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Observation of a New Kinetics to Form Ni_3Si_2 and $Ni_{31}Si_{12}$ Silicides at Low Temperature (200°C)

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The effect of prolonged annealing (10 h) at low temperature (200°C) has been studied in 20-nm Ni/Si(100) samples using Rutherford backscattering spectroscopy, X-ray diffraction, and four-point probe techniques. We observed that at 200°C a considerable amount of Ni_3Si_2 and $Ni_{31}Si_{12}$ was formed. After 10 h annealing at 200°C only a fraction of total amount of Ni has been converted into Ni_3Si_2 and $Ni_{31}Si_{12}$ phases and around 60% of nickel remains unreacted. Formation of the Ni_3Si_2 and $Ni_{31}Si_{12}$ silicides at 200°C is slow and seems to saturate after approximately 140×10^{15} atoms/cm^2. It is observed that after 2 h annealing the amount of both silicides is almost equal to that after 10 h annealing. After 10 h annealing at 300°C there is no indication of either Ni_3Si_2 or $Ni_{31}Si_{12}$, and all Ni was consumed and only the stable NiSi phase is detected.

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NiSi is an attractive material to replace $CoSi_2$ for future use in complementary metal-oxide semiconductor (CMOS) circuits for ultralarge scale integration (ULSI) because of the linewidth independence of its sheet resistance, its low resistivity, its comparatively low Si consumption,[1,2] and the absence of a bridging problem.[3]

The Ni–Si phase[4] diagram is much more complex than that of Co–Si or Ti–Si ones. While only three phases are stable at room temperature in the Co–Si system (Co_2Si, CoSi, and $CoSi_2$), one has up to eleven phases in the Ni–Si diagram, six of which being stable at room temperature (Ni_3Si, $Ni_{31}Si_{12}$, Ni_2Si, Ni_3Si_2, NiSi, and $NiSi_2$). This considerably increases the complexity of the phase formation sequence and its possible dependence on processing parameters and substrate variations (dopant type, concentration, cleaning conditions, and substrate type).

A thin NiSi film is typically formed by the solid-state reaction of a thin Ni film and Si substrate and the reaction follows the[5] sequence of Ni/Si → Ni_2Si (at 250°C) → NiSi (at 350–750°C) → $NiSi_2$ (above 750°C). While the formation of NiSi at temperatures of 300°C or above and the transformation of NiSi to $NiSi_2$ at 700–750°C has been well documented, the transition sequence between different metal-rich phases in the low-temperature regime (<300°C) is not fully understood, as highlighted by reports of contradictory results in the literature. For example, it is reported in Ref. 6 that some epitaxial $NiSi_2$ forms early in the phase sequence and is consumed by Ni_2Si or NiSi. However in Ref. 7, Lavoie et al. also tried to detect the epitaxial $NiSi_2$ formed early in the phase sequence but failed to do so.

Apart from the basic material science and reaction-kinetics-related interest, such low-temperature phases may be of technological interest, because a two-step silicidation process, i.e., Ni-rich phase formation at low temperatures, followed by selective etching of unreacted Ni and subsequent NiSi formation using higher temperature rapid thermal processing (RTP), may be important for NiSi film formation in ultrasmall/narrow structures to avoid excess silicidation.[8]

In this paper, it is reported for the first time that at 200°C, Ni_3Si_2 and $Ni_{31}Si_{12}$ phases indeed grow without any special thin-film deposition arrangement (the authors of Ref. 9 found the Ni_3Si_2 phase, but they deposited Si and Ni in the stochiometric quantities). The formation of Ni_3Si_2 from the reaction of Ni_2Si with NiSi has been investigated by Gas et al.[9] They reported that Ni_3Si_2 formation occurs at 470°C, and before reaching this temperature they detected only Ni_2Si and NiSi phases. The authors argued that Ni_3Si_2 formation is solely nucleation controlled.

Experimental

The Ni films with thickness of 20 nm were deposited by sputtering of pure Ni targets on (100) n-type Si phosphorus-doped ($\sim 2 \times 10^{15}$ cm^{-3}) wafers. The wafers were cleaned using standard RCA cleaning procedures[10] by dilute HF. A number of chips diced from these wafers were then subjected to furnace annealing in N_2 ambient for silicidation at 200 and 300°C temperatures and different time intervals varying from 1 to 10 h. Rutherford backscattering (RBS) measurements were carried out at the 3.5 MV Singletron accelerator at the Centre for Ion Beam Applications at the National University of Singapore to determine the silicides layer thickness, elemental distributions, and interface roughness. A 2 MeV He^+ beam of typically 20 nA beam current and 1 mm^2 spot size was used. RBS spectra were recorded with 50-mm^2 passivated implanted planar silicon (PIPS) detectors of 15 keV energy resolution at 130° scattering angle in IBM geometry. The sample was tilted to 32° to achieve a glancing angle geometry in order to improve depth resolution. The RBS spectra were analyzed using the simulation code RUMP.[11] To support phase identification from RBS analysis, X-ray diffraction (XRD) analysis was also carried out with Cu Kα radiation (average wavelength 1.5418 Å) in the θ-2θ geometry, and four-point probe (model 220, Keithley Instruments, Inc., U.S.A.) was employed for sheet resistance measurements.

Results

Figure 1 shows RBS spectra from 20-nm Ni/Si(100) thin films, as deposited and after 2 and 10 h furnace annealing at 200°C in N_2 ambient. For comparison, a spectrum of 20-nm Ni/Si(100) at 300°C after 10 h annealing is also shown. As shown in Fig. 1b-d, the silicide formation results in a step in the Si signal as well as a widening and lowering of the Ni signal. As the scattering cross section of Ni is higher than that of Si, it is more convenient to see silicide reaction evolution from the Ni edge instead of the Si edge. The RBS simulation is consistent with the formation of $Ni_3Si_2 + Ni_{31}Si_{12}$ phases for all samples annealed at 200°C. From the Ni to Si ratios in the silicide layer, it is estimated that after 2 h annealing $Ni_{31}Si_{12}$ is 85% and Ni_3Si_2 is 15%, and after 10 h annealing $Ni_{31}Si_{12}$ is 80% and Ni_3Si_2 20%. Therefore, though the dominant phase is $Ni_{31}Si_{12}$, a significant amount of Ni_3Si_2 is always present. From the width of the Ni peak it is observed that with increasing annealing time only a minor increase in the silicide thickness occurs, i.e., after the formation of a certain amount of $Ni_3Si_2 + Ni_{31}Si_{12}$ (140×10^{15} atoms/cm^2), the reaction virtually stops.

The RBS spectra indicate that a phase change does not happen over the entire 10 h of annealing. As seen from the spectra of all 200°C-annealed samples, a substantial quantity of Ni retains on the surface, implying that not all Ni converts to silicides. The amounts

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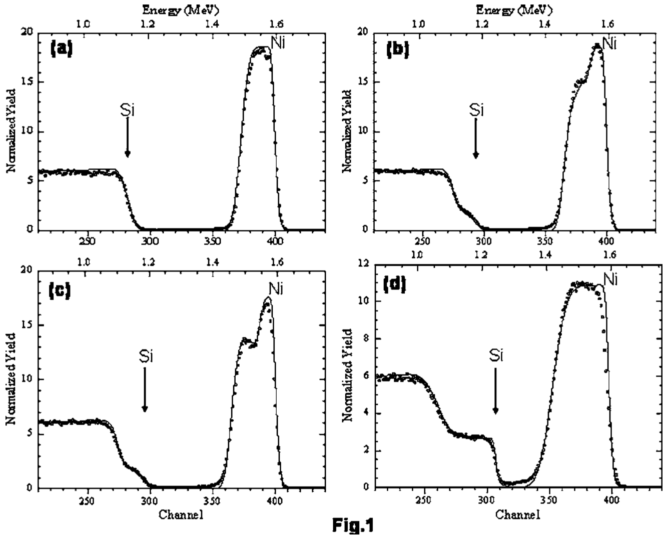

Fig.1

Figure 1. The 2-MeV 4He$^+$ RBS spectra of the 20-nm Ni/Si(100) films (a) as deposited and annealed at 200°C for (b) 2 h, (c) 10 h, and (d) annealed at 300°C for 10 h.

of Ni, $Ni_{31}Si_{12}$, and Ni_3Si_2 after various annealing time periods are displayed in Fig. 2. For comparison, after 10 h annealing at 300°C, the RBS simulation is consistent with a complete phase transformation leading to the stable NiSi phase (330×10^{15} atoms/cm^2). Due to the stable NiSi phase extending from the surface to the interface between Si and silicide, Si is at the surface, as seen in Fig. 1d.

The results of the XRD measurements are shown in Fig. 3a. Various Ni_3Si_2 and $Ni_{31}Si_{12}$ peaks were detected and there is no appreciable change of the silicide peak intensities from 2 to 10 h annealing time. The ratios of the area of the Ni_3Si_2 XRD peak to the $Ni_{31}Si_{12}$ XRD peak increases from the 2–10 h samples by 4.6%. This implies that after 7 and 10 h annealing the amount of Ni_3Si_2 is increased a little, which is perfectly consistent with RBS analysis. Figure 3b is the XRD spectrum for the 20-nm Ni/Si(100) sample annealed after 10 h at 300°C. As shown, no Ni_3Si_2 and $Ni_{31}Si_{12}$ peaks are present; only NiSi peaks emerge. Clearly, the formation of Ni_3Si_2 and $Ni_{31}Si_{12}$ phases during the heating ramp is consumed and formed NiSi at 300°C.

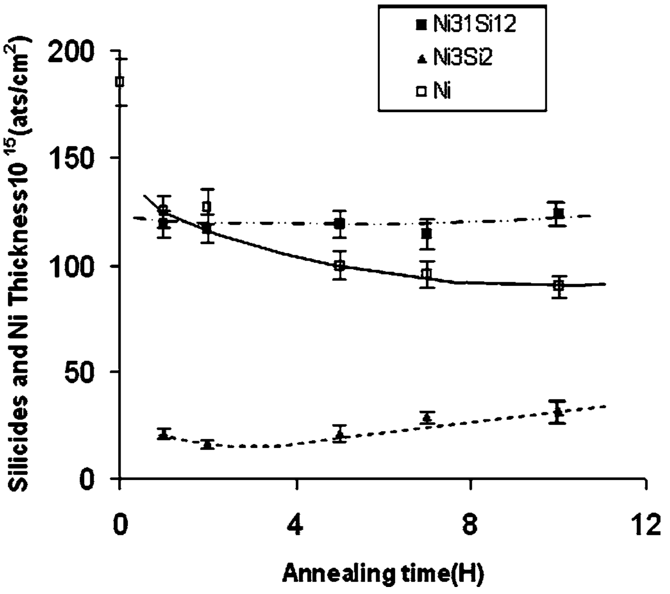

Figure 2. Growth of Ni_3Si_2 + $Ni_{31}Si_{12}$ silicides with increasing annealing time at 200°C (lines are drawn to guide the eye).

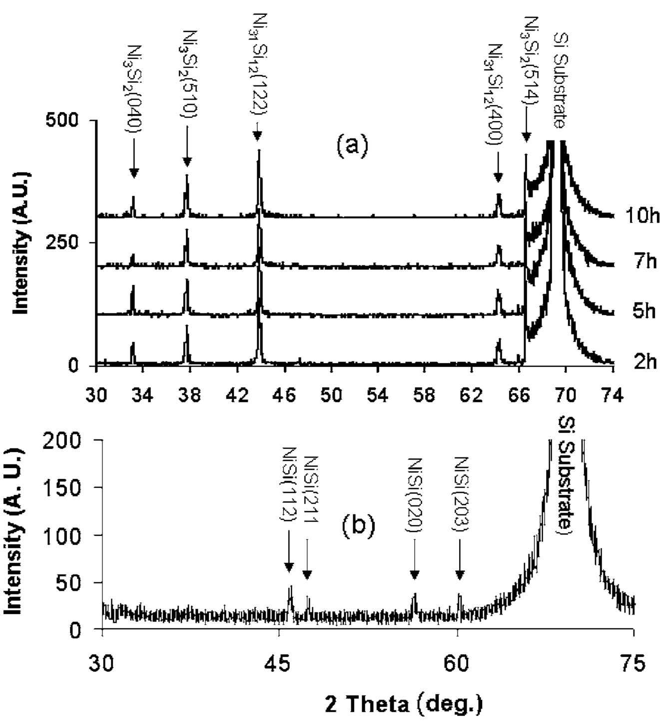

Figure 3. (a) XRD spectra of 20-nm Ni/Si(100) samples annealed for (a) 2, 5, 7, and 10 h at 200°C and (b) for 10 h at 300°C.

Sheet resistance measurements were also carried out for all samples. Figure 4 shows the sheet resistance of the various samples as a function of annealing time at 200°C. After 1, 2, 5, 7, and 10 h annealing at 200°C, sheet resistances are almost constant, indicating only slight decreases, which suggests that there is no phase change happened during 1–10 h annealing. The sheet resistance at 300°C after 10 h annealing shows a drastic lower value, confirming that stable NiSi phase formation indeed occurs.

Discussion

It was reported that[12] nickel films deposited on silicon form an intermediate layer of Ni_2Si at temperatures above 200°C with no indication of the presence of the other equilibrium phases (Ni_3Si,

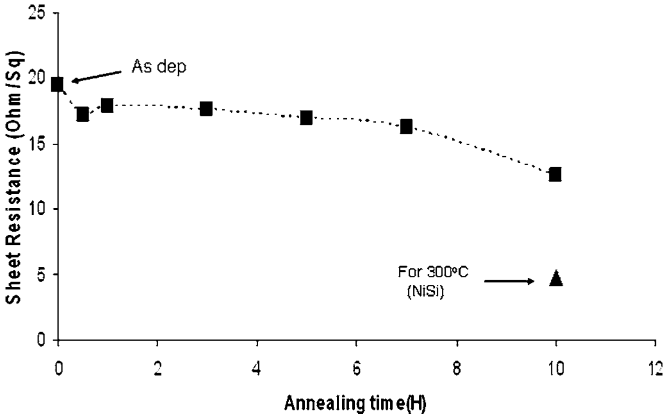

Figure 4. Sheet resistance of 20-nm Ni/Si(100) thin films as a function of annealing time at fixed annealing temperature of 200°C. Sheet resistance of one thin film of 20-nm Ni/Si(100) annealed at 300°C for 10 h is also shown.

Ni_3Si_2, $Ni_{31}Si_{12}$, NiSi, or $NiSi_2$) as long as both unreacted nickel and silicon are available. According to available theories[12] of multiphase diffusion-controlled layer growth, all equilibrium phases should be present. Various reasons have been given regarding why not all of them are observed in thin-film diffusion couples. It is argued that either all equilibrium phases are in fact present but some of them cannot be observed because of limited[13] experimental resolution, or that some of the phases could not nucleate[14] but would grow if they could overcome a nucleation barrier. It has also been claimed that the formation of the missing compound phases are thermodynamically impossible at the generally lower diffusion[15] temperatures in thin-film compared to bulk diffusion couples.

The formation of Ni-rich $Ni_{31}Si_{12}$,Ni_3Si_2 phases at low temperatures may be explained by the consideration of bond energies of NiNi and SiSi. The bond energy of Ni in the gaseous diatomic species NiNi is 203.26 ± 0.96 kJ mol^{-1}. The bond energy in the gaseous diatomic species SiSi is 326.8 ± 10.0 kJ mol^{-1}. These represent the strength of the chemical[16] bonds for NiNi and SiSi. As the removal of silicon atoms from their lattice sites is most difficult when the bonding is purely covalent (i.e., in pure silicon) and easiest when the bonding is metallic (metallic nickel), for all low-temperature silicides formation should be favorable to grow Ni-enriched silicides.

From Fig. 2 it may be concluded that in the present case Ni_3Si_2 grows via diffusion rather than nucleation. From the phase sequence of the nickel silicides, Ni_2Si should grow before Ni_3Si_2 but no Ni_2Si phase is detected. This does not completely rule out the coexistence of the Ni_2Si phase with the other two detected phases, because XRD detection only probes a very small portion of the possible grain orientations and the diffraction geometry may not allow detecting small amounts of Ni_2Si.

Another interesting point is that it may be possible that Ni_3Si_2 grows epitaxially on the Si substrate. The cubic structure of Si is $a = 5.43$ Å, and Ni_3Si_2 has an orthorhombic crystal structure with $a = 12.229$ Å, $b = 10.805$ Å, and $c = 6.924$ Å. The in-plane axis lattice parameter of Ni_3Si_2 is just double the corresponding parameter of Si; therefore, Ni_3Si_2 may grow epitaxially. The Ni_2Si lattice parameters[17] are $a = 5$ Å, $b = 3.73$ Å, and $c = 7.04$ Å, and no matches with Si are possible. Therefore it is not a surprise to detect Ni_3Si_2 but no Ni_2Si at this low temperature.

In our study, after formation of a certain amount of silicides ($\sim 140 \times 10^{15}$ atoms/cm^2) the quantities of both Ni_3Si_2 and $Ni_{31}Si_{12}$ silicides increase very little with increasing annealing time. The three well-known growth mechanisms would predict the following: for nucleation growth the whole film reacts within small a temperature range and time; for reaction-limited growth the thickness of silicide is proportional to annealing time; and for diffusion-limited growth the thickness is proportional to annealing $time^{1/2}$. Therefore, the above three well-known growth mechanisms cannot explain the $Ni_3Si_2 + Ni_{31}Si_{12}$ growth mechanism at the low temperature of 200°C. To understand the exact mechanism of the Ni_3Si_2 formation and the saturated nature of reaction kinetics in 20-nm Ni/Si(100) thin-film systems at 200°C, additional studies are needed.

Our detection of silicide phases in 20-nm Ni/Si(100) at 200°C is partially consistent with previous studies, as $Ni_{31}Si_{12}$ growth[7] is observed at 160°C but Ni_3Si_2 growth occurs through nucleation[9] at the temperature of 470°C.

Conclusion

In conclusion, upon annealing 20-nm Ni/Si(100) thin films at 200°C for various time periods, ranging from 1 to 10 h, Ni_3Si_2 and $Ni_{31}Si_{12}$ growth are observed. The amount of the silicide growth does not increase considerably with increasing annealing time period. Formation of silicides at 200°C has been compared with that at 300°C, and at 300°C after 10 h annealing only stable NiSi phase is detected.

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References

1. J. Chen, J. P. Colinge, D. Flandre, R. Gillon, J. P. Raskin, and D. Vanboenacker, *J. Electrochem. Soc.*, **144**, 2437 (1997).
2. T. Ohguro, S. Nakajima, M. Koike, T. Morimoto, A. Nishiyama, Y. Ushiku, T. Yoshitomi, M. Satio, and H. Iwai, *IEEE Trans. Electron Devices*, **41**, 2305 (1994).
3. T. Morimoto, T. Ohguro, S. Momose, T. Iinuma, I. Kunishima, K. Suguro, I. Katakabe, H. Nakajima, M. Tsuchiaki, M. Ono, Y. Katsumata, and H. Iwai, *IEEE Trans. Electron Devices*, **42**, 915 (1995).
4. *Handbook of Binary Alloy Phase Diagram*, CD version 1.0, ASM International, Materials Park, OH.
5. M.-A. Nicolet and S. S. Lau, in *VLSI Electronics Microstructure Science*, N. G. Einspruch and G. B. Larrabee, Editors, p. 329, Academic, New York (1983).
6. V. Teodorescu, L. Nistor, H. Bender, A. Steegen, A. Lauwers, K. Maex, and J. Van Landuyt, *J. Appl. Phys.*, **90**, 67 (2001).
7. C. Lavoie, F. M. d'Heurle, C. Detavernier, and C. Cabral, Jr., *Microelectron. Eng.*, **70**, 144 (2003).
8. J. P. Lu, D. Miles, J. Zhao, A. Gurba, Y. Xu, C. Lin, M. Hewson, J. Ruan, L. Tsung, R. Kuan, T. Grider, D. Mercer, and C. Montgomery, *Tech. Dig. - Int. Electron Devices Meet.*, **2002**, 371.
9. P. Gas, F. M. d'Heurle, F. K. LeGoues, and S. J. La Placa, *J. Appl. Phys.*, **59**, 3458 (1986).
10. W. Kern and D. A. Puotinen, *RCA Rev.*, **31**, 187 (1970).
11. L. Doolittle, *Nucl. Instrum. Methods Phys. Res. B*, **9**, 344 (1985).
12. U. Gösele and K. N. Tu, *J. Appl. Phys.*, **53**, 3252 (1982).
13. G. V. Kidson, *J. Nucl. Mater.*, **3**, 21 (1961).
14. J. E. E. Baglin, F. M. d'Heurle, and C. S. Peterson, in *Thin Film Interfaces and Interactions*, J. E. E. Baglin and J. M. Poste, Editors, p. 341, The Electrochemical Society, New York (1980).
15. S. U. Campisano, in *Thin Film Phenomena-Interfaces and Interactions*, J. E. E. Baglin and J. M. Poate, Editors, p. 129, The Electrochemical Society, New York (1978).
16. D. R. Lide, in *CRC Handbook of Chemistry and Physics*, 79th ed., D. R. Lide, Editor, CRC Press, Boca Raton, FL (1998).
17. W. B. Person, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, vers. 2, p. 340, Pergamon Press, New York (1967).