Improvement of the Thermal Stability of Nickel Stanogermanide by Carbon Pre-Stanogermanidation Implant into GeSn Substrate

Qingbo Liu,a,b Wang Gelei,a,• Yiluan Guo,b Xingxing Ke,b Henry Radamson,c Hong Liu,a Chao Zhao,b and Jun Luo,b,z

aKey Laboratory of Microelectronics Devices & Integrated Technology, Institute of Microelectronics of Chinese Academy of Sciences, Beijing 100029, People’s Republic of China
bState Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People’s Republic of China
cKTH Royal Institute of Technology (KTH), 16440 Kista, Sweden

An effective method to improve the thermal stability of Ni(Ge1-xSnx) by carbon pre-stanogermanidation implant into GeSn substrate is investigated systematically. As-prepared samples were characterized by means of sheet resistance measurement, X-ray diffraction (XRD), scanning electron microscopy (SEM), cross-sectional transmission electron microscopy (X-TEM) and secondary ions mass spectroscopy (SIMS). The incorporation of carbon leads to significantly improved thermal stability of Ni(Ge1-xSnx) by about 100 °C as well as to change the preferred orientations of polycrystalline Ni(Ge1-xSnx). The robust thermal stability can be attributed to the segregation of C in grain boundaries and at Ni(Ge1-xSnx)/GeSn interface after stanogermanidation.

© The Author(s) 2014. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0041503jss] All rights reserved.

To improve the performance of metal-oxide semiconductor field-effect transistors (MOSFETs), extensive research on high carrier mobility materials such as SiGe,1-4 Ge5-7 and GeSn8,9 has been carried out. Among them, GeSn has been investigated recently for boosting the performance of electronic devices and this could extend the applications of Ge based MOSFETs.10-12 Previous investigations have shown that GeSn alloys may be used either as a channel material in p-MOSFETs due to its higher mobility than Ge,10,11,13-15 or as the source/drain (S/D) stressors to introduce uniaxial compressive strain in Ge p-MOSFETs for enhancing hole mobility due to its large lattice mismatch to Ge.16-19 Either as the channel material or S/D stressors, the contact metatilization of GeSn, is however of extremely importance to improve the device performance in practical applications. It is well known that Ni-based germanides have been widely studied as the contact materials in advanced Ge-based MOSFETs.20-22 Similar to Ge, Ni stanogermanide with low contact resistance, low sheet resistance and low formation temperature has been deemed as the promising contact material for GeSn.23,24 However, an overwhelming challenge for Ni(Ge1-xSnx) is its poor thermal stability leading to agglomeration at relatively low temperature,25 especially in aggressively scaled devices in which ultrathin Ni stanogermanide films with high Sn concentration is utilized. It was reported that the precipitation of Sn atoms occurred at annealing temperature above 450 °C when Sn content in Ge1-xSnx is higher than 6.5%, which aggravates the agglomeration of NiGeSn films.23 For the back-end-of-line and high-k last process where anneals at moderately high temperature are usually performed after contact metatilization, the morphological degradation of NiGeSn films below 450 °C is not tolerable. Therefore, an effective method to improve the thermal stability of NiGeSn films is prerequisite in the fabrication of GeSn-based devices. In sharp contrast to NiGe films for which some ways like the addition of P26,27 or Z28 is used to improve the thermal stability, few studies on the improvement of the thermal stability of NiGeSn has been reported.29 In this work, a novel way to improve the thermal stability of nickel stanogermanide by carbon pre-stanogermanidation implant into GeSn substrate is proposed and studied systematically.

**Experimental**

The process flow for this experiment is schematically shown in Fig. 1. 155-nm-thick epitaxial Ge on 4-inch Si(100) (Ge-on-Si) wafer was used as the starting material. Afterwards, a 34-nm-thick p-type GeSn layer with 4% substitutional Sn composition was epitaxially grown on Ge-on-Si substrate by reduced pressure chemical vapor deposition (RPCVD). The as-grown GeSn wafers without carbon implantation as reference and with carbon implantation to a dose of 1 x 10¹⁸ cm⁻² at energy of 2 keV were dipped in 1:100 diluted HF solution for 60 s to remove oxide. After cleaning in deionized water with N₂ bubbling and rinse-dried, 8-nm-thick Ni films were sputter-deposited. The wafers were then sliced into several small pieces about 2 cm x 2 cm in size. Subsequently, the sample pieces were annealed isochronally for 30 s in a rapid thermal process (RTP) chamber in N₂ from 350 °C to 550 °C. Any unreacted Ni was selectively etched in 1:10 diluted HCl solution at 55 °C for reference samples to 500 °C. The as-prepared NiGeSn samples were characterized by means of four-point measurement for sheet resistance, X-ray diffraction (XRD), X-ray diffraction (XRD) for phase identification, scanning electron microscopy (SEM) for both surface and interfacial morphology, and cross-sectional transmission electron microscope (X-TEM) for the microscopic observations and second ion mass spectroscopy (SIMS) for the distribution of elements in NiGeSn films.

**Results and Discussion**

For as-prepared NiGeSn films with and without C, the variation of sheet resistance (Rₘₐₓ) with stanogermanidation temperature from 350 °C to 550 °C is shown in Fig. 2. For reference samples without C, the sheet resistance starts to increase at 400 °C due to the onset of agglomeration of NiGeSn films. At 450 °C and above, drastic increase in sheet resistance is salient manifesting the breakup of integrity for NiGeSn thin films, which is also proved by top-view and cross-sectional SEM images later. However, for the samples with C, the sheet resistance keeps decreasing from 14.24 Ω/□ to 12.27 Ω/□ at 350 °C ~ 500 °C and then increases sharply to 275.56 Ω/□ at 550 °C. Note that the stanogermanidation temperature where Rₘₐₓ starts to increase is shifted from 400 °C for reference samples to 500 °C for samples with C, demonstrating the great improvement on the thermal stability by the incorporation of C. Referring to NiGeSn films without C, the slightly larger Rₘₐₓ of NiGeSn films with C should be ascribed to segregated carbon atoms at grain boundaries and at the NiGeSn/GeSn interface which induce more scattering, similar to the case of NiSi with C.30

The XRD diffractograms of NiGeSn samples without C and with C are shown in Fig. 3. The XRD pattern of NiGeSn samples with C shows a remarkable difference from that of NiGeSn samples without C, which is attributed to the enhancement of the crystallinity of NiGeSn films after carbon implantation.

ECS Journal of Solid State Science and Technology, 4 (3) P67-P70 (2015) P67

*Electrochemical Society Student Member.
E-mail: luojun@ime.ac.cn
stronger for the reference samples than those for the C implanted samples, whereas some peaks e.g. NiGeSn(211) and NiGeSn(210) for C implanted samples show stronger intensity compared to their counterparts in reference samples. Noticeably, at temperature $\geq 500^\circ$C, a strong NiGeSn(112) peak appears for the C implanted samples whereas doesn’t exist at all for reference, indicating that the formation of certain preferred orientations like NiGeSn(112) may be favored in the presence of carbon. It is not unexpected that the preferred orientations of polycrystalline NiGeSn are altered by the incorporation of C thus leading to the variations in diffraction intensity of polycrystalline NiGeSn. NiGeSn films with such a preferred orientation may withstand high stanogermanidation temperature.

The cross-sectional and top-view SEM images of NiGeSn films for both reference and C implanted samples after stanogermanidation are shown in Fig. 4, respectively. It can be seen that for the reference without C, NiGeSn films are uniform and continuous until 400$^\circ$C as shown in Fig. 4a. However, at 450$^\circ$C and above obvious agglomeration takes place as depicted in Fig. 4b where some dark patches representing exposed GeSn substrate disperse in NiGeSn films. This agglomeration for reference without C results in the increase of $R_{sh}$ in Fig. 2. In sharp contrast, even after stanogermanidation at 500$^\circ$C, the C implanted samples show continuous and smooth surface morphology as well as pretty flat NiGeSn/GeSn interface as shown in Fig. 4c. This is also well consistent with the low $R_{sh}$ of NiGeSn films with C until 500$^\circ$C in Fig. 2. The significant improvement on thermal stability of NiGeSn films in the presence of C could be interpreted in the following two aspects. First, from the point of thermodynamic, segregated carbon atoms at NiGeSn grain boundaries and at NiGeSn/GeSn interface may modify and decrease the grain boundary and interface energies due to the formation of strong directional covalent bound.$^{31}$ Moreover, the presence of carbon would passivate the grain boundaries and NiGe/Ge interfaces and thereby lower the grain boundary and interface energies, thus stabilizing NiGeSn grains at high annealing temperature and improving the surface morphology. On the other hand, from the kinetics views, previous work has reported that the grain boundary diffusion can be slowed by the impurities in the CoSi grain boundaries due to the enhanced grain boundary cohesion.$^{31}$ Similar to the CoSi
In summary, the effects of carbon pre-stanogermanidation implant into GeSn substrate was investigated systematically in this work. Compared to NiGeSn films without C as reference, the thermal stability of NiGeSn films is indeed improved significantly by 100°C in the presence of C. By means of extensive characterizations, it is found that the presence of C not only leads to the improved thermal stability but also tends to change the preferred orientations of NiGeSn. The homogeneously distributed C at grain boundaries and the segregation at NiGeSn/GeSn interface are verified to account for the improved thermal stability. The improvement on the thermal stability of NiGeSn films is of great importance and significance for the development of downscaled GeSn based MOSFET devices in the future.

References

1. S.-L. Zhang, Microelectron. Eng., 70, 174 (2003).
2. V. Verdonckt-Vanderbroeck, E. F. Crabbé, B. S. Meyerson, D. L. Harame, P. J. Restle, J. M. C. Stork, and J. B. Johnson, IEEE Trans. Elec. Dev., 41, 90 (1994).
3. S. E. Thompson, Guangyu Sun, Yousung Choi, and Toshikazu Nishida, IEEE Trans. Electron Dev., 53, 1010 (2006).
4. M. L. Lee, Eugene A. Fitzgerald, Mayank T. Bulsara, Matthew T. Currie, and Anthony Lochtefeld, J. Appl. Phys., 97, 011101 (2005).
5. J. Og, P. Majhi, H. Lee, O. Yoo, S. Banerjee, C. Y. Kang, J. Yang, R. Harris, H. Tseng, and R. Jammy, IEEE Electron Device Lett. 28, 1044 (2007).
6. M. L. Lee, C. W. Leitz, Z. Cheng, A. J. Pitera, M. T. Curie, G. Taraschi, A. A. Fitzgerald, and D. A. Antoniadis, Appl. Phys. Lett. 79, 3344 (2001).
7. J. Y. Spann, R. A. Anderson, T. J. Thornton, G. Harris, S. G. Thomas, and C. Tracy, IEEE Electron Device Lett. 26, 151 (2005).
8. G. Q. Han, J. S. Xu, C. L. Zhan, Q. Zhou, Yang, L. X. Wang, P. F. Guo, W. Wei, C. P. Wong, Z. X. Shen, B. W. Cheng, and Y.-C. Yeo, JEDM, p. 16.7.1 (2011).
9. Y. Liu, H. J. Wang, J. Yan, and G. Q. Han, ECS Solid State Letters, 3(2), P11 (2014).
10. G. Han, S. Su, L. Wang, W. Wang, X. Gong, Yang, Y. Ivanov, P. Guo, C. Guo, G. Zhang, J. Pan, Z. Zhang, X. Cui, B. Cheng, and Y.-C. Yeo, Symp. on VLSI Tech., 97 (2012).
11. S. Gupta, R. Chen, B. Magyari-Kope, H. Lin, B. Yang, A. Nainani, Y. Nishi, J. S. Harris, and K. C. Saraswat, Tech. Dig. - Int. Electron Devices Meet., 398 (2011).
12. S. Winths, A. T. Tiedemann, Z. Ikonik, P. Harrison, B. Hölländer, T. Stoica, G. Mussler, M. Myronov, J. M. Hartmann, D. Grützmacher, B. Duka, and S. Mantl, Appl. Phys. Lett., 102, 192033 (2013).
13. O. Nakatsu, S. Tsutsumi, Y. Shimura, S. Takeuchi, A. Sakai, and S. Zaima, Japanese Journal of Applied Physics, 49, 04DA110 (2010).
14. G. Han, S. Su, Q. Zhou, P. Guo, and Y. Yang, IEEE electron device letters, 33(5), 634 (2012).
15. J. D. Sau and M. L. Cohen, Phys. Rev. B, 75, 045208 (2007).
16. G. H. Wang, E.-H. Toh, X. Wang, D. H. L. Seng, S. Tripathy, T. Ospiovicz, T. K. Chen, K. M. Hoc, S. Balakumar, C. H. Tung, G.-Q. Lo, G. Samudra, and Y.-C. Yeo, IEDM Tech. Dig., 131 (2007).
17. R. Loo, G. Wang, L. Sourias, J. C. Lin, S. Takeuchi, G. Brammertz, and M. Camyaz, J. Elect. Soc., 157, H13 (2010).
18. S. Takeuchi, Y. Shimura, T. Nishimura, B. Vincent, G. Eneman, T. Clarysse, J. Dumellemeester, A. Vantomme, J. Dekoster, M. Camyaz, R. Loo, A. Sakai, O. Nakatsu, and S. Zaima, Solid State Electron., 60(1), 53 (2011).

Conclusions

Figure 5. Cross-sectional TEM images of NiGeSn without C annealed at 400°C (a) and with 1·10¹⁵ cm⁻² C annealed at 500°C (b).

Figure 6. SIMS depth profiles of C for the as-I/I sample and for the sample with 1·10¹⁵ cm⁻² C after stanogermanidation at 500°C. Ni, Ge, and Sn is also included to identify NiGeSn/GeSn interface.

described in SEM section.
case, the atomic diffusivity of Ni, Ge and Sn along the grain boundary and NiGeSn/GeSn interface could also be slowed in the presence of C. As a result, the agglomeration of NiGeSn films is retarded which is similar to cases of NiSi and NiSiGe with C.32,33

In Fig. 5, the cross-sectional XTEM images of NiGeSn both for reference annealed at 400°C and for C implanted sample annealed at 500°C are displayed. As seen, the NiGeSn film with C is quite uniform whereas rugged for the NiGeSn without C. Both NiGeSn films are approximately 20 nm in average thickness which is also consistent with the conversion ratio from Ni to NiGeSn.34 For the reference without C at 400°C, the rugged film morphology indicates the agglomeration tendency at sites where two grains converge as depicted in Fig. 5a. However, for the sample with C even at high stanogermanidation temperature i.e. 500°C, pretty smooth surface and flat NiGeSn/GeSn interface is obviously displayed in Fig. 5b. In addition, it is clear that the reference without C shows an obvious interfacial layer containing lots of defects between NiGeSn and GeSn substrate. In sharp contrast, the sample with C reveals a well-defined interface with atoms orderly arranged on both sides shown in Fig. 5b, indicating the formation of atomically flat NiGeSn/GeSn interface without apparent defects.

In order to get a better insight into the role of C on the improvement of the thermal stability of NiGeSn films, the distribution of C within NiGeSn films was studied by secondary ion mass spectroscopy (SIMS). SIMS depth profiles of C for the as ion-implanted implanted sample (as-I/I) and for the C implanted sample to a dose of 1·10¹⁵ cm⁻² after annealing at 500°C are shown in Fig. 6. For the as-I/I sample, it is obviously seen that C peaks at about 6 nm below the surface of GeSn substrate in Fig. 6. For the samples annealed at 500°C, the plateaus of Ni, Ge and Sn within NiGeSn film are observed evidently indicating the formation of NiGeSn films with high uniformity after stanogermanidation. Meanwhile, a C plateau is also found in NiGeSn films which reveals homogeneous distribution of C atoms in the NiGeSn film which is similar to the case of C in NiSi.35 Considering that the solubility of C in NiGe is rather low at high temperature, C atoms should be favorable to segregate at grain boundaries of NiGeSn during the stanogermanidation process. In addition, at the NiGeSn/GeSn interface a small shoulder of C intensity in the SIMS profile occurs, which shows the segregation of C at NiGeSn/GeSn interface. Therefore, the SIMS results prove the rationality of our explanation regarding the effects of carbon on improving the thermal stability of NiGeSn film as discussed in SEM section.
19. B. Vincent, Y. Shimura, S. Takeuchi, T. Nishimura, G. Eneman, A. Ferrincieli, J. Demeulemeester, A. Vantomme, T. Clarysse, O. Nakatsuka, S. Zaima, J. Dekoster, M. Caymax, and R. Loo, *Microelectron. Eng.*, **88**(4), 342 (2011).

20. D. R. Gajula, D. W. McNeill, B. E. Coss, H. Dong, S. Jindhyala, J. Kim, R. M. Wallace, and B. M. Armstrong, *Appl. Phys. Lett.*, **100**, 192101 (2012).

21. P. S. Y. Lim, D. Z. Chi, P. C. Lim, X. C. Wang, T. K. Chan, T. Osipowicz, and Y.-C. Yeo, *Appl. Phys. Lett.*, **100**, 192101 (2012).

22. T. Yamamoto, Y. Yamashita, M. Harada, N. Tsuka, K. Ikeda, K. Suzuki, O. Kiso, N. Sugiyama, and S. Takagi, *Tech. Dig. - Int. Electron Devices Meet.*, 1041 (2007).

23. J. Demeulemeester, A. Schrauwen, O. Nakatsuka, S. Zaima, M. Adachi, Y. Shimura, C. M. Comrie, C. Fleischmann, C. Detavernier, K. Temst, and A. Vantomme, *Appl. Phys. Lett.*, **99**, 211905 (2011).

24. Y. Tong, G. Q. Han, B. Liu, Y. Yang, L. X. Wang, W. Wang, and Y.-C. Yeo, *IEEE Transactions on Electron Devices*, **60**(2), 746 (2013).

25. T. Nishimura, O. Nakatsuka, Y. Shimura, S. Takeuchi, B. Vincent, A. Vantomme, J. Dekoster, M. Caymax, R. Loo, and S. Zaima, *Solid-State Electronics*, **60**, 46 (2011).

26. L. J. Lin, K. L. Pey, W. K. Choo, E. A. Fitzgerald, D. A. Antoniadis, A. J. Pitera, M. L. Lee, D. Z. Chi, Md. A. Rahman, T. Osipowicz, and C. H. Tung, *Journal of Applied Physics*, **98**, 033520 (2005).

27. Y. Y. Zhang, J. Oh, S.-G. Li, S.-Y. Jung, K.-Y. Park, G.-W. Lee, P. Majhi, H.-H. Tseng, R. Jammy, and H.-D. Lee, *IEEE Transactions on Nanotechnology*, **9**, 258 (2010).

28. S. L. Liew, R. T. P. Lee, K. Y. Lee, B. Balakrishnan, S. Y. Chow, M. Y. Lai, and D. Z. Chi, *Thin Solid Films*, **504**, 104 (2006).

29. L. X. Wang, G. Q. Han, S. J. Su, Q. Zhou, Y. Yang, P. F. Guo, W. Wang, Y. Tong, P. S. Y. Lim, B. Liu, E. Y.-J. Kong, C. L. Xue, Q. M. Wang, B. W. Cheng, and Y.-C. Yeo, *Electrochemical and Solid-State Letters*, **15**(6), H179 (2012).

30. J. Luo, Z.-J. Qiu, J. Deng, C. Zhao, J. F. Li, W. W. Wang, D. P. Chen, D. P. Wu, M. Ostling, T. C. Ye, and Shi-Li Zhang, *Microelectronic Engineering*, **120**, 178 (2014).

31. C. Detavernier, R. L. Van Meirhaeghe, H. Bender, O. Richard, B. Brijs, and K. Maex, *J. Appl. Phys.*, **92**(3), 1207 (2002).

32. B. Zhang, W. Yu, Q. T. Zhao, D. Busa, B. Holländer, J.-M. Hartmann, M. Zhang, X. Wang, and S. Mantl, *Interconnect Technology Conference and 2011 Materials for Advanced Metallization (IITC/MAM) IEEE International*, pp. 1–3 (2011).

33. J. Hålstedt, M. Blomqvist, P. O. Å. Persson, L. Hultman, and H. H. Radamson, *J. Appl. Phys.*, **95**, 2397 (2004).

34. V. Carron, M. Riberto, P. Besson, G. Rolland, J.-M. Hartmann, V. Loup, S. Minoret, L. Clavelier, C. Leroyer, and T. Billon, *ECS trans.*, **7**, 643 (2006).

35. S. Zaima, O. Nakatsuka, A. Sakai, J. Murota, and Y. Yasuda, *Applied Surface Science*, **224**, 215 (2004).