Stability of Amorphous Chalcogenide Materials : Phase Transition and Fragility

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ABSTRACT

Present-day application of phase change random access memory (PCRAM) strongly demands the development of phase materials with superior capabilities in high switching speed, large set/reset contrast and low power consumption. Amorphous $Ge_2Sb_2Te_5$ (GST) alloys are most promising candidate in this respect, however, still suffered from inherent phase instability issues. Even though the study on the phase instability of amorphous GST is critical to many reliability issues in PCRAM devices, such as retention loss and resistance drift, it has not yet been thoroughly analyzed due to the difficulties in analysis of amorphous states and measurement of thin film forms. Here the *in-situ* mechanical stress analysis with continuous heating were utilized in order to measure the glass transition temperature (T_g), structural relaxation, crystallization temperature (T_x) and fragility (m) for pure and N-doped $Ge_2Sb_2Te_5$ alloys in amorphous state. According to the values of T_g, T_x and m, we revealed that the phase stability was enhanced with N doping concentration. Presented results on the phase and structural changes in amorphous $Ge_2Sb_2Te_5$ alloys provide further understanding on the reliability issues of PCRAM.

Key words: Phase change materials, Phase stability, $Ge_2Sb_2Te_5$, Mechanical stress analysis, Glass transition, Fragility

1. INTRODUCTION

$Ge_2Sb_2Te_5$ (GST) has been actively pursued for phase change materials for the development of phase change random access memories (PCRAM) due to its high phase change speed, large contrast between properties of crystalline/amorphous state, and low power consumption required to cause phase transition. However, there are still many reports on many reliability issues of PCRAM such as resistance drift and retention issues. Recent studies on the origin of the resistance drift and retention loss, inherent phase instability of amorphous GST strongly affects these issues[1,2], therefore, high stability of amorphous state in amorphous GST is highly required.

The instability of amorphous state is defined as vulnerability against phase and structural changes which include three behaviors, i) the structural relaxation; structural change to reach more stable state, ii) the glass transition; 2nd order phase transition to super-cooled liquid, and iii) the crystallization; phase transition to crystalline phase. Most common way to detect these behaviors is thermal analysis; differential scanning calorimetry (DSC), however, it is hardly applicable to thin film. Moreover, it is hard to detect the slight signal changes associated with the glass transition and the structural relaxation. Here we clearly observed the volume change associated with those phase and structural changes in amorphous GST film by using *in-situ* mechanical stress analysis, because biaxial stress evolution due to volume change in film/substrate system is easily detected.

By detecting these behaviors, quantitative parameters to evaluate the stability of amorphous GST were provided. Those are crystallization temperature (T_x), glass transition temperature (T_g), and fragility (m). The fragility is the universal parameter for the stability of amorphous materials and can be expressed by using activation energy of glass transition at T_g, E as follows[3,4],

$$m = E/(2.303RT_g) \tag{1}$$

where R is the gas constant. E could be obtained by well-known Moynihan's plot[5],

$$\frac{d\ln\beta}{d(1/T_g)} = -\frac{E}{R} \tag{2}$$

where β is the heating rate in units of K/min. For m ~16, the glass is strong glass with high stability, and the larger m is fragile glass with less stability.

In this work, we observed structural relaxation, glass transition, and crystallization of amorphous GST film by using *in-situ* mechanical stress analysis. Based on the measured quantitative parameters, the phase stability of amorphous GST and effect of N doping has successfully been evaluated.

2. EXPERIMENTS

Amorphous $Ge_2Sb_2Te_5$ films were deposited on silicon wafer by DC magnetron sputtering at room temperature. The gun power and the chamber pressure were 80 W and 3 mTorr, respectively. The gas mixing ratio was Ar/N_2 = 40/2, 40/6, and 40/12 for the preparation of N-doped GST and N contents were determined to be 1.35, 4.32, and 10.1 at. %, respectively. The phase of as-deposited GST thin films was observed to be amorphous state, as confirmed by Grazing Incident X-ray Diffraction (GIXRD, New D8 Advance). The wafer curvature measurement with multi-beam leaser technique was used (kSA Multibeam Optic System, depicted in Fig. 1 to determine mechanical stress of the film during thermal cycling in the N_2 atmosphere at 10 Torr. The biaxial stress changes (σ) were determined by the changes of curvature according to Stoney's equation given by as follows[6],

$$\sigma = \frac{1}{6}\cdot Y_s \cdot \frac{t_s^2}{t_f}\cdot \kappa \tag{3}$$

where t_f is thickness of film, Y_s and t_s are biaxial modulus and thickness of substrate, respectively. Resolution of mechanical stress analysis was determined to be approximately 0.1 MPa for stress change during heating, approximately 5 MPa for absolute stress.

3. RESULTS & DISCUSSION

To investigate the thermally-induced phase and structural changes in amorphous GST thin film, stress-temperature curve of 500 nm-thick amorphous GST thin film on 100 μm-thick silicon substrate is measured as seen in Fig. 2. Positive value of stress means tensile stress and volume shrinkage of film, and negative value means compressive stress and volume expansion of film. Red circles indicate the stress-temperature curve of pure GST, as the temperature increases up to ~ 70 °C during the heating, the stress changes toward compressive direction was detected because the film has larger coefficient of thermal expansion (CTE) than silicon substrate. For further heating up to 130 °C, tensile stress evolution due to structural relaxation also detected.

As the temperature approaches 130 °C, significant amount of tensile stress evolution distinguished from the stress changes associated with structural relaxation was detected, this phenomenon is well-known densification accompanied with crystallization of amorphous GST. The crystallization at this point is confirmed with the abrupt optical reflectivity and GIXRD data. Further heating of crystalline GST leads to stress relaxation toward compressive direction and slight tensile stress evolution due to hexagonal transition around 250 °C. However, the stress change associated with glass transition was

not observed, it is likely due to too small region of super-cooled liquid region of pure GST; T_g exhibit similar value with T_x.

In Fig. 2, yellow, green, and blue circles indicates the stress-temperature curve of N 1.35, 4.32, and 10.1 at. % doped GST, respectively. It is well-known that N doping on the GST retards the crystallization behavior of GST, therefore it is likely the phase stability of GST will also be developed by N doping. N doping on the amorphous GST leads to the extension of super-cooled liquid region, and enables the clear measurement of glass transition temperatures because it leads to the separation of glass transition temperature and crystallization temperature. For the N 1.35 at. % doped GST indicated in yellow circles, stress change toward compressive direction was detected at approximately 150 °C. This gradual stress change is due to the volume expansion associated with glass transition at T_g. The crystallization temperature of N-doped GST also deviated from pure GST, manifested in the shift of the temperature which evolution of tensile stress occurs. These results of deviated T_g and T_x in N-doped GST indicate that N doping can significantly enhance the phase stability of amorphous GST.

The T_g of N-doped GST shows clear heating rate dependence for 1, 2.5, 6.5, and 13 K/min. Measured heating rate dependence of T_g can be used to extract the fragility (m). The fragility of N-doped GST was determined in accordance with Eq.(1) and Eq.(2). Compared to the fragility value of approximately 90 for pure GST obtained by using ultrafast heating DSC by other researcher[7], N-doped GST exhibits much lower fragility of 55, 33, and 29 for N 1.35, 4.32, and 10.1 at. % doped GST, respectively. Fragility measured for N-doped GST and extrapolated viscosity (η) changes according to Vogel-Fulcher relation ($\eta \sim \exp\{D \cdot T_0/(T-T_0)\}$, where D and T_0 are fitting parameters) is indicated as gray dashed line in Fig. 3. As the fragility is defined as a universal classification of glass by its stability against the structural reconfiguration, fragility data for N-doped GST show more stable nature compared to pure GST.

4. CONCLUSION

The structural relaxation, glass transition temperature (T_g), crystallization temperature (T_x), and fragility (m) were successfully detected from the *in-situ* mechanical stress analysis with continuous heating. Compared to pure GST, T_g and m of N-doped GST shows that the N doping effectively enhance the amorphous phase stability of GST. Instability in PCRAM can be evaluated by this methodology and can further be developed using the material optimization in this respect. In addition, discovering exact role of dopant can achieve successful selection of dopant for improving the reliability.

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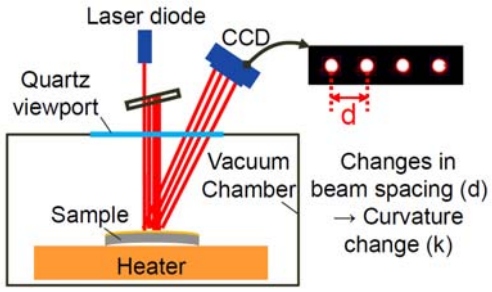

Fig. 1 Schematic of kSA multibeam optic system for *in-situ* mechanical stress analysis.

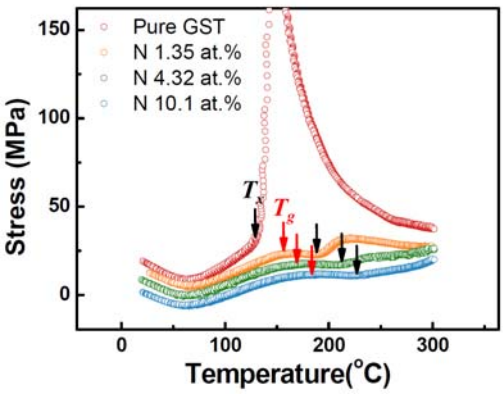

Fig. 2 Stress-temperature curve of pure and N-doped GST during heating. Black arrows indicate T_x and red arrows indicated T_g.

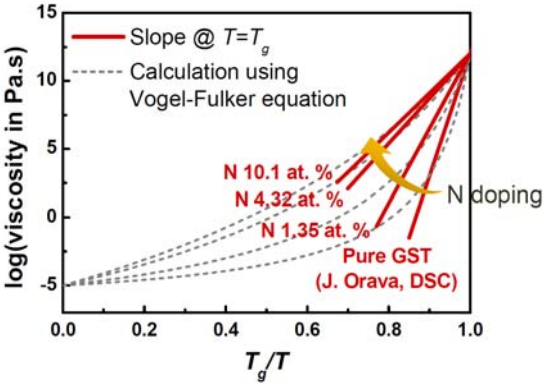

Fig. 3 Fragility measured for pure and N-doped GST and extrapolated viscosity changes according to Vogel-Fulcher relation.

Biographies

Ju-Young Cho received his B.S. degree in Department of Materials Science and Engineering at Seoul National University, Seoul, Korea in 2009. He is currently Ph. D. student in Department of Materials Science and Engineering at Seoul National University. His research interests have been the characterization of the phase stability in chalcogenide glass and amorphous oxide semiconductors.

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