Nitrogen and Silicon Co-Doping of $Ge_2Sb_2Te_5$ Thin Films for Improving Phase Change Memory Performance *

CAI Yan-Fei(蔡燕飞)[1], ZHOU Peng(周鹏)[1], LIN Yin-Yin(林殷茵)[1**], TANG Ting-Ao(汤庭鳌)[1], CHEN Liang-Yao(陈良尧)[2], LI Jing(李晶)[2], QIAO Bao-Wei(乔保卫)[3], LAI Yun-Feng(赖云峰)[3], FENG Jie(冯洁)[3], CAI Bing-Chu(蔡炳初)[3], CHEN Bomy(陈邦民)[4]

[1]*Department of Microelectronics, ASIC & System State Key Lab, Fudan University, Shanghai 200433*
[2]*Department of Optical Science and Engineering, Fudan University, Shanghai 200433*
[3]*Research Institute of Micro/Nanometer Technology, Shanghai Jiao Tong University, Shanghai 200030*
[4]*Silicon Storage Technology, Inc., 1171 Sonora Court, Sunnyvale, CA94086, U.S.A.*

(Received 10 October 2006)

Electrical properties and phase structures of (Si+N)-codoped $Ge_2Sb_2Te_5$ (GST) for phase change memory are investigated to improve the memory performance. Compared to the films with N or Si dopants only in previous reports, the (Si+N)-doped GST has a remarkable improvement of crystalline resistivity of about 10^4 mΩcm. The Fourier-transform infrared spectroscopy spectrum reveals the Si–N bonds formation in the film. X-ray diffraction patterns show that the grain size is reduced due to the crystallization inhibition of the amorphous GST by SiN_x, which results in higher crystalline resistivity. This is very useful to reduce writing current for phase change memory applications.

PACS: 61. 43. Dq, 61. 72. Ww, 81. 30. Hd, 84. 37. +q

Phase change memory (PCM), one of the best candidates for next generation non-volatile memory, has advantages of high density, write/read performance, endurance, scalability, process simplicity, and CMOS compatibility.[1] As a typical phase change material used in both PCM and DVD optical storage systems, $Ge_2Sb_2Te_5$ (GST) has been investigated for decades.[2−4] It can be reversibly converted between highly resistive amorphous phase and low resistive crystalline phase under the energy effect. For optical storage applications, the phase of GST can be changed by laser pulses, and the signals can be read out through the reflectivity difference. As to PCM applications, the phase change is executed by electrical pulses while the signals can be identified by resistance variation.[5] However, a large reset current is necessary for the pure GST compound to transform crystalline to an amorphous state,[6] which challenges the wide use of PCM. Up to date, many solutions have been proposed for reduction of the programming currents, such as doping impurities,[7] sandwiching a high-resistive heater such as amorphous carbon,[8] decreasing the contact area between GST and the electrode.[9] Among them, impurity doping is proven to be an effective way for reduction of writing current[7,10] without complicating the fabrication process and without increasing the cost of products too much.

Impurity doping initially carried out with N is subsequently extended to O-, and Si-dopings[11] among which N- and Si-dopings are identified to increase the crystalline resistivity of the GST film considerably. Horii *et al.*[7] demonstrated that the crystalline resistivity of N-doped GST (N=7at.%) can increase up to 20 mΩcm in comparison to 2 mΩcm of a pure GST. Moreover, our group has successfully obtained a value of 11 mΩcm by Si-doping,[11] more than one order higher than that of pure GST. However, those important efforts do not meet the practical application requirement of PCM entirely yet, because it is difficult to increase the crystalline resistivity further by excessive doping of one single element. For example, excessive N-doping could result in lower crystalline resistivity[12] and excessive Si-doping also has little effect on the further resistivity increase. Our simulation shows that the reset current could be reduced by one order in a conventional 1T1R cell only when the crystalline resistivity is increased by two orders. Thus, the development of a new doping method to obtain much higher crystalline resistivity is high on the agenda.

In this Letter, we report codoping of Si and N to increase the resistivity of crystalline GST by two orders compared to Si- or N-doping with an appropriate on-off ratio. The effects of (Si+N)-codoping on structural properties of GST are also discussed.

The (Si+N)-doped GST films were deposited on SiO_2/Si (100) wafers by magnetron co-sputtering of two targets of GST alloy and Si single crystal. The deposition atmosphere is a mixture of N_2 and Ar gases with an optimized flow rate of 5 sccm for N_2 and 25 sccm for Ar at room temperature. The base pres-

* Supported by the National Natural Science Foundation of China under Nos 60206005, 60376017, and 60676007, the Shanghai Applied Materials Research and Development Foundation and Silicon Storage Technology, Inc.

** To whom correspondence should be addressed. Email: yylin@fudan.edu.cn

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sure in the chamber and working pressure for sputtering were 5×10^{-6} and 6×10^{-3} mbar, respectively. The sputtering power is 100 W for GST and 50 W for Si. Additionally, pure GST, N-doped GST, and Si-doped GST films were deposited under the same conditions with an adjusted gas mixture. The film thickness of all the samples was about 200 nm. All the samples were annealed by rapid temperature annealing (RTA) after deposition at various temperatures for 10 min under a protective argon atmosphere. The annealing temperature is ranged from 140°C to 490°C to achieve a good crystalline nature of all the samples inspected by XRD patterns. Fourier transform infrared spectroscopy (FTIR) was employed to study the Si–N compounds using Nexus 470. X-ray diffraction (XRD) of the films was carried out in a Rigaku D/MAX 2550 V diffractometer using Cu K_α radiation to inspect the GST crystal structures. The I–V characteristics of thin films were investigated by using a semiconductor parameter analyser (Keithley S4200) in the device sandwiched with two tungsten electrodes.

Figure 1 and Table 1 show the effect of (Si+N)-codoping on the resistivity of the films measured by four-point probing technique under different annealing temperatures. The typical resistivity of (Si+N)-codoped GST is about 10^9 mΩcm below 180°C and the value decreases rapidly by 5 orders of magnitude at around 300°C above which it levels off. The crystallization temperature of GST is also increased after Si or (Si+N) codoping, as shown in Fig. 1, which indicates a better thermal stability for the improvement of memory-cell reliability. Table 1 shows the resistivity of all the films after annealed at 400°C. The highest resistivity is (Si+N)-codoped GST, reaching 10^4 mΩcm, nearly two orders higher than 17 mΩcm of Si-doped GST as well as the best value of N-doped GST in the previous reports.[7]

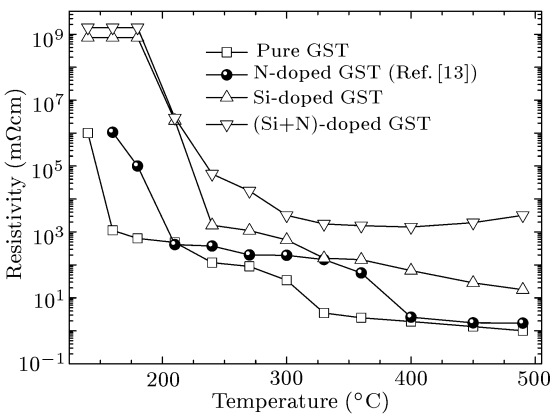


Fig. 1. Dependence of the resistivity on annealing temperature.

Figure 2 shows the FTIR transmission spectrum for pure and (Si+N)-codoped GST annealed at 490°C for 10 min. With the codoping of Si and N, the vibration mode at approximately 850 cm^{-1} appears, which can be attributed to the Si–N stretching mode.[14] It is proposed that the N atoms came into the film during the co-sputtering of Si and GST. Inevitably, some N atoms bonded to Si atoms; as a result, SiN_x compounds are formed.

Table 1. Resistivity of pure, N-doped, Si-doped and (Si+N)-codoped GST films after being annealed at 400°C for 10 min.

Specimens	Pure GST	N-doped GST (Ref. [13])	Si-doped GST	(Si+N)-codoped GST
Resistivity (mΩ cm)	1.3	1.7	28.5	1920

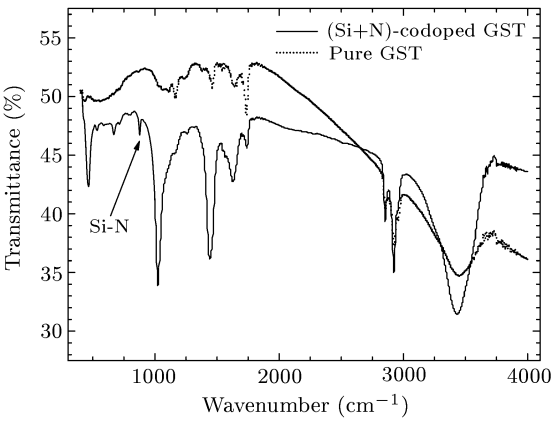


Fig. 2. Infrared absorption spectrum of pure and (Si+N)-codoped GST film annealed at 490°C for 10 min.

For comparison, the XRD patterns of the above samples are shown in Fig. 3. The samples were annealed at 450°C for 20 min in Ar atmosphere. Generally, there are two phase symmetries of hexagonal-close-packed (*hpc*) and meta-stable face centred cubic (*fcc*) structures for crystallized GST.[15] Here the phase symmetry is hexagonal for the pure GST, as shown by XRD pattern in Fig. 3, while the face-centred cubic structure for both Si-doped GST and (Si+N)-codoped GSTs. It is supposed that the incorporation of Si plays a key role in stabilization of the *fcc* structure. Meanwhile, characteristic peaks of (Si+N)-codoped GST are much broader than others. From the calculation from of Scherrer formula, the grain size of (Si+N)-codoped GST is much smaller than those of pure and Si-doped GSTs, just as listed in Table 2. The reason for the reduction of crystalline GST grain size is related to the incorporation of Si and N atoms into the structures, which facilitate the formation of Si–N compounds. The nitrides are of great importance in suppressing the grain growth.[12] It is reasonable that the incorporated Si, N and SiN_x work as inhibitors to the crystallization of the amorphous chalcogenide materials. However, as observed in our experiment and as reported in the literature,[13] a single element such as Si and N cannot induce such small grains. Thus it is suggested that SiN_x plays a key role of suppressing the grain growth among these inhibitors. As a result, the

density of grain boundaries is increased remarkably, which scatter carriers more effectively and lower their mobility.[16] Thus, the bulk resistivity is enhanced.

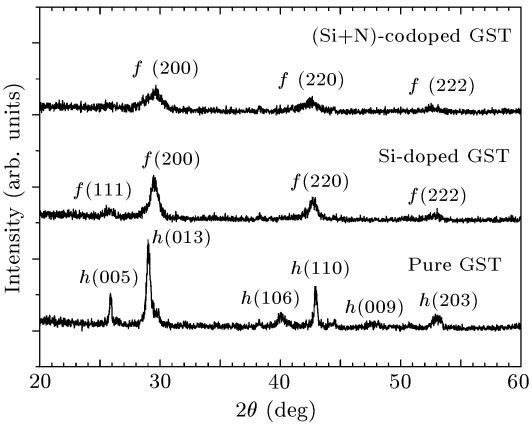


Fig. 3. XRD spectra of pure, Si-doped and (Si+N)-codoped GST films after 450°C annealing for 20 min (*fcc* and *hcp* represented by f and h, respectively).

Table 2. Average crystal grain size of pure, Si-doped and (Si+N)-codoped GST films after 400°C annealing for 10 min.

Specimens	Pure GST	Si-doped GST	(Si+N)-codoped GST
Average Grain size (nm)	20.4	10.7	5.6

The static current–voltage (I–V) characterizations of the device with pure and (Si+N)-codoped GST films in thickness 100 nm are shown in Fig. 4. Since the initial amorphous state of the (Si+N)-codoped GST film is of high resistance, the current flowing through the device is very small when the applied voltage is lower than the threshold voltage $V_{\rm th}$. However, when $V_{\rm th}$ is reached, filament formation,[20] combined with crystallization of the film, lowers the resistance of the material and switches the chalcogenide film into a low resistive state that persists even if the voltage is removed and the material is cooled. This is the typical characteristics of memory switching effect. The dynamic resistance of the GST film increases from 90Ω to 130Ω by codoping Si and N, which would supply more Joule heat for phase change in reset operation and results in smaller writing current.[11] Additionally, it is interesting that the difference of their crystalline resistance is not so large as the difference of their resistivity shown in Fig. 1. This is proposed to be related to the crystallization process of the film. As we know, the thermal conductivity of amorphous GST is lower than GST,[10] so the heat dissipation of the (Si+N)-codoped GST film is smaller than the pure GST, the former has smaller grain size and is more amorphous than the latter. Therefore, the crystallization of the (Si+N)-codoped GST film is much easier during the set process and the resistance decreases. It is also seen from Fig. 4 that the threshold voltage increases from 2 V to 3.9 V by codoping Si and N, which may be attributed to the higher amorphous resistance of the film.

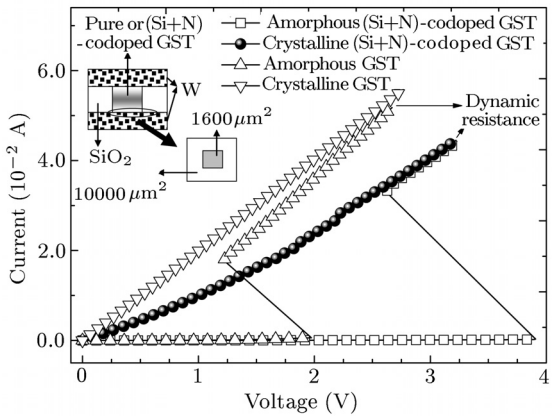


Fig. 4. I–V characteristics of the device with (Si+N)-codoped GST film.

In conclusion, the resistivity of crystalline GST can be increased significantly by codoping of Si and N, which is 2 orders higher than Si- or N-doped GST. FTIR spectra show the formation of Si–N bonds which would be important for suppressing of the grain growth in the films, in agreement with XRD measurements. Small grain size is proven to be effective in enhancement of crystalline resistivity, which is helpful for the reduction of writing current for the phase change in (Si+N)-codoped GST for PCM performance.

We thank Professor A. Q. Jiang for his help of this study.

References

[1] Lai S and Lowrey L 2001 *IEDM* 803-6
[2] Weidenhof V, Friedrich I, Ziegler S and Wutting M 2001 *J. Appl. Phys.* **89** 3168
[3] Jeong T H, Kim M R, Seo H, Kim S J and Kim S Y 1999 *J. Appl. Phys.* **86** 774
[4] Friedrich I, Weidenhof V, Njoroge W, Franz P and Wuttig M 2000 *J. Appl. Phys.* **87** 4130
[5] Privitera S et al 2003 *J. Appl. Phys.* **94** 4409
[6] Lai S 2003 *IEDM Tech. Digest.* 255
[7] Horii H, Yi J H, Park J Het al 2003 *Symposium on VLSI Technology Digest of Technical* paper 177
[8] Kang D H, Ahn D H, Kim K B, Webb J F and Yi K W 2003 *J. Appl. Phys.* **94** 3536
[9] Pellizzer F, Pirovano A et al 2004 *Symposium on VLSI Technology Digest of Technical* paper 18
[10] Hwang Y N, Lee S H, Ahn S J, Lee S Y, Ryoo K C, Hong H S et al 2003 *IEDM Tech. Digit.* p 893
[11] Qiao B W et al 2006 *Chin. Phys. Lett.* **23** 172
[12] Kim S M et al 2004 *Thin Solid Films* **469** 322
[13] Lai Y F et al 2005 *J. Electron. Mater.* **34** 176
[14] Molinari M, Rinnert H and Vergnat M 2001 *Appl. Phys. Lett.* **79** 2172
[15] Yamada N et al 1991 *J. Appl. Phys.* **69** 2849
[16] Mayadas A F and Shatzkes M 1970 *Phys. Rev.* B **1** 1382