CrystEngComm

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](http://www.rsc.org/Publishing/Journals/guidelines/AuthorGuidelines/JournalPolicy/accepted_manuscripts.asp).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](http://www.rsc.org/help/termsconditions.asp) and the Ethical quidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

www.rsc.org/crystengcomm

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012, Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A Novel Silicide and Germanosilicide by NiCo Alloy for Si and SiGe Source/Drain Contact with Improved Thermal Stability

Chi-Hsuan Cheng and Cheng-Lun Hsin^a

NiCo (10 at.% of Co) alloy was employed for the formation of the metal silicide and germanosilicide as the contact layer for future CMOS source/drain. The resistivity and structure evolution of NiCo silicide and germanosilicide were investigated, and the performance of the NiCo silicide is better than conventional NiSi and comparable with NiPt silicides, as well as NiPt germanosilicide below 700 ℃. The thermal stability and enhanced sheet resistance of NiCo silicide and germanosilicide were found to be up to 900℃ and 700℃, respectively. The low sheet resistance at high temperature was attributed to the lowtemperature CoSi by enhancing the thermal stability and uniformity of the Ge. The influence of Ge concentration was studied in different $Si_{1-x}Ge_x$ substrates, and the low sheet resistance can be reliable up to 650 ℃.

Introduction

The feature size of the transistor keeps scaling down and following Moore's law while employing new materials and structures. The evolution of the transistor architecture has incorporated the $3D$ structure¹, silicon-germanium (SiGe) source/drain², high K/metal gate³ etc. to boost the performance of the device. With the decrease of the source/drain contact area, the series and contact resistance is getting more critical $4, 5$. Metal silicides have been used as contact materials in the complementary metal-oxide-semiconductor (CMOS) technology for many decades while nickel silicide (NiSi) has been used since the 90-nm technology node due to its low resistivity, formation temperature and silicon consumption^{6, 7}. However, the poor thermal stability of the nanoscaled thin film has become a serious issue in recent years, especially for the contemporary $Si_{0.8}Ge_{0.2} source/drain of P-channel MOS^{8, 9}.$ NiPt alloy has been employed and the incorporation of new element is a solution to improve the thermal stability and process window¹⁰. Nevertheless, the removal of the residual unreacted alloy on the spacer is another problem for the etching process of self-aligned silicide (salicide) technology¹¹, as well as the cost of the noble metal. Compared with Pt, $CoSi₂$ was also employed before the 0.13-micron technology nodes. Besides, cobalt(Co) is low-cost and easier to be selectively etched in the silicide process with no significant damage to the silicon substrate by buffered oxide etcher or HNO₃-based solutions¹². Previous reports has proved that $Ni_{0.9}Co_{0.1}$ thin film or $Ni_{0.5}Co_{0.5}$ interlayer has the merit to improve the electrical and thermal property^{13, 14}. In this report, $Ni_{90}Co_{10}$ alloy was

employed for the formation of the metal silicide and germanosilicide as the contact layer for Si and SiGe. The resistivity and structure evolution of NiCo silicide and germanosilicide were investigated, as well as the counterparts of Ni and NiPt. The incorporation of Co was found to enhance the sheet resistance by enhancing the high temperature thermal stability of the thin film and uniformity of the Ge. The property of the silicides formed by NiCo alloy is comparable with that of NiPt alloy. The influence of Ge concentration was studied in different $Si_{1-x}Ge_x$ substrates. This observation provides a novel silicide and germanosilicide by NiCo alloy for Si and SiGe source/drain contact in the future.

Experimental

P-type Si(100) wafers with resistivity of ~ 1 Ω \cdot cm were used. SiGe substrate was grown in the ultra-high-vacuum chemical vapor deposition system with a buffer layer. Before loading in to the sputtering chamber, the wafers were cleaned by standard cleaning process^{15, 16}, followed by diluted-HF to remove the native oxide. A 12 nm-thick NiCo (10 at.% of Co) film were sputtered on Si and $\text{Si}_{1-x}\text{Ge}_{x}$ (x = 0.1, 0.2, 0.4, 0.5, and 1.0) substrates. A 12 nm-thick Ni and NiPt (10 at.% Pt) alloy was sputtered and evaporated, respectively, on the Si and $\mathrm{Si}_{0.8}\mathrm{Ge}_{0.2}$ substrates. After the deposition, rapid thermal annealing (RTA) was conducted at temperatures of 300-900 ℃ for 30 s in N_2 ambient separately for each sample. The deposited alloy would be consumed completely.

 Sheet resistance was measured by a four-point-probe system. The surface morphologies of silicide were investigated by field emission scanning electron microscope (FESEM, JEOL 7000F). Field-emission transmission electron microscope (TEM, JEOL 2100F) installed with energy dispersive spectroscope (EDS) were used to examine the structures and chemical composition. The plane-view TEM samples were thinned down by mechanical grinding and chemical etching technique. The cross-sectional TEM sample was prepared by coating it with $Si₃N₄$ to provide better image contrast at the surface, followed by the ion-milling in the focus-ion-beam system.

Results and discussion

Figures 1(a) and (b) are the sheet resistance of the NiCo silicides and germanosilicides as a function of the annealing temperatures from 300°C to 900°C on Si substrate and $Si_{0.8}Ge_{0.2}$ substrate, respectively, as well as the characteristics of the counterparts of Ni and NiPt. The error bar is due to the ingenuity of the instrument and uncertainty of the operation. However, for the case of Ni, the silicide and germanide thin film became islands, resulting in the large deviation of the measured value. It is obvious that the performance of NiPt silicides is better than NiSi, which is stable up to 550° C. However, the property of NiCo silicide can be comparable with NiPt silicides, and thermally stable up to 900℃. In Fig. 1(b), Ni germanosilicide deteriorated due to the Ge segregation and reactivity, and the sheet resistance of NiCo germanosilicide is higher than the counterpart of NiPt but lower than Ni. The sheet resistance of NiCo germanosilicide is stable up to 700℃, and dramatically increased at 750 ℃ . Besides, the formation temperature of NiCo silicide and germanosilicide could be as low as 550 ℃ and 500 ℃, respectively.

Figure 1. The sheet resistance of silicide made by Ni, NiCo, and NiPt on (a) Si, and (b) $Si_{0.8}Ge_{0.2}$ substrates at different annealing temperatures.

Fig. 2 shows the plan-view SEM images of NiCo silicide and NiCo germanosilicide at different annealing temperature from 600℃ to 700℃, indicating the instability and agglomeration of NiCo germanosilicide at high temperature. This observation explains the increase of the sheet resistance from 650℃ to 700 ℃ for NiCo germanosilicide.

Fig. 3 is a series of cross-sectional TEM images of NiCo silicides $((a), (b),$ and $(c))$ and germanosilicides $((d), (e),$ and (f)) at different annealing temperatures from 600℃ to 700℃, respectively. The consumption ratio of NiCo/Si and NiCo/SiGe is \sim 1.5, comparable with that of NiPt and Ni. The agglomeration of the NiCo germanosilicide illustrated the high

Figure 2. Plan-view SEM images of NiCo silicide grown on Si substrates at (a) 600 ℃, (b) 650 ℃, and (c) 700 ℃. Plan-view SEM images of NiCo germanosilicide grown on $Si_{0.8}Ge_{0.2}$ substrates at (d) 600°C, (e) 650°C, and (f) 700°C.

Figure 3. Cross-sectional TEM images of NiCo silicide grown on Si substrates at (a) 600℃, (b) 650 ℃, and (c) 700 ℃. Cross-sectional TEM images of NiCo germanosilicide grown on Si_{0.8}Ge_{0.2} substrates at (d) 600℃, (e) 650 ℃, and (f) 700 ℃.

temperature instability and the increase of resistance, which is consistent with our previous observations. The stability and low resistance of the NiCo was revealed by the phase of the silicide and germanosilicide.

Fig. 4 is a series of plan-view TEM images of NiCo silicides and germanosilicides with corresponding diffraction patterns in the inset at temperatures from 600℃ to 700℃ and 650℃ to 750℃, respectively. The discontinuity of the silicide film is due to the sample preparation process. From the identification of diffraction patterns, Ni silicide are in majority while the Ni germanide, Co silicide, Co germanide are in minority. Furthermore, the low-resistivity NiSi is still one of the constituent parts of the film, and the presence of lowtemperature CoSi could contribute to the stability of the thin film at high temperatures, which is similar to the case of P_i ISi⁶.

In order to unravel the distribution of Co and the concern of Ge precipitation, Fig. 5 illustrates the cross-sectional TEM images and corresponding EDS mapping of NiCo silicide and germanosilicide at annealing temperature of 650℃ and 700℃, respectively, revealing the uniform distribution and no precipitation of Ge in germanosilicide. The sparse distribution of the Co signal suggested that the intensity is beyond detection

Journal Name ARTICLE

limit, and there is no Co silicide accumulation. For the further application on different SiGe substrates, the sheet resistance of the germanosilicides as a function of the Ge concentration (Si_{1-x})

Figure 4. Plan-view TEM images of NiCo silicide grown on Si substrates at (a) 600 ℃, (b) 650 ℃, and (c) 700 ℃. Plan-view TEM images of NiCo germanosilicide grown on Si_{0.8}Ge_{0.2} substrates at (d) 650℃, (e) 700 ℃, and (f) 750 ℃. The inset is the corresponding diffraction pattern and the color dashed-lines highlighted the

Ge_x, $x = 0.1, 0.2, 0.4, 0.5,$ and 1.0) at annealing temperatures from 550℃ to 700℃ was illustrated in Fig. 6. Generally, the sheet resistance decreases with the increase of the Ge concentration except for the $Si_{0.6}Ge_{0.4}$ substrate at 700 °C due to the instability and agglomeration of the thin film, as shown in the SEM image of the inset. In this study, $Si₆₀Ge₄₀$ may result in severe Ge segregation for $\text{Ni}_{90}\text{Co}_{10}$. For substrates with higher Ge concentration more than 50%, Ni will react with Ge preferentially to form the nickel germanide so the segregation could be suppressed. However, the low sheet resistance can be reliable up to 650 ℃, which indicates NiCo germanosilicide also a good candidate for SiGe/Ge contact. Our observation provides a novel silicide and germanosilicide for Si and SiGe source/drain contact in the future.

Conclusions

diffraction rings of each phase.

In this report, NiCo (10 at.% of Co) silicide and germanosilicide were investigated for future applications in source/drain contact. On the Si substrates, the performance of the NiCo silicide is better than conventional NiSi and comparable with NiPt silicides, as well as NiPt germanosilicide

Figure 5. (a) Cross-sectional TEM image of the NiCo silicide grown at 650 ℃, and (b) Cross-sectional TEM image of the NiCo germanosilicide grown at 700 ℃. The corresponding plots of the EDS mapping showing the element distribution of Ni, Co, and Ge.

Figure 6. The sheet resistance of NiCo as a function of different Ge concentrations of substrates at different annealing temperatures.

below 700 ℃ . The thermal stability and enhanced sheet resistance of NiCo silicide and germanosilicide were found to be up to 900℃ and 700℃, respectively, which provides a feasible process window for the IC fabrication with acceptable cost. The presence of low-temperature CoSi could contribute to the stability of the thin film at high temperatures, similar to the functionality of PtSi. The uniform distribution of Co and Ge indicates the suppression of Ge precipitation. For different SiGe substrates, the low sheet resistance can be reliable up to 650 ° \degree C.

Acknowledgements

The research is supported by the Republic of China National Science Council (grant no. NSC 101-2218-E-008 -014 -MY2). The authors also thanks for the technical discussion with Prof. S. W. Lee and P. W. Li in National Central University.

Notes and references

Department of Electrical Engineering, National Central University, Taoyuan, 32001, Taiwan

a Corresponding Author E-mail: clhsin@ee.ncu.edu.tw

- 1. D. H. Kim, K. Athikulwongse and S. K. Lim, *IEEE Trans. Very Large Scale Integr.*, 2013, **21**, 862-874.
- 2. S. Baudot, F. Andrieu, O. Weber, P. Perreau, J. F. Damlencourt, S. Barnola, T. Salvetat, L. Tosti, L. Brevard, D. Lafond, J. Eymery and O. Faynot, *IEEE Electr. Device Lett.*, 2010, **31**, 1074-1076.
- 3. H. Nam and C. Shin, *IEEE Electr. Device Lett.*, 2013, **34**, 1560-1562.
- 4. Q. Zhou, S. M. Koh, T. Thanigaivelan, T. Henry and Y. C. Yeo, *IEEE Trans. Electr. Devices*, 2013, **60**, 1310-1317.
- 5. J. Pan, A. Topol, I. Shao, C. Y. Sung, J. Lacoponi and M. R. Lin, *IEEE Electr. Device Lett.*, 2007, **28**, 691-693.
- 6. S. L. Zhang and U. Smith, *J. Vac. Sci. Technol. A*, 2004, **22**, 1361- 1370.
- 7. H. Iwai, T. Ohguro and S. Ohmi, *Microelectron. Eng.*, 2002, **60**, 157- 169.
- 8. F. F. Zhao, J. Z. Zheng, Z. X. Shen, T. Osipowicz, W. Z. Gao and L. H. Chan, *Microelectron. Eng.*, 2004, **71**, 104-111.
- 9. F. Deng, R. A. Johnson, P. M. Asbeck, S. S. Lau, W. B. Dubbelday, T. Hsiao and J. Woo, *J. Appl. Phys.*, 1997, **81**, 8047-8051.
- 10. K. Akarvardar, M. Rodgers, V. Kaushik, C. S. Johnson, H. Chong, I. Ok, K. W. Ang, S. Gausepohl, C. Hobbs, P. Kirsch and R. Jammy, *IEEE Electr. Device Lett.*, 2012, **33**, 631-633.
- 11. M. M. Chu and J. H. Chou, *Jpn. J. Appl. Phys.*, 2010, **49**. 06GG16.
- 12. S. L. Hsia, T. Y. Tan, P. Smith and G. E. McGuire, *J. Appl. Phys.*, 1992, **72**, 1864-1873.
- 13. J. B. Lee, S. Y. Jeong, B. J. Park, C. J. Choi, K. Hong, S. J. Whang and T. Y. Seong, *Superlattices Microstruct.*, 2010, **47**, 259-265.
- 14. O. Song, K. Yoon and S. Kim, *Met. Mater.-Int.*, 2009, **15**, 285-291.
- 15. C. L. Hsin, C. W. Huang, C. H. Cheng, H. S. Teng and W. W. Wu, *Crystengcomm*, 2014, **16**, 1611-1614.
- 16. C. L. Hsin, W. W. Wu, L. W. Chu, H. C. Hsu and L. J. Chen, *Crystengcomm*, 2011, **13**, 3967-3970.

Page 5 of 5 CrystEngComm

Cross-sectional TEM images of NiCo germanosilicide grown on Si0.8Ge0.2 substrates at different temperatures, showing the structural stability and evolution. 289x82mm (96 x 96 DPI)