Nitrogen-implanted $Ge_2Sb_2Te_5$ film used as multilevel storage media for phase change random access memory

2004 Semicond. Sci. Technol. 19 L61

(http://iopscience.iop.org/0268-1242/19/6/L01)

INSTITUTE OF PHYSICS PUBLISHING SEMICONDUCTOR SCIENCE AND TECHNOLOGY

Semicond. Sci. Technol. **19** (2004) L61–L64 PII: S0268-1242(04)75607-2

LETTER TO THE EDITOR

Nitrogen-implanted $Ge_2Sb_2Te_5$ film used as multilevel storage media for phase change random access memory

Bo Liu[1], **Ting Zhang**[1], **Jilin Xia**[1], **Zhitang Song**[1,2], **Songlin Feng**[2] **and Bomy Chen**[3]

[1] Research Center of Functional Semiconductor Film Engineering and Technology,
Shanghai Institute of Micro-system and Information Technology, CAS, Shanghai 200050,
People's Republic of China
[2] State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of
Micro-system and Information Technology, CAS, Shanghai 200050,
People's Republic of China
[3] Silicon Storage Technology, Inc., 1171 Sonora Court, Sunnyvale, CA 94086, USA

E-mail: lb73sd@yahoo.com.cn

Received 3 February 2004
Published 21 April 2004
Online at stacks.iop.org/SST/19/L61 (DOI: 10.1088/0268-1242/19/6/L01)

Abstract
$Ge_2Sb_2Te_5$ films were deposited by RF magnetron sputtering on $Si(100)/SiO_2$ substrates. N^+ ion was implanted into $Ge_2Sb_2Te_5$ films. Two obvious steps were observed in the resistance–temperature curve of the $Ge_2Sb_2Te_5$-N film with a minor nitrogen implant dose. The two steps may change into one step because the phase transition from FCC to hexagonal structure was suppressed by nitrogen implantation if the nitrogen implant dose is higher than 4.51×10^{16} cm^{-2}. The favourite nitrogen implant dose is about 6.44×10^{15} to 1.92×10^{16} cm^{-2} in our study. This phenomenon is very important for multilevel storage. Three-level storage with $Ge_2Sb_2Te_5$-N media for chalcogenide random access memory (C-RAM) can be performed easily, and hence, the capacity of C-RAM will be dramatically increased.

1. Introduction

In 1968, Ovshinsky discovered a new order–disorder memory phenomenon in chalcogenide film materials, later termed 'ovonic memory' and subsequently found a laser optical memory effect [1–4]. As phase changes occur in these materials, the change in optical constants is accompanied by a much larger change in electrical conductivity. So chalcogenide semiconductor films can also be applied to electrical write and erase nonvolatile memory devices, which are named 'chalcogenide random access memory' (C-RAM) or 'ovonic unified memory' (OUM). This electrical phase change technology has been developed for commercial and space applications by Ovonyx, Inc. at Intel and Lockheed Martin, respectively, since 1999 [5]. C-RAM is a possible substitute for all kinds of current memory devices such as dynamic random access memory (DRAM), static random access memory (SRAM), flash memory, and others. C-RAM has a simple cell structure with high scalability; it is nonvolatile, has a relatively high read/write operation speed and a long cycle life [6, 7]. Furthermore, superior radiation tolerance makes it attractive for space-based applications [8].

Many studies on C-RAM using chalcogenide semiconductors such as GeTeAsSi [1, 9], GeTe [10], GeSbTe [6, 8, 11], GeTeBi [12, 13], GeSb (Cu, Ag) [14], GeTeAs [15], In-Te [16], AsSbTe [17, 18], SeSbTe [19], PbGeSb [20], GeSbTe-N [21], etc have been reported. But all of the above chalcogenide semiconductors were used only as single-level storage media for C-RAM. In this letter, we report for the first time that the nitrogen-implanted $Ge_2Sb_2Te_5$ film can be used as multilevel storage media for C-RAM.

0268-1242/04/060061+04$30.00

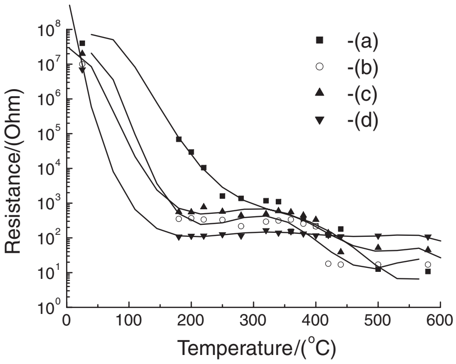

Figure 1. Dependence of the sheet resistance of the nitrogen-implanted $Ge_2Sb_2Te_5$ film on annealing temperature: (a) $Ge_2Sb_2Te_5$ film and nitrogen implant dose was 6.44×10^{15}; 1.93×10^{16} and 4.51×10^{16} cm^{-2} for (b)–(d), respectively.

2. Experiments

In our experiments, $Ge_2Sb_2Te_5$ thin film was deposited by RF sputtering on a $Si(100)/SiO_2$ substrate and the temperature of the substrate was controlled at room temperature. The background pressure is below 2×10^{-4} Pa. The sputtering parameters of the film are sputtering power of 300 W and Ar sputtering pressure of 0.15 Pa. The thickness of the film before implantation is 200 nm, which is determined using a Tencor Alpha-Step 500 Profiler. The film growth rate is 0.7 nm s^{-1}. N^+ ion was implanted into $Ge_2Sb_2Te_5$ films with the implant dose ranging from 6.44×10^{15} to 4.51×10^{16} cm^{-2}. The nitrogen implant dose was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The implantation energy was 65 keV. The samples were crystallized by rapid thermal annealing under Ar atmosphere for 1 min. The film resistance is measured with a four-point probe. The structure of the films was examined by x-ray diffraction (XRD) analyses using a Rigaku D/MAX 2550 V diffractometer. For XRD experiments, Cu Kα ($\lambda = 0.154\,18$ nm) radiation was used.

3. Results and discussions

Figure 1 shows the dependence of the sheet resistance of the nitrogen-implanted $Ge_2Sb_2Te_5$ films on annealing temperature. The sheet resistance of the amorphous (R_{amo}) $Ge_2Sb_2Te_5$-N film is larger than 1×10^7 Ω. For the $Ge_2Sb_2Te_5$ film without nitrogen implantation, the resistance decreases with increasing temperature and reaches a steady value when the temperature is higher than 500 °C. But for the nitrogen-implanted $Ge_2Sb_2Te_5$ film, the dependence of resistance on temperature is different from that for the $Ge_2Sb_2Te_5$ film without nitrogen implantation. When the annealing temperature increases, the resistance of the $Ge_2Sb_2Te_5$-N film with a nitrogen implant dose of 6.44×10^{15} cm^{-2} first decreases quickly and then reaches a steady value after 180 °C; the resistance further decreases quickly at about 400 °C and then reaches another steady value again at temperature higher than 420 °C. The change of resistance with temperature for the $Ge_2Sb_2Te_5$-N film with a nitrogen implant dose of 1.92×10^{16} cm^{-2} is similar to that for the $Ge_2Sb_2Te_5$-N film with a nitrogen implant dose of 6.44×10^{15} cm^{-2}. However, when the nitrogen implant dose reaches 4.51×10^{16} cm^{-2}, the second step of resistance decreasing disappears. The resistance changes very slightly and is almost the same at temperature higher than 180 °C.

Figure 2 shows the XRD patterns for the nitrogen-implanted crystalline $Ge_2Sb_2Te_5$ films. From figure 2(*a*), the structure of the crystalline $Ge_2Sb_2Te_5$ film is identified as a face-centred cubic (FCC) structure at low annealing temperature [22] and the lattice parameter is calculated as $a = 0.599\,06$ nm. However, the structure changes into a hexagonal structure with lattice parameters $a = 0.4216$ nm and $c = 1.7174$ nm when the annealing temperature is high. The crystal structure of the $Ge_2Sb_2Te_5$-N film is also identified as a FCC structure at low annealing temperature. The lattice parameter increases slightly with increasing nitrogen implant dose. The increase of the lattice parameter is due to the fact that a doped nitrogen atom occupying the tetrahedral interstitial site distorts the unit cell and the volume of the tetrahedral site is not large enough for a nitrogen atom to occupy [23]. From figures 2(*b*) and (*c*), when the nitrogen implant dose is below 1.92×10^{16} cm^{-2}, the crystal structure of the $Ge_2Sb_2Te_5$-N film is still identified as a hexagonal structure at high annealing temperature. But the intensity of the peaks for the hexagonal structure decreased greatly with increasing nitrogen implant dose. However, the peaks for the hexagonal structure totally disappeared and the crystal structure of the $Ge_2Sb_2Te_5$-N film is identified as a FCC structure at high annealing temperature when the nitrogen implant dose reaches 4.51×10^{16} cm^{-2} (see figure 2(*d*)). The phase transition from FCC to hexagonal structure was suppressed by nitrogen implantation at high implant dose. We first report this result.

Ovshinsky [5] has supposed that multi-state phase change memory can be realized using $Ge_2Sb_2Te_5$ film because the resistance difference between the amorphous and crystalline state is very large. But there is no resistance steady state with large temperature tolerance in the resistance–temperature curve for the $Ge_2Sb_2Te_5$ film. This is not beneficial for realizing multilevel storage. However, if there are obvious steps in the resistance–temperature curve and the resistance in each step almost remains constant in a wide temperature range, the multilevel storage will be realized easily. From the above we can see that there are two obvious steps in the resistance–temperature curve of the $Ge_2Sb_2Te_5$-N film with a minor nitrogen implant dose, for example, about 6.44×10^{15} to 1.92×10^{16} cm^{-2}. This phenomenon is very important for multilevel storage. We can define the amorphous state with high resistance as the ‘0’ state, the crystalline state with medium resistance as the ‘1’ state and the crystalline state with low resistance as the ‘2’ state. The resistance ratio of ‘0’ to ‘1’ or ‘0’ to ‘2’ state is about 10^4–10^6 and the resistance difference between ‘1’ state and ‘2’ state is at least of order 1 (see figure 1). The ratio is sufficiently large for application to the memory devices. Then multilevel storage with $Ge_2Sb_2Te_5$-N media for C-RAM can be performed easily. Three-level storage can be realized: level 1 (0 to 1), level 2 (0 to 2) and level 3 (1 to 2), just as shown in figure 3. However, the nitrogen implant dose must be selected correctly because the two steps may change into one step if the nitrogen implant dose is higher than 4.51×10^{16} cm^{-2}. This phenomenon is also very important for single-level storage because the resistance of the crystalline $Ge_2Sb_2Te_5$-N film is almost constant, that is, the recording voltage margin is large.

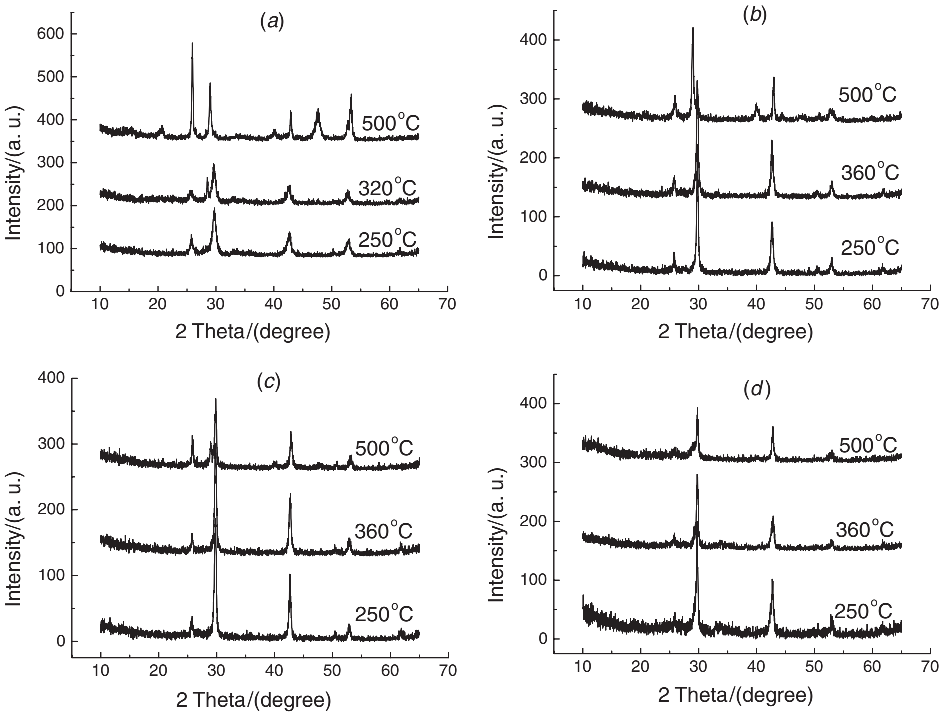

Figure 2. XRD patterns for the crystalline nitrogen-implanted $Ge_2Sb_2Te_5$ films with different nitrogen implant doses: (*a*) 0, (*b*) 6.44×10^{15} cm^{-2}, (*c*) 1.93×10^{16} cm^{-2} and (*d*) 4.51×10^{16} cm^{-2}.

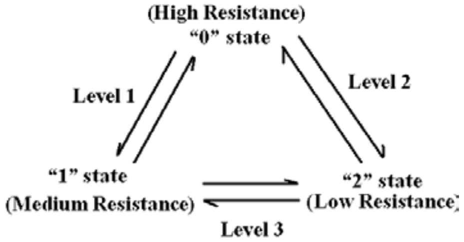

Figure 3. Outline diagram of three-level storage of C-RAM using the nitrogen-implanted $Ge_2Sb_2Te_5$ film.

The $Ge_2Sb_2Te_5$ films in the amorphous, the FCC and the HCP structures show a semiconductor, semi-metallic and metallic behaviour, respectively [24]. Obviously, the metal has much higher conductivity than the semi-metal and the semiconductor. The results from resistance measurements compared well to those from XRD. The detailed reason of nitrogen implantation affecting the resistance–temperature curve for the $Ge_2Sb_2Te_5$ film is not very clear now. This may be due to the structure change of $Ge_2Sb_2Te_5$ film caused by nitrogen implantation because we have found the existence of Ge_3N_4 in $Ge_2Sb_2Te_5$-N film. Further research about the effect of nitrogen implantation on the structure or resistance and the multilevel storage behaviour of memory cell using $Ge_2Sb_2Te_5$-N film is underway.

4. Conclusions

In summary, N^+ ion was implanted into $Ge_2Sb_2Te_5$ films and two obvious steps were observed in the resistance–temperature curve of the $Ge_2Sb_2Te_5$-N film with a minor nitrogen implant dose. The two steps may change into one step because the phase transition from FCC to hexagonal structure is suppressed by nitrogen implantation if the nitrogen implant dose is higher than 4.51×10^{16} cm^{-2}. The favourite nitrogen implant dose is about 6.44×10^{15} to 1.92×10^{16} cm^{-2} in our study. This phenomenon is very important for multilevel storage. Three-level storage with $Ge_2Sb_2Te_5$-N media for C-RAM can be performed easily. This multilevel storage technology will dramatically increase the capacity of C-RAM. In addition, the resistance of the crystalline $Ge_2Sb_2Te_5$-N film with a nitrogen implant dose higher than 4.51×10^{16} cm^{-2} is almost constant, which is also very important for single-level storage because the recording voltage margin is greatly improved.

Acknowledgments

This work is supported by National 863 Project under contract of 2003AA32720, Shanghai Nanotechnology Promotion Center (0352nm016, 0359nm004, 0252nm084), China Postdoctoral Foundation (2003034308), K C Wong Education Foundation (Hong Kong), the special Funds for Major State Basic Research Project (no 001CB610408), Fore-research of basic research project (2001CCA02800) and Science and Technology Council of Shanghai (03dz11009). The authors thank Miss Jing Chen at Shanghai Institute of Technical Physics, CAS, for help in the experiment of resistance measurement.

References

[1] Ovshinsky S R 1968 *Phys. Rev. Lett.* **21** 1450
[2] Feinleib J deNeufville, Moss S C and Ovshinsky S R 1971 *Appl. Phys. Lett.* **18** 254

[3] Ohta T, Nishiuchi K, Narumi K, Kitaoka Y, Ishibashi H, Yamada N and Kozaki T 2000 *Japan. J. Appl. Phys.* **39** 770

[4] Maeda T, Terao M and Shimano T 2003 *Japan. J. Appl. Phys.* **42** 1044

[5] Ovshinsky S R and Czubatyj W 2001 *Proc. SPIE* **4085** 15

[6] Wicker G 1999 *Proc. SPIE* **3891** 2

[7] Lai S and Lowrey T 2001 *IEEE Conf. Proc. Int. Electron Devices Meeting* 36.5.1

[8] Bernacki S, Hunt K and Tyson S 2000 *IEEE Trans. Nucl. Sci.* **47** 2528

[9] Bunton G V and Quilliam R M 1973 *IEEE Trans. Electron Devices* **20** 140

[10] Gosain D P, Nakamura M and Shimizu T 1989 *Japan. J. Appl. Phys.* **28** 1013

[11] Kang D H, Ahn D H and Kim K B 2003 *J. Appl. Phys.* **94** 3536

[12] Bhatia K L, Singh M and Katagawa T 1995 *Semicond. Sci. Technol.* **10** 65

[13] Bhatia K L, Kishore N and Malik J 2002 *Semicond. Sci. Technol.* **17** 189

[14] Ramesh K, Asokan S and Sangunni K S 1999 *Appl. Phys.* A **69** 421

[15] Tsendin K D, Lebedev E A and Kim Y H 2001 *Semicond. Sci. Technol.* **16** 394

[16] Rajesh R and Philip J 2003 *Semicond. Sci. Technol.* **18** 133

[17] Nakayama K, Kitagawa T and Ohmura M 1993 *Japan. J. Appl. Phys.* **32** 564

[18] Nakayama K, Kojima K and Hayakawa F 2000 *Japan. J. Appl. Phys.* **39** 6157

[19] Nakayama K, Kojima K and Imai Y 2003 *Japan. J. Appl. Phys.* **42** 404

[20] Saheb P Z, Asokan S and Gowda K A 2003 *Appl. Phys.* A **76** 665

[21] Horii H, Yi J H and Park J H 2003 *Symposium on VLSI Technology Digest of Technical Papers* 177

[22] Yamada N, Ohno E, Nishiuchi K, Akahira N and Takao M 1991 *J. Appl. Phys.* **69** 2849

[23] Jeong T H, Kim M R and Seo H 2000 *Japan. J. Appl. Phys.* **39** 2775

[24] Galvan A M and Hernandez J G 2000 *J. Appl. Phys.* **87** 760