\) and \(t_m\) are the thickness of the substrate and film, respectively. This equation assumes that the substrate is isotropic and that the film is much thinner than the substrate. The GST films were thermally cycled by ramping at the rate of 2 °C/min in a vacuum chamber with the base pressure of 10⁻³ Pa. The mechanical properties of the GST film, such as the biaxial modulus \((M_b = E_s / (1-\nu_s))\) and CTE, were determined by measuring the temperature dependence of the thermal stress for the two different substrates, as previously reported [9]. A nanoindenter was also used for determining the hardness and the elastic modulus [10]. Nano XP™ (MTS Nano Innovation Center, Oak Ridge, TN) with a Berkovich indenter was utilized to measure indentation load, contact stiffness and depth simultaneously. Hardness and elastic modulus of 300 nm GST films on Si were determined using the Oliver and Pharr analysis [11].

FEA was carried out to estimate the distributions of the thermal and phase-change stresses of a real PRAM device using a commercial code, ABAQUS 6.2 [12]. Fig. 1 shows the 2-dimensional model geometry of the PRAM device structure. The line width scales of the GST element and the bottom TiN electrode were modeled as 900 nm and 90 nm, respectively. The number of total element generated from meshing was 3270 in the modeling. The GST element was constituted with 125 elements. Axi-symmetry was assumed as the boundary condition on the left side. For the right side, it was assumed that the structure was repeated periodically and infinitely to the direction of right. The properties of the materials used in this study are summarized in Table 1. Each material was assumed to be isotropic and linearly-elastic. The change in the thermal stress at 500 °C was calculated assuming that the system is stress-free at room temperature. It was assumed that the temperature of the PRAM device was reached at 500 °C during process. For the thermal stress, the properties of crystalline GST film were used because the phase of the entire GST element (inside and outside hemisphere) was assumed as crystalline phase. The volume of the phase-change was assumed to be hemispherical, with a footprint area again assumed to be equivalent to that of the bottom electrode (TiN); volume strain for the phase-change was assumed to be 6.8% calculated from the difference between the density of the amorphous and crystalline states [5]. Phase-change stress was examined from the calculated volume strain. Based on these assumptions, the volume-averaged stress of the entire GST element and the gradient of the stress along the bottom edge of the GST element contacting the bottom TiN electrode (distance along path: 0–45 nm) were evaluated and are discussed below.

3. Results and discussion

3.1. Stress evolutions of GST film during thermal cycling

Fig. 2 shows the stress–temperature characteristics of a GST film on a Si substrate heated with the ramping rate of about 2 °C/min. The GST film was thermally cycled between room temperature and 200 °C in vacuum. The GST film was amorphous in the as-deposited state. The onset of plastic deformation of the amorphous GST occurred at approximately 100 °C. Stress of the film increased slightly in the direction of tensile stress because stress relaxed by viscous flow

![Fig. 1. Model geometry for the test structure of PRAM device used for the finite element analysis.](image1)

![Fig. 2. Stress–temperature characteristics of GST film on Si substrate heated with the ramping rate of about 2 °C/min between room temperature and 200 °C.](image2)
A abrupt change of stress then occurred at about 170 °C due to crystallization, where the volume shrinkage due to crystallization [4] resulted in development of a large tensile stress. The stress change calculated based on the densities of the amorphous GST (5.87±0.05 g/cm³) [5] and the crystalline GST (6.27±0.02 g/cm³) [5] is approximately 170 MPa, which agrees well with the experimental results. This large tensile stress due to crystallization then relaxed rapidly to be about 120 MPa in the temperature range of 170–180 °C. From 180 °C to 200 °C, the stress of the crystalline GST decreased with different slope of stress vs. temperature from that of the amorphous GST. During the cooling segment from 200 °C, the crystalline GST showed only elastic deformation and the stress progressed in the tensile direction with constant slope of stress vs. temperature that is different from that of the amorphous GST.

3.2. Biaxial modulus, elastic modulus, and coefficient of thermal expansion of GST films

The biaxial modulus (\(M_f = E_f / (1 - \nu_{fi})\)) and CTE of the GST thin film were determined by measuring the temperature dependence of the thermal stress for the GST films on two different substrates. In the elastic deformation part, the slope of stress–temperature curve calculated from Eq. (1) can be expressed as

\[
\frac{d\sigma}{dT} = k = (\alpha_f - \alpha_i)M_f
\]

where the \(\alpha_f\) and \(\alpha_i\) are the CTE of the substrate and film and \(M_f\) is the biaxial modulus of the film. In Eq. (2), there are two unknowns, the CTE and biaxial modulus of the film. By measuring the stress–temperature behavior of GST films on two different substrates, two different values of \(d\sigma/dT\) (\(k\)) can be obtained. The CTE and the biaxial modulus of the film can then be determined from the following expressions:

\[
\alpha_f = \frac{k_2\alpha_1 - k_1\alpha_2}{k_2 - k_1}
\]

\[
M_f = \frac{k_2 - k_1}{\alpha_2 - \alpha_1}
\]

Here, the scripts of 1 and 2 refer to the two different substrate cases.

In this study, GST thin films deposited on Si and glass substrates were selected to determine the CTE and biaxial modulus using wafer curvature analysis. The stress vs. temperature plots for the amorphous and the crystalline states of the GST films are shown in Fig. 3, from which the slopes \(d\sigma/dT\) can be determined. The GST films were first thermally cycled in the amorphous region between room temperature and 120 °C to remove plastic stress changes, and the slopes of amorphous state were measured in the second thermal cycles. Similarly, the slopes of the crystalline state were measured in the second thermal cycles after GST films were thermally cycled in the crystalline region between room temperature and 200 °C to remove any plastic stress change. The slopes of stress vs. temperature were measured for second cycles from several samples and averaged. For the amorphous state, the slopes were obtained between 30 °C and 150 °C and the slopes for the crystalline state were obtained between 50 °C and 200 °C. The averaged slopes of the GST film on Si and glass substrates were \(-0.358±0.008\) MPa C\(^{-1}\) and \(-0.350±0.011\) MPa C\(^{-1}\) respectively for the amorphous state and \(-0.593±0.034\) MPa C\(^{-1}\) and \(-0.582±0.023\) MPa C\(^{-1}\) respectively for the crystalline state. The slope of the GST film on Si substrate is larger than that on glass substrate for both the amorphous and the crystalline states because the difference of CTE between GST and Si is larger than that between GST and glass. The CTEs of Si and glass substrates are 2.61×10\(^{-6}\) K\(^{-1}\) [20] and 3.25×10\(^{-6}\) K\(^{-1}\) [21]. Based on these informations, the CTE and biaxial modulus of the GST films could be determined using Eqs. (3) and (4), and are tabulated in Table 2. The CTE and the biaxial modulus of the amorphous GST film are 13.3×10\(^{-6}\) K\(^{-1}\) and 29.5 GPa, and those of the crystalline state are 17.4×10\(^{-6}\) K\(^{-1}\) and 36.8 GPa. These values from this study are in good agreement with the results of Kalb et al. [6].

A nanoindenter with a Berkovich tip was also used to determine the hardness and the modulus of the GST thin film deposited on Si substrate. A series of indentations were carried out at a strain rate of 0.05 s\(^{-1}\) with indentation depths ranging from 3 to 280 nm depending on the thickness of the GST film. From the measured load (\(P\)), contact stiffness (\(S\)), and displacement (\(h\), the hardness and the elastic modulus were calculated using the Oliver and Pharr model:

\[
H_{OP} = \frac{P}{A_{c}(h_c)}
\]

\[
E_{OP} = \frac{\sqrt{\pi}}{2h_{c}} \frac{S}{\sqrt{A_{c}(h_c)}}
\]

\[
A_{c}(h_c) = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/8}
\]
where $A_c$ is the calibrated tip area function, and the contact depth $h_c$ is given by

$$h_c = h_{tot} - h_f = h_{tot} - \frac{P}{E_r}$$

(8)

where $h_{tot}$ is the total displacement, $\varepsilon$ is a tip shape dependent parameter ($\varepsilon=0.75$ for a Berkovich tip). The reduced modulus $E_r$ is defined as

$$\frac{1}{E_r} = \frac{(1-\nu_f^2)}{E_f} + \frac{(1-\nu_i^2)}{E_i}$$

(9)

where $E$ and $\nu$ are elastic modulus and Poisson’s ratio, respectively and the subscripts of $f$ and $i$ refer to the film and the diamond indenter tip respectively. Since $E_f$ and $\nu_f$ of the diamond indenter tip are known, the film modulus $E_i$ as a function of depth can be calculated by inputting the Poisson’s ratio of the film. In this relation, the Poisson’s ratio of the GST film was assumed as 0.3.

The Oliver and Pharr hardness and modulus for the crystalline and the amorphous GST films were plotted against the displacement normalized by the film thickness in Fig. 4. The elastic moduli of the amorphous and crystalline GST films measured over defined range using nanoindentation were about $27.8 \pm 6.49$ GPa and $48.6 \pm 4.73$ GPa. Both the Oliver and Pharr hardness and modulus values rise with indentation depth, indicating incorrect estimates of contact area due to pile-up and substrate effects [22,23]. Nevertheless, a reasonable estimate of the modulus of the thin film can be obtained by extracting the modulus of the film at zero indentation depth, where the substrate effects are minimal. In order to minimize a contacting problem, we removed the first 5 data points and extract the modulus values down to zero indentation depth by doing a fit to the rest of the data in the shallow indentation depth region. The elastic moduli of the amorphous and the crystalline films thus determined are $33.9 \pm 0.67$ GPa and $58.7 \pm 0.48$ GPa, respectively. The nanoindentation results reveal that the modulus of the crystalline state is larger than that of the amorphous state, and these results are consistent with previous studies showing larger biaxial modulus for the crystalline state than for the amorphous state [24].

A comparison can now be made for the CTE and the moduli of GST measured in this study to those of other materials. The thermal expansion behavior of the GST is similar to that of metal such as Cu (CTE = $17.7 \times 10^{-6}$ K$^{-1}$ [25]), but the biaxial modulus of Cu (107.8 GPa [17,25]) is larger than that of the GST.

3.3. Stress distribution of PRAM device

Using the measured mechanical properties of the GST films from the substrate curvature method, the stress distribution in the PRAM device was determined from FEA simulations. The hydrostatic stress ($\sigma_{hi}$) can be obtained as the arithmetic average of the three normal stress components ($\sigma_{xx}$, $\sigma_{yy}$, $\sigma_{zz}$) when shear stresses are zero, and expressed as

$$\sigma_{hi} = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3}$$

(10)

Because the hydrostatic stress will result in volume changes, a large hydrostatic stress is known to be the greatest threat to the reliability of interconnects. Especially, a large hydrostatic stress is known to be a driving force for the stress voiding nucleation, and the gradient in the hydrostatic stress is a driving force for stress voiding growth [26]. Therefore, it is important to estimate the hydrostatic stress in the GST element, where the volume change due to local phase transition evolves. Fig. 5 shows the volume-averaged hydrostatic stresses for the entire GST element induced by thermal and phase-change stresses. The thermal stress was 112 MPa and the phase-change stress was 3 MPa. The thermal stress was two orders of magnitude larger than the phase-change stress, because the phase-change stress developed locally around the bottom TiN electrode for the entire GST element. Here, because the volume-averaged stresses were for the entire GST element, the magnitudes of the stresses were estimated as small values. In terms of the volume-averaged stress, the thermal stress contributes mostly to the mechanical failure in PRAM devices. The gradient of the hydrostatic stress, which plays a greater role in mechanical failure rather than the magnitude of the stress [26], was also evaluated and shown in Fig. 6. The path of the hydrostatic stress

![Fig. 4. The result of the Oliver and Pharr a) hardness and b) elastic modulus of the crystalline and amorphous GST films plotted as a function of the indentation depth normalized by the film thickness using nanoindentation.](image)

![Fig. 5. Volume-averaged hydrostatic stress of GST element in modeled PRAM device for the thermal stress and phase-change stress.](image)
stress is considered at the bottom of the GST element along a path in radial direction, as shown in the Fig. 6 (a). As shown in Fig. 6(c), the phase-change stress was abruptly increased in the direction of the tensile stress due to the phase transition at the interface between the GST element and TiN (distance along path: 0–45 nm). The thermal stress was gradually increased to the distance along the path of 0 nm. The gradient in the phase-change stress were larger than that of the thermal stress. Mechanical failure accompanied by volumetric change such as void and hillock of PRAM devices can therefore be attributed to the phase-change stress, as well as the thermal stress. Both the thermal and the phase-change stresses should be taken into consideration for understanding the mechanism of mechanical failure and optimizing the mechanical reliability of the PRAM device.

4. Conclusions

In this study, the mechanical stress evolution and thermomechanical properties of GST thin films were evaluated. Mechanical stresses of the GST films have different behaviors in its amorphous and crystalline states. It was found that large tensile stress evolved due to crystallization. The biaxial modulus and CTE of the GST films were determined by measuring stress vs. temperature of the amorphous and the crystalline GST films deposited on two different substrates using the substrate curvature method. The elastic moduli of the amorphous and the crystalline GST films were also determined from nanoindentation. The biaxial modulus and the elastic modulus were higher for the crystalline state than for the amorphous state. The stress distribution in the PRAM structure was also examined using the FEA simulations. It was found that the magnitude of the thermal stress was higher than that of the phase-change stress in the PRAM, but the gradient of the phase-change stress is higher than the gradient of the thermal stress. Therefore, both the thermal and phase-change stresses should be taken into consideration for understanding the mechanism of mechanical failure and optimizing the mechanical reliability of the PRAM device.

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