Ni Metallization on SiGe Nanowire

Y. Li, K. Buddharaju, and X. P. Wang

Abstract—The mechanism of nickel (Ni) metallization in silicon-germanium ($Si_{0.5}Ge_{0.5}$) alloy nanowire (NW) was studied. Transmission electron microscope imaging with in-situ annealing was conducted at temperatures of $200^{o}C$ to $600^{o}C$. During rapid formation of Ni germanosilicide, loss of material from from the SiGe NW occurred which led to the formation of a thin Ni germanosilicide filament and eventual void. Energy dispersive X-ray spectroscopy analysis along the SiGe NW before and after annealing determined that Ge atoms tend to out-diffuse from the Ni germanosilicide towards the Ni source in the course of annealing. A model for the Ni germanosilicide formation in SiGe NW is proposed to explain this observation.

Keywords—SiGe, nanowires, germanosilicide.

I. Introduction

SEMICONDUCTOR NANOWIRES (NWs) have attracted significant attention in the area of thermoelectricity recently [1]. Apart from thermoelectric studies of individual NWs, recent literature has started to report studies on complete silicon (Si) NW based thermoelectric power generators (TEGs) [2], [3]. Apart from interest in SiNWs, there are a number of theoretical works that highlight the advantages of silicon-germanium (SiGe) NW in the thermoelectric properties compared to SiNWs [4]. However, in a practical thermoelectric device, one of the factors in defining the device performance is the electrical contacts quality [5]. In the reported work on SiNW-based TEGs, the fabrication process involves the silicidation of the top and bottom of the SiNW array using nickel (Ni) due to the advantage in having low sheet resistivity, low silicon consumption and low processing temperature [6], [7]. Considering the progress demonstrated so far of a complete SiNW-based TEG, research into higher-performance CMOS-compatible materials like SiGe is natural. Similarly, Ni was found to be a suitable silicide metal due to its ability to yield a lower contact resistivity at temperatures < $700^{o}C$ as compared to other metal titanium and cobalt [8].

In several works that studied the reaction between Ni and SiNWs, it was observed that the Ni silicide phase formation is dependent on the Si orientation; this is different from that of bulk Si [9], [10]. We would expect it to be the same for SiGe

as well. However, due to the relative infancy of SiGe NW technology as compared to SiNW, reports of similar work for SiGe NW are lacking. Hence, an understanding of the growth mechanism of Ni germane silicide arising from the reaction of Ni and SiGe NW is desired. In this paper, we report on the investigation of such growth mechanism using transmission electron microscopy (TEM) with in-situ annealing. Energy dispersive X-Ray spectroscopy (EDX) analysis was conducted along the length of the SiGe NW to better understand the whole process of phase transformation.

II. Experimental

A. Sample Preparation

A $Si_{0.5}Ge_{0.5}$ layer (~$0.5\mu m$ thick) was deposited on an 8", Si (100) wafer using an epitaxy process. A SiGe NW array was then formed using deep ultraviolet lithography and a dry etching method; the process is documented in [2], [3]. We use high-density-plasma oxide to fill the air gap, and an anisotropic oxide etch to exposed the SiGe NW tip for contact with a ~3000Å thick layer of Ni. The HDP oxide filler was deposited to prevent any Ni deposition at the sidewalls of the SiGe NW, which would otherwise affect the quality of the TEM images. The sample was then transferred to a Si nitride membrane window grid from SPI Supplies® to facilitate the in-situ annealing process. A final oxide etching process using vapor hydrofluoric acid was used to remove the HDP oxide filler. Fig. 1 shows TEM images of the prepared sample (a) before and (b) after the removal of the HDP oxide. In Fig. 1 (a), the bright regions are air gaps which could not be filled completely by the HDP oxide while in Fig. 1 (b) the "branches" are residues of the HDP oxide after the oxide etching process. We observe that the NW formed has a total length of ~650nm, of which the top ~450nm is the epitaxy SiGe layer and the bottom 200nm is from the Si substrate.

The SiGe NW samples were placed in the TEM while the in-situ annealing was carried out using a TEM holder with a heating stage. During the experiment, the temperature of the heating stage was raised to $200^{o}C$, $400^{o}C$, and $600^{o}C$, during which, TEM images of the samples were taken at 10s intervals. Fig. 2 shows TEM images of the SiGe NW sample after having been annealed at (a) $200^{o}C$, (b) $400^{o}C$, and (c) $600^{o}C$ for 500s. The insets of Figs. 2 (a) and (b) are the magnified view of the SiGe NW near the tip area. It can be observed from the insets of Figs. 2 (a) and (b) that the formation of Ni germanosilicide when the sample was annealed at $200^{o}C$ and $400^{o}C$ was trivial. At $600^{o}C$ however, the growth was much accelerated, and the formation of Ni germanosilicide in the SiGe NW was accompanied by voids. Apart from the SiGe

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World Academy of Science, Engineering and Technology
International Journal of Electronics and Communication Engineering
Vol:7, No:9, 2013

NWs that have been severed completely by void formation, some exhibited a filament-like structure. Apart from voids and the filament-like structure, we can also observe that close to the tips of the SiGe NW, there is bulging of material. This observed phenomenon was not reported before in relevant literature which studied the interfacial reaction of Ni and SiGe layer, [6], [7], [11]-[14] nor in the fabrication process of the SiNW TEG [2], [3]. Such voids are detrimental to a device's performance as it acted as open circuit.
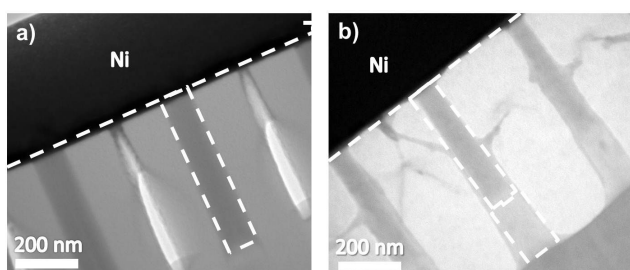

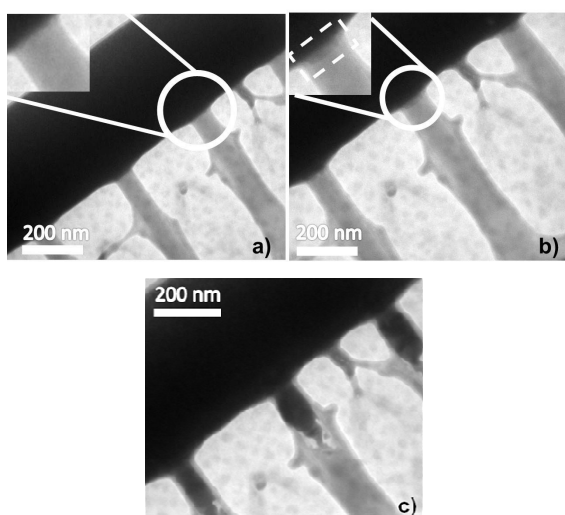Fig.1 TEM image of the prepared sample (a) before and (b) after the removal of the HDP oxide

Fig. 2 TEM images of the SiGe NW sample annealed at (a) 200°C, (b) 400°C, and (c) 600°C after 500s. The insets of Fig. 2 (a) and (b) are the magnified view of the SiGe NW near the tip area
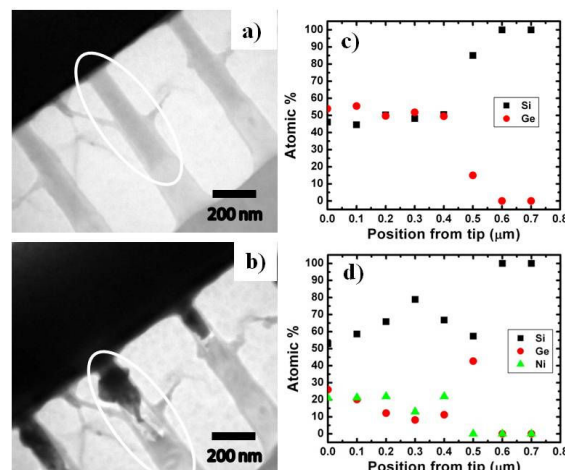

Fig. 3 (a) and (b) show the TEM image of the SiGe NW and composition before the experiment respectively while (c) and (d) show the same after the experiment

Thereafter, EDX was used to determine the Ni, Si, and Ge composition along the SiGe NW before and after the experiment. The location of the EDX analysis along the SiGe NW and the corresponding composition are shown in Fig. 3. Figs. 3 (a) and (b) show, respectively, the TEM image of the SiGe NW and EDX results before annealing while Figs. 3 (c) and (d) show the same analysis after the experiment. We observe that there is an increase in the Si concentration as the Ge concentration decreased, all the while with the Ni concentration being relatively constant at ~21% along the Ni germanosilicide portion.

III. RESULTS AND DISCUSSION

Aldrich and co workers proposed a solid state reaction model for titanium with a SiGe layer [15]. For prolonged annealing, segregation of Ge atoms into the grain boundaries occurs and eventually leads to the formation of a SiGe layer which renders the Ni germanosilicide film discontinuous. However, the extensive works done on SiGe layers do not explain the voids observed in the SiGe NW after annealing [6], [7], [11]-[14]. However, the results obtained reveal that the bulk Ni germanosilicide model proposed by Aldrich and co-workers [15] does not quite apply to SiGe NW. As opposed to the formation of SiGe grains between Ni germanosilicide grain boundaries, voids were formed instead. In fact, our observation are more in line with the study of formation of Ni germanide on Ge NW, where a break in the Ge wire near the Ni germanide-Ge interface was always observed at temperatures > 450°C [16]. It is more reasonable to propose that instead of Ge atoms preferentially segregating at the grain boundaries, the Ge atoms in the SiGe NW have a tendency to segregate near the Ni germanosilicide-Ni source interface, as seen by the buldging near the tips after annealing. Considering the observations, the Ni germanosilicide formation mechanism can be summarized by the modified model shown in Fig. 4 [6].

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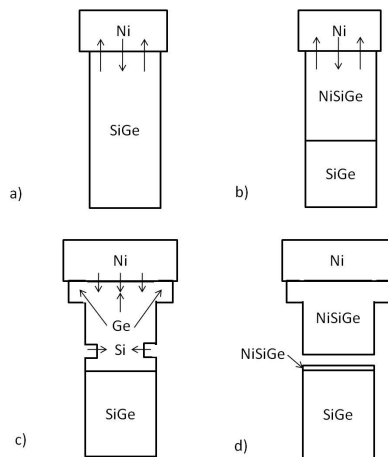Vol:7, No:9, 2013

Fig. 4 Schematic of the formation of Ni-germanosilicide in SiGe NW. a) during annealing, Ni and SiGe interdiffuse to form b) Ni-germanosilicide. c) A neck in the Ni-germanosilicide starts to form with bulging near the tips. d) Upon prolonged heating, a break occurs in the SiGe NW

IV. CONCLUSION

In summary, the mechanism of Ni metallization on SiGe NW was studied for temperatures of $200^{o}C$ to $600^{o}C$. The growth mechanism is significantly different from that of SiGe-layer studies. In SiGe layers, voids were not observed after reacting with Ni metallization. In SiGe NW however, voids that severed the top Ni germanosilicide portion from the bottom SiGe NW portion were observed after prolonged annealing. In addition, the Ge, Si and Ni composition along the SiGe NW determined using EDX shows that there was a drastic drop in Ge concentration which explains the loss of materials from the sides of the SiGe NW. It seems that Ge atoms segregate/out-diffuse from the Ni germanosilicide towards the Ni source during annealing and caused the bulging observed. The observation suggests that in the case of the SiGe layer, the presence of a continuous layer provides a compressive strain sideways, which in turn suppresses excessive out-diffusion of the Ge atoms and thus voids. Further studies on the effect of the compressive strain in Ni germanosilicide for the suppression of voids formation will be highly desired to develop processes for future SiGe-NW based devices.

REFERENCES

[1] A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. Yang, Nature, 451, 163 (2008).
[2] Y. Li, K. Buddharaju, N. Singh, G. Q. Lo, and S. J. Lee, Electron Dev. Lett., 32, 674 (2011).
[3] Y. Li, K. Buddharaju, B. C. Tinh, N. Singh, and S. J. Lee, IEEE Electron Dev. Lett., 33, 715 (2012).
[4] L. Shi, D. Yao, G. Zhang, and B. Li, Appl. Phys. Lett., 96, 173108 (2010).
[5] T. Schwamb, B. R. Burg, N. C. Schirmer, and D. Poulikakos, Appl. Phys. Lett., 92, 243106 (2008).
[6] K. L Pey, S. Chattopadhyay, W. K. Choi, Y. Miron, E. A. Fitzgerald, D. A. Antoniadis, and T. Osipowicz., J. Vac. Sci. Technol. B, 22, 852 (2004).
[7] H. B. Zhao, K. L. Pey, W. K. Choi, S. Chattopadhyay, E. A. Fitzgerald, D. A. Antoniadis, and P. S. Lee. J. Appl. Phys., 92, 214 (2002).
[8] C. K. Maiti, Silicon Hetrostructure Handbook, John. D. Cressler, Ed. CRC Press, ch 2 (2005).
[9] Y. Wu, J. Xiang, C. Yang, W. Lu, and C. M. Lieber, Nature, 430, 61 (2004).
[10] N. S. Dellas, B. Z. Liu, S. M. Eichfeld, C. M. Eichfeld, T. S. Mayer, and S. E. Mohney, J. Appl. Phys. 105, 094309, (2009).
[11] C. H. Jang, D. O. Shin, S. I. Baik, Y-W. Kim, Y-J. Song, K-H. Shim, and N-E. Lee, Japanese J. Appl. Phys., 44, 4805 (2005)
[12] J. S. Luo, W. T. Lin, C.Y. Chang, and W. C. Tsai., J. Appl. Phys.82, 3621, (1997).
[13] K. L. Pey, W. K. Choi, S. Chattopadhyay, H. B. Zhao, E. A. Fitzgerald, D. A. Antoniadis, and P. S. Lee, J. Vac. Sci. Technol. A, 20, 1903 (2002).
[14] C. Y. Lin, W. J. Chen, C. H. Lai, A. Chin, and J. Liu. IEEE Electron Dev. Lett., 23, 464 (2002).
[15] D. B. Aldrich, Y. L. Chen, D. E. Sayers, R. J. Nemanich, S. P. Ashbun, and M. C. Ozturk, J. Appl. Phys., 77, 5107 (1995).
[16] N. S. Dellas, S. Minassian, J. M. Redwing, and S. E. Mohney, Appl. Phys. Lett., 97, 26 (2010).