I O U R N A L O F

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Investigation on the effect of silicon doping in Sb₂Te₃ phase change materials

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The crystallization behavior and physical properties of Si-doped Sb₂Te₃(Si : ST) materials applicable to phase change random access memory (PCRAM) was studied with the purpose of overcoming their current weaknesses regarding use in PCRAM. Phase change materials were prepared by DC magnetron sputtering. Si-doped Sb₂Te₃materials have anSb₂Te₃(ST) rhombohedral structure regardless of Si content and a segregated region consisting of Si was founded. The Si amorphous phase located at grain boundaries interrupted grain growth, therefore the grain size became smaller. These crystal structures and their bonding characteristics were confirmed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Increasing the amount of Si in Sb₂Te₃ increased the sheet resistance, crystallization temperature (T_c) and crystallization activation energy (E_a), which was confirmed by a 4-point probe measurement. Furthermore, Metal-Insulator-Metal (MIM) devices based on ST and Si : ST were fabricated and the measured threshold voltage (V_{th}) of Si : ST was higher than ST. These results showed that Si doping improved thermal stability.

Key words: PCRAM, Si doped SbTe, Crystallization temperature, Thermal stability.

Introduction

In the semiconductor industry, the memory market has been dominated by dynamic random access memory (DRAM) and flash memory. However these types of devices have reached a limit resulting from the high density integration of the process. The main shortcomings of DRAM and flash memory are their volatility and slow speed, respectively [1, 2]. Therefore, a new memory type is needed and should be investigated to overcome these shortcomings. Phase change random access memory (PCRAM) is one of the several promising new memory technologies that have nonvolatile properties, fast speed and low power consumption [2-4].

The PCRAM is operated via the phase change of chalcogenide glass.[4] GeSbTe is one of the most studied phase change materials [5]. Many new phase change materials have been investigated with the aim of improving their properties, such as phase change speed, electrical resistance of the crystal and crystallization temperature [6-8]. Electrical resistance in the crystalline phase and the crystallization temperature are important parameters used to determine the power consumption and thermal stability of the device, respectively [2]. Our research team chose Sb₂Te₃(ST)-based phase change materials because of high crystallization speed [9]. However, ST also has disadvantages of relatively low electrical resistivity and low crystallization temperature, but it has been found that these problems can be solved

through doping elements. Generally the doping of heterogeneity elements has been known to increase the crystal resistivity and crystallization temperature. N, Ag, Si and other elements have been used as dopants [9-12]. Our research team selected Si as a dopant, and changes in crystal structure and physical properties were investigated by adding a small amount of Si to Sb2Te3 (Si:ST), because large amounts of Si are known to decrease phase change speed [13].

Experimental details

Sb₂Te₃(ST) and Si-doped Sb₂Te₃(Si : ST)thin films were deposited by DC magnetron sputtering (SHS-M3-400D, Samvac, Korea) on TiN, carbon grid mesh and glass substrates at room temperature. The composition of the Si in the films was controlled by changing the sputtering power. The base pressure was maintained below $\sim 10^{-6}$ Torr. The working pressure and Ar gas flow rate were 8.0×10^{-3} Torr and 40 sccm, respectively. Annealing was performed by a halogen heater at 0.3 Torr and 80 sccm of Ar gas flow with a heating rate of 10 °C/min and was maintained for 20 min. The thickness of the films was about 130 nm as measured by a surface profiler (AS500, KLA-Tencor Co.). The film compositions were measured by transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDS, JEM-2100, Jeol). The differences in the crystal structure as a result of Si doping were identified by glancing mode X-ray diffraction (XRD, Ultima IV, Rigaku). The chemical bonding state of the Si in the films was analyzed by X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo U.K.). Transmission electron microscopy (TEM, JEM-2100, Jeol) 50,000X, 600,000X

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images and their corresponding selective area electron diffraction (SAED) patterns were observed using a 200-KeV electron beam. The change of the sheet resistance with respect to temperature and the amount of Si was identified by an ex-situ method measured after annealing and an in-situ method measured simultaneously with annealing by a 4-point probe (CMT-SR 200N, Korea). A metal-insulator-metal(MIM) cell was fabricated by applying a phase change material as an insulator and current-voltage (I-V) characteristics were analyzed by a semiconductor parameter analyzer (Agilent B1500A).

Results and Discussion

Fig. 1(a) shows the four XRD patterns which detail a different chemical composition before and after annealing at 350 °C for 20 min. The as-deposited film showed amorphous characteristics. All annealed films had only an Sb₂Te₃ rhombohedral structure and main peaks correspond to a family of (015), (1010) and (110) planes. These patterns showed that Si could not form a crystal structure in the films regardless of Si-doping content. The decrease in the main peak intensity with an increase of Si indicates that the crystallization of Sb₂Te₃ films was disturbed by Si. The full width at half maximum (FWHM) value showed an opposite trend compared to peak intensity. The crystalline grain size of each Si : ST was calculated by the Debye-Scherrer formula,

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos \theta}$$

Where D_{hkl} is the grain size of the (hkl) plane, λ is the wavelength (0.15406 nm), β is the FWHM, and θ is the diffraction angle, respectively. Fig. 1(b) indicates that the grain size decreased with an increase in the amount of Si. The drastic decrease of the grain size occurred at an Si composition between 2.3% and 4.3% in particular. The XPS analysis showed how the chemical bonding state of Si in the Si : ST film changed after annealing in terms of crystallization. Fig. 2 shows the results of the chemical state through the peak separation of the Si 2p narrow scan. Peak position of the as-deposited Si : ST



Fig. 1. (a) X-ray diffraction analysis of the ST and Si : ST films with various Si content and (b) the value of FWHM and grain size according to Si content.

film is 102.46 eV and 103.54 eV, which apply to the Si-N and Si-O bonding, respectively, can been seen in Fig. 2(a) [14-15]. Peak position and number changed after annealing. Fig. 2(b) shows crystalline Si : ST bonding peaks for Si-Si, Si-N and Si-O at 100.65eV, 101.56eV and 102.86eV, respectively [16-18]. Si-N bonding and Si-O bonding were found in both as-dep film and annealed film. This bonding likely came from surface contamination, because very low amounts of N and O were determined by the TEM-EDS analysis. However, Si-Si bonding was shown in the annealed film,



Fig. 2. Result of the XPS Si 2p narrow scan of the (a) as-deposited Sb_{36.4}Te_{55.2}Si_{8.4} and (b) Sb_{36.4}Te_{55.2}Si_{8.4} annealed at 350 °C.



Fig. 3. TEM images and their corresponding SAED pattern of (a) as-deposited $Sb_{39,5}Te_{60.5}$, (b) annealed $Sb_{39,5}Te_{60.5}$, (c) annealed $Sb_{38,7}Te_{59,0}Si_{2.3}$, (d) annealed $Sb_{37,6}Te_{58,1}Si_{4.3}$ and (e) annealed $Sb_{36,4}Te_{55,2}Si_{8,4}$.

therefore Si segregated and formed a Si-Si phase in the Sb₂Te₃ phase change material.

Fig. 3 shows the TEM plane view image and their corresponding SAED patterns of as-deposited ST,

annealed ST and various compositions of Si : ST annealed films. As seen in the plane view, the as deposited state was found to be amorphous which does not include the grains, however grains had appeared after annealing and the grain size decreased with increasing Si content. This tendency was confirmed by the SAED pattern, where the as deposited ST had a halo-type pattern, indicating it was amorphous and the annealed film had a dotted ring pattern due to crystallization. Increasing the amount of Si in the ST dotted pattern yielded close to a perfect ring pattern. This indicated a decreasing the grain size. The ring radius from the SAED pattern provided a crystal plane in the film by the following formula, where d is the interplanar spacing, L is the camera length, λ is the wavelength



of the electron beam, r is the radius of ring pattern [18]. The interplanar spacing was calculated as 3.2, 2.24 and 2.07 Å corresponding to the (015), (1010) and (110) planes of the Sb₂Te₃ rhombohedral structure, respectively, which was in accordance with the results of the XRD analysis. The HRTEM image of ST and Si : ST is depicted in Fig. 4. Fig. 4(a) depicts one large grain, which is shown in the image, however, as seen in Fig. 4(b) many small grains and several amorphous regions appeared. This image indicated that the grain size decreased as a result of increasing Si. The amorphous



Fig. 4. HRTEM image of (a) ST and (b) Sb_{36.4}Te_{55.2}Si_{8.4} after annealing at 350 °C.



Fig. 5. Sheet resistance as a function of temperature by (a) ex-situ and (b) in-situ methods.



Fig. 6. Sheet resistance of (a) ST and (b) $Sb_{38.7}Te_{59.0}Si_{2.3}$ was a function of temperature with changing heating rate; (c) corresponding Kissinger's plot.



Fig. 7. I-V curves of (a) ST and (b) Sb_{36.4}Te_{55.2}Si_{8.4} by memory switching in the (c) MIM cell device.

region in Si-doped Sb_2Te_3 is thought to be segregated Si which did not crystalize. This segregated amorphous Si is located between the grains and interrupted grain growth, therefore decrease in grain size corresponded to an increasing Si content.

As shown in Fig. 5, the sheet resistance of Sb₂Te₃ and Si-doped Sb₂Te₃ with a change in temperature was measured by an ex-situ and in-situ 4-point probe method. Fig. 5(a) shows the sheet resistance of films annealed at 100 °C, 150 °C, 200 °C, 250 °C, 300 °C and 350 °C. Sheet resistance of every film decreased as temperature increased. In addition, crystallization temperature (T_c) which occur abrupt drop of resistance increased with an increasing Si contents. Fig. 5(b) shows an in-situ method using a heating rate of 10 °C/min. The T_c of ST and Si2.3:STwas found to be approximately 205 °C and 215 °C, respectively.

Fig.s 7(a) and (b) show the in-situ four-point probe measurements for ST and Si2.3:STat various heating rates. It was found that T_c increased with an increasing

heating rate. The activation energy for crystallization was obtained by Kissinger's analysis that is indicated by the following formula [19-20].

$$\ln \frac{dT/dt}{T_c^2} = C + \left(\frac{E_a}{k_B T_c}\right)$$

Where dT/dt is the heating rate, T_c is the crystallization temperature, C is a constant, E_a is the activation energy, and k_B is the Boltzmann constant. As shown in Fig. 6(c), the slopes of the linear lines in the Kissinger's plot represent the E_a of ST and Si2.3ST, which were calculated as 0.318 eV and 0.839 eV, respectively. Si doping appears to lead to increased activation energy for crystallization.

The I-V curves of ST and Si : ST are shown in Fig. 7. The threshold voltage increased from 1V to 1.6V with Si doping, suggesting that Si-doped St needed more energy for switching. T_c , E_a and V_{th} increased with increasing Si content, since the covalent bonds in the amorphous phase were strengthened by the Si atoms. The bond strengths that included Si were larger than Sb-Sb, Sb-Te and Te-Te, and the coordinate number of Si was more than Sb and Te [21]. Therefore, cohesion of the atoms was reinforced because the strength and number of covalent bonds had increased, leading to an increase of T_c , E_a and V_{th} .

Conclusions

The crystal structure and physical properties of Sidoped Sb₂Te₃ were studied. According to the results, the crystalline phase of Sb₂Te₃ was not changed by Si doping, however grain size decreased. T_c, E_a and V_{th} increased with an increasing Si content, since the covalent bonds in the amorphous phase were strengthened by the Si atoms. This strengthening led to improved thermal stability. In conclusion, Si doping of Sb₂Te₃ enhanced the thermal and electrical characteristics of the phase change material.

Reference

- M. H. R. Lankhorst, B. W. S. M. M. Ketelaars and R. A. M. Wolters, Nat. Mater. 4 (2005) 347.
- 2. H. S. P. Wong, S.Raoux, S. B. Kim et al., *Proc. IEEE* 98 (2010) 2201.
- 3. M. H. Kryder and C. S. Kim, *IEEE Trans. Magn.* 45 (2009) 3406
- 4. S. R. Ovshinsky, Phys. Rev. Lett. 21 (1968) 1450.

- 5. A. V. Kolobov, P.Fons, A. I. Frenkel et al., *Nat. Mater.* 3 (2004) 703.
- 6. M.Wuttig and N. Yamada, Nat. Mater. 6 (2007) 824.
- 7. G C. Sosso, GMiceli, S. Caravati et al., *Phys. Rev. B* 85 (2012) 174103.
- 8. C. W. Sun, J. Y. Lee, M. S. Youm and Y. T. Kim, *Phys. Stat. Sol.* 1 (2007) R25.
- 9. Y. Zhang, J. Feng, Z. Zhang et al., *Appl. Surf. Sci.* 254 (2008) 5602.
- 10. J. H. Jeong, H. K. Kim and D. J. Choi, J. Mater. Sci. 48 (2013) 6167.
- 11. H. Y. Kim, N. H. Kim, J. S. Roh and D. J. Choi, *Curr. Appl. Phys.* 11 (2011) S404.
- Y. Gu, S. Song, Z. Song, Y. Cheng, X. Du et al, J. Appl. Phys. 111 (2012) 054319.
- Y. Cheng, N. Yan, X.D. Han et al, J. Non-Cryst. Solids 356 (2010) 884
- 14. M. S. Donle, D. R. Baer, T. G. Stoebe, *Surf.Interface. Anal.*11 (1998) 335.
- 15. Y. S. Jin, Q. J. Yan, Z. R. Yin, Y. Chen, J. Chem. Soc. Faraday Transactions 91 (1995) 381.
- R. Alfonsettia, L. Lozzib, M. Passacantandobet al, *Appl. Surf. Sci.*70 (1993) 222.
- 17. T. N. Wittberg, J. R. Hoenigman, W. E. Moddeman et al, J. Vac. Sci& Tech.15 (1978) 348.
- 18. X. R. Yu, H. Hantsche, Surf. Interface. Anal. 20(1993)555
- F. Rao, Z. Song, K. Ren et al, Nanotechnology 22 (2011) 145702.
- 20. Z. Zhang, S. Song, Z. Song, Y. Cheng et al, Appl. Phys. Lett. 102 (2013) 252106.
- 21. A. D., in"John,Lange's handbook of chemistry"(McGraw-Hill, New York, 1992) p. 4.41.