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Epitaxial growth of Ni(Al)Si$_{0.7}$Ge$_{0.3}$ on relaxed Si$_{0.7}$Ge$_{0.3}$/Si(100) substrates was achieved via an Al interlayer mediated epitaxy. After annealing, most of the Al atoms from the original 3 nm interlayer diffused toward the surface but the remaining Al atoms in the epitaxial monogermanosilicide distributed uniformly, independent of the annealing temperatures. The incorporation of Al increases the transition temperature from the Ni-rich germanosilicide phase to the monogermanosilicide phase. The reduced Ni diffusion, the increased lattice constant due to substitutional Al, and the increased thermal expansion of monogermanosilicide are assumed to be the main mechanisms enabling the epitaxial growth of the quaternary silicide. © *2011 American Institute of Physics.*
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Single crystalline SiGe has been implemented into advanced complementary metal oxide semiconductor (CMOS) devices at source/drain in order to induce uniaxial compressive strain in the Si channel,[1] or, alternatively, as channel material due to its high hole mobility.[2] One of the challenges for the SiGe devices poses the formation of germanosilicide with pristine electrical and structural properties, namely, a low electrical resistivity, an abrupt and uniform interface to SiGe, as well as a low contact resistance.

Ni silicide is the most employed contact material in state-of-the-art CMOS devices. In the solid-state reaction of the binary Ni/Si system, Ni is the dominant diffusing species and several silicide phases, i.e., Ni$_2$Si, NiSi, NiSi$_2$, of different resistivity may form. In the ternary Ni/Si$_{1-x}$Ge$_x$ systems, the phase reactions and morphological transformations are more complex.[3] Island structures and Ge segregation (out diffusion) have been observed following high-temperature treatments.[4,5] The failure of the Ni/Si$_{1-x}$Ge$_x$ system to form a highly uniform, low-resistivity silicide was ascribed to the larger absolute enthalpy of formation of NiSi (-45 kJ mol^{-1}) than that of NiGe (-32 kJ mol^{-1}), which means that NiSi is more favorable and more stable than NiGe.[6] Therefore, it is considered that the Ge is incorporated in the Ni(Si$_{1-x}$Ge$_x$) phase when formed at lower temperatures while at higher temperatures out-diffusion of Ge occurs, allowing a minimization of the Gibbs free energy by the formation of thermodynamically stable phases like NiSi.[7]

Consequently, it is of particular interest for the ternary NiSiGe system to achieve a uniform layer with atomically flat interface to the SiGe layer and improve the thermal stability. Recently, several attempts have been made to improve the morphology and thermal stability of NiSiGe layers by the addition of metal elements such as Pt, Pd, or by C ion implantation into the SiGe layer.[8–10] Furthermore, epitaxial silicides and germanosilicides have superior properties due to the excellent interface sharpness, the lack of grain boundaries, and the concomitant high thermal stability. Single crystalline CoSi$_2$ and NiSi$_2$, which have small lattice mismatches to Si, can be realized on Si substrates using Ti interlayer mediated epitaxy[11,12] or very thin metal layers.[13] However, the epitaxial growth of ternary silicides is difficult due to the complicated reactions. Erbium germanosilicide layers in disilicide phase have been epitaxially grown on SiGe substrates.[14,15] Epitaxial monogermanosilicide NiSi$_{1-x}$Ge$_x$ layers on Si$_{1-x}$Ge$_x$ have not been reported as yet.

In this letter, we present a simple but efficient way to form *epitaxial* Ni-germanosilicide films using Al interlayer mediated epitaxy. High-quality epitaxial Ni-monogermanosilicide films were obtained.

Intrinsic strain relaxed Si$_{0.7}$Ge$_{0.3}$ layers with a thickness of about 800 nm were grown by reduced pressure chemical vapor deposition on $\sim$2 μm thick, linearly graded Si$_{0.7}$Ge$_{0.3}$ buffer layers on Si(100) substrates. Prior to the deposition of Ni films, samples were cleaned by standard Si process, followed by a 30 s dip in 1% HF solution. A 3 nm Al layer and a subsequent 11 nm Ni film were deposited on Si$_{0.70}$Ge$_{0.30}$/Si substrates by electron beam evaporation. 11 nm Ni layers were also deposited directly on Si$_{0.70}$Ge$_{0.30}$/Si substrates without Al for comparison. Solid-phase reactions between Ni or Ni/Al and Si$_{0.7}$Ge$_{0.3}$ during rapid thermal processing (RTP) in N$_2$ ambient for 30 s were studied at temperatures ranging from 300 to 750 °C. The unreacted remaining Ni was selectively etched in solution of H$_2$SO$_4$:H$_2$O$_2$ (1:4) before layer characterization.

The influence of an Al interlayer on the germanosilicide formed on Si$_{0.7}$Ge$_{0.3}$ substrates was primarily investigated by sheet resistance measurements. Figure 1 illustrates the sheet resistance of Ni/SiGe and Ni/Al/SiGe systems as a function of the annealing temperature. For the Ni/SiGe system, the layer resistance exhibits a rapid decrease at 400 °C, attributed to the monogermanosilicide (NiSi$_{0.7}$Ge$_{0.3}$) phase formation as concluded from Rutherford backscattering spectros-

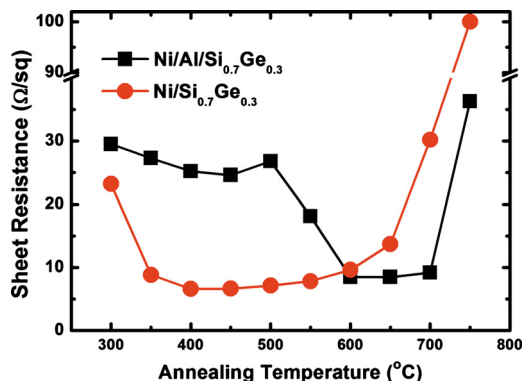a)Electronic mail: q.zhao@fz-juelich.de.

FIG. 1. (Color online) Sheet resistance of Ni/SiGe and Ni/Al/SiGe systems as a function of silicidation temperature.

copy (RBS) data (not shown). The layer suffers pronounced degradation when the temperature increases above 600 °C. Cross-section transmission electron microscopy images are presented in Fig. 2. Agglomeration of polycrystalline NiSi$_{0.7}$Ge$_{0.3}$ grains is observed for Ni/SiGe systems at silicidation temperatures at 400 °C [Fig. 2(a)]. Interestingly, for the Ni/Al/SiGe system, the sheet resistance remains at a higher value in a temperature window from 300 to 500 °C due to the formation of a Ni rich germanosilicide phase (Ni$_2$Al$_x$Si$_y$Ge$_z$) as indicated by RBS measurements. The sheet resistance then decreases abruptly after annealing at 600 °C and remains at this value up to 700 °C. Only a few Ni germanosilicide grains were observed after a 600 °C anneal in an otherwise homogeneous continuous layer with sharp surface and interface to the SiGe substrates [Fig. 2(b)]. After annealing at 700 °C, the grains completely disappeared and a very uniform single crystalline germanosilicide layer with a thickness of 24 nm formed, as shown in the inset of Fig. 2(c). The high resolution TEM image in Fig. 2(c) clearly indicates an atomic flat crystalline NiAl$_x$Si$_y$Ge$_z$/Si$_{0.70}$Ge$_{0.30}$ interface for the Ni/Al/SiGe system. Considering the sheet resistance and the thickness of the Ni germanosilicide layer, a specific resistivity of ~22 $\mu\Omega$ cm is obtained,
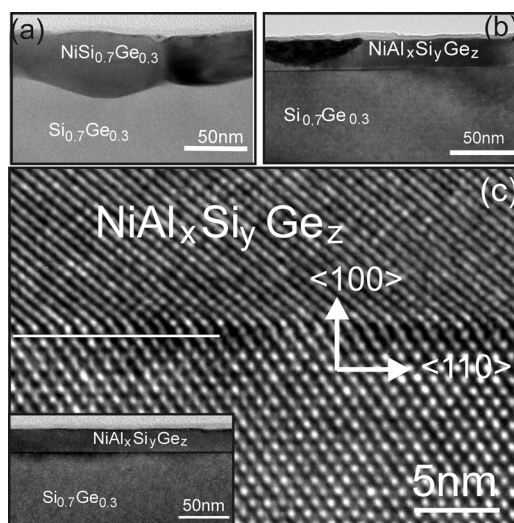

FIG. 2. Cross-section TEM image of (a) Ni/SiGe sample annealed at 400 °C, (b) Ni/Al/SiGe sample annealed at 600 °C, (c) high-resolution TEM image for Ni/Al/SiGe sample annealed at 700 °C, indicating an epitaxial Ni(Al)SiGe layer with an atomically flat interface to the SiGe. The inset shows a very uniform Ni(Al)SiGe layer on a larger scale.
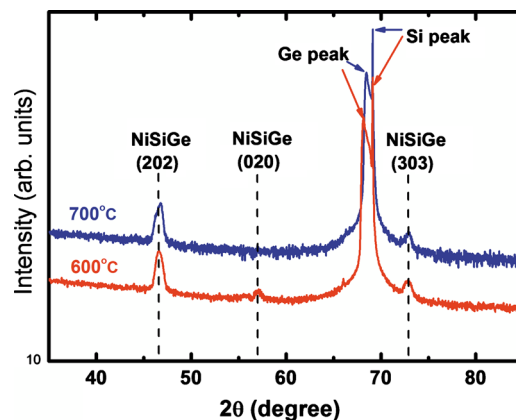

FIG. 3. (Color online) XRD curves of Ni(Al)SiGe layers formed at 600 °C and 700 °C. The main (101) orientation for both silicide layers is determined.

which is similar to the resistivity of polycrystalline Ni-germanosilicide.

X-ray diffractometry (XRD) in θ-2θ geometry (Bragg–Brentano) was employed for the analysis of the Ni-germanosilicide phase. The x-ray diffractograms acquired for Ni/Al/SiGe layer structures after annealing at temperatures of 600 and 700 °C are shown in Fig. 3. For the lower temperature anneal the XRD curve show, in addition to the peaks corresponding to the SiGe substrate, two sharp peaks at 46.6° and 72.9°, and one low intensity peak at 57.1°. The peaks at 46.6° and 72.9° correspond to NiSiGe (202) and (303) planes, respectively, while the peak at 57.1° is attributed to the NiSiGe (020) reflection. This indicates a certain degree of polycrystallinity of the germanosilicide layer. However, the combined information from TEM and XRD allows to affirm that the germanosilicide layer has predominant (101) base plane and a minor fraction of observed grains has the (020) orientation. For the Ni germanosilicide layer formed at 700 °C the small peak at 57.1° vanishes and only the sharp (202) and (303) peaks are visible. This confirms a highly oriented single-crystalline germanosilicide film as shown in the TEM images in Figs. 2(c). In conclusion, the epitaxial NiAl$_x$Si$_y$Ge$_z$ layer is in a monogermanosilicide phase with x+y+z=1, assuming that Al atoms occupy the substitutional lattice sites of Si in SiGe as demonstrated for the NiAl$_x$Si$_{2-x}$ case.[16] Further measurements indicate that y ≈ 0.7 and z ≈ 0.3, which corresponds closely the Si/Ge ratio of the substrate. Hence, we assume a very small Al content distributed in the germanosilicide layer.

To gain further insight into the mediating role of Al, depth distributions were determined by secondary ion mass spectrometry (SIMS). The SIMS results of Fig. 4 indicate that most of the Al segregated at the surface of the germanosilicide layer. An integration of the Al signal indicates that only ~2% of the Al atoms are distributed uniformly in the germanosilicide layer. Most of the Al atoms diffused to the surface, where they form an oxide with Si and Ge during annealing due to the residual oxygen in the RTP chamber. This indicates that the deposited Ni layer was completely reacted. A comparison of the remaining Al atom distributions in the epitaxial germanosilicide layers formed at 600 and 700 °C indicates that the Al contents in the germanosilicide layers do not change with the annealing temperature, possibly due to the formation of the most stable phase and solubility limitations. The uniform Ni and Ge distributions after
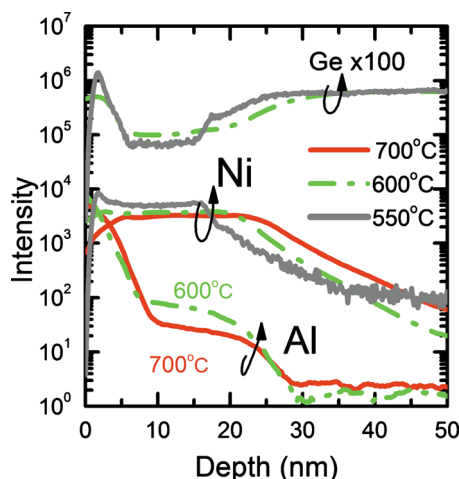
FIG. 4. (Color online) Depth distributions of Al, Ni, and Ge in the Ni germanosilicide layers formed at different temperatures. The Ge intensity is 100 times higher than the measured values for clarity.

600 and 700 °C anneals reveal that only one phase was formed. However, after 500 °C anneal, a Ni-rich phase was formed indicated by the high Ni content and lower Ge and Si contents (Si distributions are not shown in the figure for clarity) but at the interface monogermanosilicide phase is present as indicated by the shoulder steps in the Ni and Ge distributions close to the interface. At 550 °C the germanosilicide phases start to transfer from Ni-rich to monogermanosilicide phases, as already shown in Fig. 1.

In the case of Ti-interlayer or oxide mediated epitaxy of NiSi$_2$ and CoSi$_2$ single crystalline layers, the mediated layer (Ti and oxide) behaves as a diffusion barrier to reduce the diffusion of Ni or Co.[11,12,17] Obviously, the formation of the epitaxial disilicide phase (Si-rich) is preferred when the metal diffusion is reduced. This is contrary to the present results where a Ni-rich germanosilicide is the preferred phase at low temperatures when an Al interlayer is present. During annealing of Ni/Al/SiGe layer stack, Al diffuses through the Ni layer to the surface, while Ni diffuses simultaneously through the Al and germanosilicide toward the SiGe substrate. Possibly, the Al interlayer has the following effects. First, it reduces the Ni diffusion and, second, the presence of Al–Ni, Al–Si, and Al–Ge bonds in the reacted layer alters also the reactions of Al with the SiGe layer. Normally the Ni–Si reaction is faster than the Ni–Ge reaction due to its more negative enthalpy.[6] Al could be more favorable to bond with Si because of their similar atomic size. In this case, the reactions of Ni–Si and Ni–Ge are modulated and balanced. Third, Al atoms occupying the substitutional lattice sites of Si in NiSiGe could enlarge the lattice constant as in the case of NiAl$_x$Si$_{2-x}$.[16] The final lattice enlargement is very small because only <2% of Al atoms are incorporated in the layer.[16] However, we found that more Al atoms are present in the Ni-rich germanosilicide phase formed at low temperatures. During the transfer from Ni-rich germanosilicide phase to monogermanosilicide phase, the large amount of Al atoms could increase the lattice constant of NiSiGe. Finally, the Al incorporation in NiSiGe could increase the thermal expansion.[18] The first two effects can increase the activation energy of forming monogermanosilicide phases, leading to Ni-rich phase formation at low temperatures. Our results show clearly that the monogermanosilicide phase is formed only after complete formation of Ni-rich phases, as described

by d'Heurle *et al.* for NiSi.[19] NiSi has an orthorhombic structure with lattice constants of a=5.233 Å, b=3.258 Å, and c=5.659 Å.[19] Indeed, XRD polar figure results (not shown) indicate that NiAl$_x$Si$_y$Ge$_z$ has an orthorhombic structure with a (101) base plane rotated by 45° with respect to the (100) Si$_{0.7}$Ge$_{0.3}$ substrate. The latter two effects as discussed above are helpful in adjusting the lattice mismatch of the NiAl$_x$Si$_y$Ge$_z$ layer to the SiGe substrate. The crystal alignment of the NiAlSiGe layer to the SiGe substrate and the strain in the layer are still not fully understood and require further investigations.

In summary, we have shown that an epitaxial Ni monogermanosilicide layer can be formed on a relaxed SiGe substrate. A 3 nm thin Al interlayer was successfully used to mediate the epitaxial growth of (101) oriented single-crystal Ni(Al)SiGe layers with a sheet resistivity equal to low temperature formed polycrystalline NiSiGe layers. Considering the atomically flat interface between the Ni(Al)SiGe layer and the SiGe substrate, the approach presented may have wide applications for the next generation of CMOS devices.

[1] P. Packan, S. Akbar, M. Armstrong, D. Bergstrom, M. Brazier, H. Deshpande, K. Dev, G. Ding, T. Ghani, O. Golonzka, W. Han, J. He, R. Heussner, R. James, J. Jopling, C. Kenyon, S.-H. Lee, M. Liu, S. Lodha, B. Mattis, A. Murthy, L. Neiberg, J. Neirynck, S. Pae, C. Parker, L. Pipes, J. Sebastian, J. Seiple, B. Sell, A. Sharma, S. Sivakumar, B. Song, A. St. Amour, K. Tone, T. Troeger, C. Weber, K. Zhang, Y. Luo, and S. Natarajan, Tech. Dig. - Int. Electron Devices Meet. **2009**, 659.

[2] L. Gomez, P. Hashemi, and J. L. Hoyt, IEEE Trans. Electron Devices **56**, 2644 (2009).

[3] S. L. Zhang, Microelectron. Eng. **70**, 174 (2003).

[4] J. Seger, S. L. Zhang, D. Mangelinck, and H. H. Radamson, Appl. Phys. Lett. **81**, 1978 (2002).

[5] Q. T. Zhao, D. Buca, S. Lenk, R. Loo, M. Caymax, and S. Mantl, Microelectron. Eng. **76**, 285 (2004).

[6] J. Li, Q. Z. Hong, J. W. Mayer, and L. Rathbun, J. Appl. Phys. **67**, 2506 (1990).

[7] F. R. Deboer, R. Boon, W. C. Mattens, A. R. Miedema, and A. K. Niessen, *Cohesion in Metals: Transition Metal Alloys* (North-Holland, Amsterdam, 1988).

[8] L. J. Jin, K. L. Pey, W. K. Choi, E. A. Fitzgerald, D. A. Antoniadis, A. J. Pitera, M. L. Lee, D. Z. Chi, M. A. Rahman, T. Osipowicz, and C. H. Tung, J. Appl. Phys. **98**, 033520 (2005).

[9] L. J. Jin, K. L. Pey, W. K. Choi, E. A. Fitzgerald, D. A. Antoniadis, A. J. Pitera, M. L. Lee, and C. H. Tung, J. Appl. Phys. **97**, 104917 (2005).

[10] B. Zhang, W. Yu, Q. T. Zhao, D. Buca, B. Holländer, J. M. Hartmann, M. Zhang, X. Wang, and S. Mantl, Electrochem. Solid-State Lett. **14**, H261 (2011).

[11] O. Nakatsuka, K. Okubo, Y. Tsuchiya, A. Sakai, S. Zaima, and Y. Yasuda, Jpn. J. Appl. Phys., Part 1 **44**, 2945 (2005).

[12] J. E. Burnette, S. Kiesel, D. E. Sayers, and R. J. Nemanich, Thin Solid Films **516**, 1809 (2008).

[13] L. Knoll, Q. T. Zhao, S. Habicht, C. Urban, B. Ghyselen, and S. Mantl, IEEE Electron Device Lett. **31**, 350 (2010).

[14] A. Travlos, N. Boukos, G. Apostolopoulos, C. J. Aidinis, and L. Bischoff, Nucl. Instrum. Methods Phys. Res. B **196**, 174 (2002).

[15] E. J. Tan, K. L. Pey, D. Z. Chi, P. S. Lee, Y. Setiawan, and K. M. Hoe, J. Electrochem. Soc. **155**, H26 (2008).

[16] K. W. Richter and K. Hiebl, Appl. Phys. Lett. **83**, 497 (2003).

[17] R. T. Tung, Appl. Phys. Lett. **68**, 3461 (1996).

[18] A. Schubert, Diploma thesis, Tech. Univ. Chemnitz, 2005.

[19] F. d'Heurle, C. S. Petersson, J. E. E. Baglin, S. J. La Placa, and C. Y. Wong, J. Appl. Phys. **55**, 4208 (1984).