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# Transmission electron microscopy of the formation of nickel silicides

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#### ABSTRACT

The formation of Ni<sub>2</sub>Si, NiSi and NiSi<sub>2</sub> on Si has been studied by TEM, particularly with cross-sectional specimens and by high-resolution imaging. Both Ni<sub>2</sub>Si and NiSi showed an oriented growth on {111} substrates, while NiSi<sub>2</sub> grew epitaxially on {111} and {100} Si. Ni<sub>2</sub>Si assumed two different pseudo-hexagonal orientations whereas NiSi was found to be truly hexagonal instead of orthorhombic on {111} Si. TEM of cross-sectional specimens showed that all the silicide–Si interfaces were quite rough, except in the case of NiSi<sub>2</sub> where it was highly facetted. When Ni<sub>2</sub>Si and NiSi were present simultaneously, they often were separated by an interfacial layer, ~3 nm thick, which might be related to Kirkendall voids or to remainders of the native oxide on the Si substrate. Cross-sectional views of misfit dislocations in the epitaxial interfaces have been obtained and analysed in terms of their Burgers vector and spacing.

# § 1. INTRODUCTION

Recently wide-spread interest has developed in studying the properties of silicon-silicide interfaces, especially for near-noble-metal silicides. These silicides are finding applications in microelectronic devices as rectifying and Ohmic contacts. Many technically important properties of these contacts, such as Schottky barrier height, contact resistance and corrosion stability are controlled by the silicon-silicide interfaces, consequently there is an impetus to advance our understanding about these interfaces. Most silicide studies have been concentrated on reaction kinetics and identification of phases formed during reaction. A large body of information has been obtained about activation energies of silicide growth, sequence of phase formation and the predominant diffusing species during the reaction, yet much less is known about the structural and morphological aspects of silicide-silicon or silicide-silicide interfaces.

Many silicides can grow epitaxially on Si substrates, e.g.  $Pd_2Si$  on {111} Si and  $NiSi_2$  on {111} and {100} Si. Epitaxial silicides offer an opportunity to investigate their interfaces by cross-sectional high-resolution transmission electron microscopy (TEM). First results of such an investigation have been published (Föll, Ho and Tu 1980). In this paper, a systematic TEM study of Ni silicides and their interfaces is now described. The Ni–Si system has already received much attention in the past (Tu, Alessandrini, Chu, Kräutle

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and Mayer 1974, Tu, Chu and Mayer 1975, Olowolafe, Nicolet and Mayer 1976, Pretorius, Ramiller, Lau and Nicolet 1977, Canali, Catellani, Ottaviani and Prudenziati 1978, Ishiwara, Nagatomo and Furukawa 1978, Pretorius, Ramiller and Nicolet 1978, Canali, Majni, Ottaviani and Celotti 1979, Chiu, Poate, Feldman and Doherty 1980) and it is generally agreed that the first compound formed is orthorhombic Ni<sub>2</sub>Si (at 200–350°C), followed by orthorhombic NiSi (at 300–700°C) and finally by cubic NiSi<sub>2</sub> (at >700°C). NiSi<sub>2</sub> has a lattice constant very close to that of Si and consequently grows epitaxially on low-index Si surfaces (Tu *et al.* 1974, Ishiwara *et al.* 1978, Chiu *et al.* 1980, Föll *et al.* 1980). It has been shown that the NiSi<sub>2</sub>–Si interface is highly facetted and contains misfit dislocations (Föll *et al.* 1980). It is rather rough on  $\{100\}$  Si but on  $\{111\}$  Si the interface is much smoother and the lattice of NiSi<sub>2</sub> is twinned with respect to the Si (Föll *et al.* 1980). No information is available about the interfacial structure of the two earlier phases.

In this paper the results of a transmission electron microscopy study of  $Ni_2Si$ , NiSi and  $NiSi_2$  on  $\{100\}$  and  $\{111\}$  Si substrates are reported. Besides 'conventional' or 'flat-on' TEM (i.e. electron beam perpendicular to the silicide interface), extensive use has been made of 'cross-sectional' or 'edge-on' TEM (i.e. electron-beam parallel to the silicide interface) and direct-lattice-imaging techniques.

#### § 2. Experimental procedures

Commercial Si wafers (1 in. diameter, 10  $\Omega$  cm, n-type) were degreased and dipped in buffered HF solution prior to evaporation. Ni was evaporated by e-beam on both {100} and {111} Si wafers to a thickness of 50 nm at room temperature. All wafers were then annealed at 300°C for 20 min in a He atmosphere to form Ni<sub>2</sub>Si. Subsequently, the wafers were cleaved into two halves and one set of the halves annealed at 400°C for 20 min to form NiSi. After that the half-wafers were cleaved again and one set of the resulting quarter-wafers was finally annealed at 800°C for 1 hour to form NiSi<sub>2</sub>.

Conventional TEM specimens were prepared by chemical thinning from the back side of the samples. Cross-sectional specimens were prepared using the procedure outlined by Sheng and Chang (1976) and Föll *et al.* (1980). Electron microscopy was performed in a JEOL 200B microscope operated at 200 kV beam voltage or in a Siemens 102 at 125 kV beam voltage.

#### § 3. Results

#### 3.1. {100} wafer orientation : 300 and 400°C annealing ; conventional TEM

The electron diffraction patterns of conventional specimens (fig. 1) showed that orthorhombic Ni<sub>2</sub>Si (a = 0.704 nm, b = 0.5 nm, c = 0.375 nm) was formed after the 300°C anneal and orthorhombic NiSi (a = 0.562 nm, b = 0.518 nm, c = 0.334 nm) was formed after the 400°C anneal. The Ni<sub>2</sub>Si diffraction showed only Debye–Scherrer rings (fig. 1 (a)), whereas the NiSi diffraction pattern was textured (fig. 1 (b)). The latter, however, was only seen if the  $\langle 100 \rangle$  direction of the Si substrate was almost parallel to the electron beam. This is usually not the case because the thin areas of the sample invariably are bent, due to stresses in the silicide layer. The texture therefore is easily overlooked and



Diffraction patterns of (a) Ni<sub>2</sub>Si present after the 300°C annealing and of (b) NiSi present after the 400°C annealing.

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Fig. 2



Silicide layers on  $\{100\}$  Si (a) after the 300 °C annealing and (b) after the 400 °C annealing.

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has not been reported before. The texture can be explained by assuming an occasional epitaxial growth of NiSi grains with the NiSi  $\{121\}$  planes (spacing 0.191 nm) matching the Si  $\{220\}$  planes (spacing 0.192 nm).

Figure 2 shows bright-field micrographs of the silicide layers. As can be seen, the films are polycrystalline with a grain size of 30-70 nm for the Ni<sub>2</sub>Si and 30-100 nm for the NiSi.

# 3.2. {111} wafer orientation ; 300 and 400°C annealing ; conventional TEM

Figure 3 shows the electron diffraction patterns of the silicides formed on  $\{111\}$  Si after the 300 and 400°C annealings. Clearly, in both cases an epitaxial relationship between Si and the silicides is observed. The diffraction pattern for the 300°C case (fig. 3 (a)) will be discussed first.



Fig. 3

Diffraction pattern of (a) epitaxial Ni<sub>2</sub>Si and NiSi present on {111} Si after the 300°C annealing and of (b) epitaxial and polycrystalline NiSi after the 400°C annealing For details see the text.

The most prominent reflections, labelled 1, 2 and 3 (4 will be discussed later) correspond to lattice spacing of ~0.35 nm (spot 1), 0.33 nm (spot 2), and 0.28 nm (spot 3). These spacings compare favourably with the (200) and (101) plane of Ni<sub>2</sub>Si (0.352 nm and 0.331 nm spacing) and the (002) plane of NiSi (0.284 nm spacing). Although there are other possible choices, if we assume that these planes are responsible for the observed spots, they must belong to a hexagonal or pseudo-hexagonal subsystem of the orthorhombic unit cell. Such a hexagonal symmetry can indeed be found for both Ni<sub>2</sub>Si and NiSi, fig. 4 shows a projection of the Ni<sub>2</sub>Si unit cell on the (010) plane. (The atom positions are taken from Wyckoff (1963) and the unit-cell dimensions from Tu *et al.* (1974).) On this projection, the pseudo-hexagonal symmetry can be seen and the (200) and (101) planes form a slightly distorted hexagon in agreement with the observed diffraction pattern. Preferred growth of epitaxial Ni<sub>2</sub>Si grains with this orientation is probably favoured Fig. 4





Ni<sub>2</sub>Si lattice projected on the (010) plane. The large circles correspond to Si atoms, the small circles represent Ni atoms. The atoms are in various positions above and below the plane of the paper.

because of the close match of the second-order prismatic planes ( $\{301\}$  and  $\{\overline{102}\}$  with spacings 0.199 nm and 0.181 nm, respectively) with the Si  $\{220\}$  planes (spacing 0.192 nm). The basic geometry of this pseudo-hexagonal system is quite similar to that of epitaxial PtSi on  $\{111\}$  Si (Sinha, Marcus, Sheng and Haszko 1972).

The interpretation of diffraction spot 3 in fig. 3 (a) is less straightforward. In contrast to spots 1 and 2 it is fairly sharp thus strongly suggests a true hexagonal symmetry of the underlying lattice. This spot cannot be assigned to Ni<sub>2</sub>Si or NiSi<sub>2</sub> (nor, for that matter, to Ni<sub>3</sub>Si, Ni<sub>31</sub>Si<sub>12</sub> or Ni<sub>5</sub>Si<sub>2</sub>) and thus must originate from NiSi. The problem is that NiSi is reported to be orthorhombic and not hexagonal. However, hexagonal lattices can be viewed as sublattices of an orthorhombic unit cell and a 'true' hexagonal lattice will be obtained if the ratio between two of the three orthorhombic unit axes is equal to  $\sqrt{3} = 1.732$ . From the reported lattice parameters of orthorhombic NiSi, ratios of 1.747 (Wyckoff 1963) and 1.682 (Tu et al. 1974) can be calculated, i.e. just below and above the required ratio for a hexagonal symmetry. It therefore seems justified to assume that the NiSi unit cell is truly hexagonal with a = 0.323 nm and c = 0.516 nm (these values were chosen for optimal agreement with literature values and our own observations). In addition to the a/c ratio, atom positions have to obey a hexagonal symmetry too. Unfortunately, the atom positions for NiSi are not tabulated. Figure 5 therefore shows the (orthorhombic) unit cell of NiSi with the atom positions of NiGe (which is supposedly similar to NiSi) as given by Wyckoff (1963). It can be seen that only a small change of the atom positions is needed to create a truly hexagonal unit cell. It is therefore suggested here that NiSi either is hexagonal or can at least exist under stress in a hexagonal form closely related to its reported orthorhombic structure.



PROPOSED ATOM POSITIONS IN NISI

Proposed NiSi lattice projected on the (010) plane. The atomic positions of NiGe and the proposed positions for NiSi are shown. The large circles represent Si or Ge atoms, respectively, the small circles correspond to Ni atoms.

The hexagonal NiSi is not well matched to the Si {111} geometry. The misfit between the NiSi {1120} planes (henceforth the hexagonal indexing will be used for NiSi) and the Si {220} planes is  $\sim 15\%$ , a rather large value. Nevertheless the high degree of epitaxy observed indicates that the gain in interfacial energy is larger than the energy spent on strain and misfit dislocations.

In conclusion, fig. 3 (a) demonstrates that at 300°C both Ni<sub>2</sub>Si and NiSi are present on  $\{111\}$ Si and both show a high degree of epitaxy with the Si substrate. This is unexpected because NiSi has not been reported to form at all at 300°C (Tu *et al.* 1974, Tu *et al.* 1975, Coe and Rhoderick 1976, Olowolafe *et al.* 1976, Berning and Levenson 1978). However, it is known that electron microscopy is more sensitive in detecting the early stage growth of silicide, especially if this occurs epitaxially.

The interpretation of the diffraction pattern in fig. 3 (b) now becomes straightforward. The Ni<sub>2</sub>Si spots have disappeared and the NiSi spots appear stronger. Thus, after the 400°C anneal, the NiSi becomes fully reacted and is the only phase present. Sometimes a ring pattern belonging to NiSi is observed in addition to the epitaxial pattern, indicating that polycrystalline NiSi can be formed, too. Figure 6 shows the bright-field images of the layers formed after the 300°C and 400°C annealing. The average grain size is  $\sim 50$  nm after the 300°C annealing and  $\sim 100$  nm after the 400°C annealing.



Fig. 6

Silicide layers on  $\{111\}$  Si (a) after the 300°C annealing and (b) after the 400°C annealing.

3.3.  $\{100\}$  wafer orientation; 300 and 400°C annealing; cross-sectional TEM

Figure 7 shows cross-sectional views of the silicide layers formed after the 300 and 400°C annealing procedure. Whereas the 300°C silicide forms a rather homogeneous polycrystalline layer, the silicide formed at 400°C is clearly divided into a two-layer structure. Before further discussing the implications of fig. 7, two shortcomings of cross-sectional microscopy should be noted. First, the total area investigated is extremely small. Whereas a conventional specimen may have an electron-transparent area of up to  $10^5 \,\mu\text{m}^2$  (i.e.  $\sim 0.10\%$  of a macroscopic 1 cm<sup>2</sup> sample), cross-sectional specimens have a much smaller interfacial area which is transparent to the electron beam, typically in the order of  $1-10 \,\mu\text{m}^2$  (i.e.  $\sim 10^{-40}\%$  of the sample area). Moreover, in preparing conventional samples it is usually possible to locate the electron-transparent area of the TEM sample in a region of particular interest, but this is not the case

Fig. 7



• Cross-sectional view of (a) Ni<sub>2</sub>Si on {100} Si after the 300°C annealing and of (b) NiSi and Ni<sub>2</sub>Si after the 400°C annealing. For details see the text.

for cross-sectional specimens. In general, if the macroscopic sample is not completely homogeneous, cross-sectional samples may not always be representative and the statistical significance of cross-sectional data is not always clear. Second, it is difficult to obtain interpretable electron-diffraction patterns from cross-sectional samples because of the thinness of the silicide layer. Even the smallest possible selected-area diffraction apertures of  $\sim 1 \,\mu$ m in diameter encompass the silicide, its substrate plus the adjacent layer and sometimes also the epoxy glue between them. If the silicide film is polycrystalline, only a few grains will contribute to the diffraction pattern, producing a few diffraction spots but no well-developed rings. Only for epitaxial silicide films can an easily interpretable diffraction pattern be expected.

Both difficulties have been encountered in the present study. As indicated in fig. 7, cross-sections from different areas of the same wafer look indeed different. This behaviour was also observed for the  $\{111\}$  case and at present not all observations are understood. It may be concluded, however, that the formation of Ni-silicide is not entirely homogeneous over a Si wafer. The diffraction patterns, as far as they could be evaluated, show the presence of Ni<sub>2</sub>Si at 300°C and of NiSi and Ni<sub>2</sub>Si at 400°C. This is in basic agreement with the findings from conventional specimens, although in the latter case the presence of  $Ni_2Si$  was uncertain at 400°C. However, since the diffraction patterns of  $Ni_2Si$  and NiSi are similar, weak  $Ni_2Si$  rings can be easily overlooked in the presence of stronger NiSi reflections.

The layered structure of the silicide at 400°C is striking, though sometimes it is very clear as in fig. 7 (c) and sometimes more subtle as in fig. 7 (b). It is likely that the thick innermost layer consists of NiSi and the outer layer of Ni<sub>2</sub>Si (the top layer in the figures is Si). The two layers in fig. 7 (c) appear to be separated by an intermediate layer,  $\sim 3$  nm wide, which could consist of SiO<sub>2</sub> (Föll and Ho 1981) or even of voids. The Si-silicide interface is sharply defined although rough, with an amplitude of  $\sim 50$  nm and a typical roughness wavelength of  $\sim 100$  nm. In contrast, the silicide surface (the bottom surface in fig. 7) is rather flat.

# 3.4. {111} wafer orientation ; 300 and 400°C annealing ; cross-sectional TEM

Figure 8 shows representative examples of the 300 and 400°C samples with the top layer being Si. The 300°C (fig. 8 (*a*)) sample shows a layered structure reminiscent of the 400°C/{100} case. According to the findings of conventional TEM, the silicides should be epitaxial in this case and a correspondingly simple diffraction pattern is to be expected.

Figure 9 shows typical diffraction patterns from these cross-sectional specimens. Based on the epitaxial geometry discussed above, the Ni<sub>2</sub>Si (010) and the NiSi (0002) spots (0.250 nm, no. 1; and 0.258 nm, no. 2, respectively)



Fig. 8

Cross-sectional view of (a) Ni<sub>2</sub>Si and NiSi after the 300°C annealing and of (b) NiSi after the 400°C annealing.





Diffraction patterns from cross-sectional specimens. (a) and (b) show the diffraction pattern of epitaxial Ni<sub>2</sub>Si and NiSi on  $\{111\}$  Si for (a)  $\{110\}$  and (b)  $\{112\}$  specimen orientation. (c) shows the diffraction pattern of epitaxial NiSi after the 400°C annealing for  $\{110\}$  specimen orientation. For details see the text.







should be aligned with the Si {111} systematic reflections. At a right angle to this row of reflections, the Ni<sub>2</sub>Si (101) and (200) spots (0.331 nm, 0.352 nm, not visible on print) and the NiSi (1100) spot (0.284 nm, no. 3) should be visible for {110} substrate orientations; for {112} substrate orientations the Ni<sub>2</sub>Si (301) and ( $\overline{102}$ ) spots (0.199 nm, no. 4; 0.181 nm, no. 5), and the NiSi (1120) spot (0.164 nm, no. 6) should be present.

All these reflections can be found although they may be very weak. However, there is an additional reflection (no. 7), comparatively strong and not expected, which also is in line with the Si {111} reflections. The spacing of the set of lattice planes producing this spot is 0.203 nm. This only fits the Ni<sub>2</sub>Si (110) plane and thus indicates the possibility of an additional epitaxial system of Ni<sub>2</sub>Si, overlooked so far, with (110) Ni<sub>2</sub>Si parallel to (111) Si.

Figure 10 shows that there is indeed the possibility of a pseudo-hexagonal system on the Ni<sub>2</sub>Si (110) plane. A slightly distorted hexagon is formed by Si and Ni atoms in this case. The prismatic planes are not exactly perpendicular to the (110) basal plane, but the deviations from a right angle are only a few degrees. The prismatic planes are the (210) and (324) planes and the characteristic dimensions of the hexagon are 0.353 nm and 0.329 nm which are very close to those of the (010) pseudo-hexagonal system. Therefore, the difference in the diffraction patterns between the (010) (fig. 3) and the (110) pseudo-hexagonal systems would only show up among high-order reflections. In fact, the Si {440} spot (labelled no. 4 in fig. 3) is surrounded not only by two, but by



Dark-field images of the Ni<sub>2</sub>Si and NiSi on  $\{111\}$  Si after the 300°C anneal. (a) was taken with a NiSi reflection (spot no. 3 in fig. 9 (a)) and (b) was taken with a Ni<sub>2</sub>Si reflection (spot no. 7 in fig. 9 (a)).

Fig. 11

four epitaxial silicide reflections. This is the only clue to the presence of two epitaxial systems in this diffraction pattern, something easily overlooked or misinterpreted without the use of cross-sectional TEM.

As in the case of the  $\{100\}$  samples, the Si-silicide interface is not particularly flat whereas the interface between the two layers and the silicide surface is quite straight.

Because of well-developed and identifiable silicide reflections present in this case, dark-field microscopy with both Ni<sub>2</sub>Si and NiSi diffraction spots is possible, an example is shown in fig. 11. It can be seen that the layer adjacent to the silicon consists of NiSi, whereas the top layer is composed of the Ni<sub>2</sub>Si/(110) system (the bottom layer in the figures is Si). Again, an interfacial layer between the NiSi and the Ni<sub>2</sub>Si, some 3 nm thick, gives the impression that the two phases are hardly connected.

A comparison of fig. 8 (a) with (b) suggests that only NiSi is left after the 400°C annealing. This is confirmed by the diffraction pattern (fig. 9 (c)) which shows only NiSi spots. The interface again is quite uneven, but the NiSi layer is remarkably free of macroscopic defects. Sometimes the regions near the NiSi surface seem to be more disordered; this probably corresponds to the polycrystalline NiSi occasionally detected in the diffraction pattern of conventional specimens (fig. 3 (b)).





Lattice fringe image of the epitaxial NiSi-Si interface. The dislocation symbols denote ending NiSi {1100} fringes.

Despite the large misfit of ~15%, the epitaxial growth of NiSi on {111} Si is rather perfect, however, this requires the presence of a dense network of misfit dislocations. These dislocations have to be common to both crystal systems and therefore most likely belong to the  $\mathbf{b} = a/2\langle 110 \rangle$  type in the Si lattice which corresponds to  $\mathbf{b} = a/3\langle 11\overline{2}0 \rangle$  in the hexagonal NiSi lattice. Their spacing then would be ~1.5 nm; i.e. every sixth NiSi lattice plane should terminate at the interface. Figure 12 shows a lattice-fringe image of the Si–NiSi interface. The Si {111} and the NiSi {T100} fringes are visible and as predicted, about every sixth NiSi {1100} fringe terminates at the interface.

#### 3.5. $800^{\circ}C$ annealing

For completeness, a brief description of the silicide formed at 800°C will be given ; additional details can be found elsewhere (Föll *et al.* 1980). Figure 13 shows cross-sections of the NiSi<sub>2</sub> formed at this temperature. The NiSi<sub>2</sub>–Si interface is highly facetted on {111} and {100} planes. The silicide surfaces are smoother and also show small facets. The interface for the {100} substrate is much rougher than that of the {111} substrate. In both cases almost perfect epitaxy is observed even though the NiSi<sub>2</sub> on {111} Si is mostly twinned with respect to the substrate orientation. Within a facet, the interface is perfectly straight and confined to one atomic plane. This can be seen from the lattice images in fig. 14, which shows also directly the twinning in the {111} substrate case (fig. 14 (*b*)).



Cross-sectional view of NiSi<sub>2</sub> present after the 800°C anneal on (a) {111} Si and on (b) {100} Si.

Observations by conventional TEM show the presence of misfit dislocations. In the {111} substrate case, their geometry again confirms the twin-boundary nature of the interface, an example shown in fig. 15. The relatively regular hexagonal network consists of  $\mathbf{b} = a/2\langle 112 \rangle$  edge-dislocations, the type of dislocation required in a twin boundary. Patches of dislocation networks, more irregular and with a larger spacing, are also present. These patches contain dislocations with  $\mathbf{b} = a/2\langle 110 \rangle$  which outline areas where direct epitaxial growth has taken place. The dislocation nodes in this case are extended, see insert in fig. 15. The 'stacking-fault' energy estimated from these nodes

(see, for example, Föll and Carter 1979) is in the order of  $\sim 20 \text{ mJ/m^2}$ . This energy represents approximately the interface energy of a twinned interface.



Fig. 14

Lattice images of NiSi<sub>2</sub>-Si interfaces. (a) shows NiSi<sub>2</sub> on {100} Si; a large facet on a {100} plane and a small facet on a {111} plane is visible. (b) shows NiSi<sub>2</sub> on {111} Si; the NiSi<sub>2</sub> is twinned with respect to the Si matrix.

#### § 4. DISCUSSION

The results presented here are in general agreement with previous findings but there are significant differences in details. Whereas the sequence of silicide formation is identical to that reported in the literature, the formation temperatures for Ni<sub>2</sub>Si and NiSi on {111} Si appear to be lower than for {100} Si substrates. This is, at least for NiSi, in contrast to what is stated in the literature (Olowolafe *et al.* 1976). The reason for this discrepancy may be due to the surprisingly high degree of epitaxial growth (or more precisely a textured growth of polycrystallites) of Ni<sub>2</sub>Si and NiSi in our case. A polycrystalline textured growth of Ni silicides has been reported previously (Tu *et al.* 1975), but without the crystallographic relationship with the Si substrate.

The literature contains contradictory statements about the growth kinetics of NiSi. Whereas Coe and Rhoderick (1976) found that the growth of NiSi is linear with time, J. E. Baglin (1981, private communication) reported a squareroot time dependence. In the first case the reaction would be interfacecontrolled, e.g. by the rate at which Si atoms can be released at the NiSi-Si interface; in the second case the reaction would be diffusion-controlled. It



Weak-beam image of the misfit dislocation network in the NiSi<sub>2</sub>-Si interface for {111} oriented substrates. The inset shows an enlarged view of the dislocation network in the area with non-twinned NiSi<sub>2</sub>. For details see the text.

appears plausible that the reaction rate and/or the temperature of NiSi formation can be substantially different for different interface configurations and that the reaction kinetics may depend on the NiSi layer thickness and/or the reaction temperature. Our findings suggest that an epitaxial interface between NiSi and Si can lower the reaction temperature and may significantly increase the NiSi growth rate. This provides an opportunity to study the growth kinetics at a low reaction temperature which would be more sensitive for resolving the growth mechanism.

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The reason for the good epitaxial growth of Ni<sub>2</sub>Si and NiSi in our case is not clear. The effect of impurity content in the Ni film, cleanliness of the Ni/Si interface and annealing conditions may be contributing factors. Nevertheless, the perfection of epitaxy observed for Ni<sub>2</sub>Si and NiSi on {111} Si is not comparable to the single-crystal silicides observed for Pd<sub>2</sub>Si or NiSi<sub>2</sub> on {111} Si.

The reason for a faster growth of epitaxial Ni<sub>2</sub>Si and NiSi on {111} Si than their non-epitaxial growth on {100} Si is also unclear. One can argue that since an epitaxial interface is in general lower in energy than a non-epitaxial interface, the driving force for an epitaxial growth will be larger if all other factors affecting the growth are equal. Furthermore, since misfit dislocations must climb in order to remain in, or close to, the advancing epitaxial interface, the climb motion requires interaction with point defects. If we assume that the interaction can promote the mixing between the metal and the Si substrate atoms, a faster interfacial mobility is possible. With a larger driving force and a better mobility, a faster growth can be expected. However, the details of the growth mechanism are far from clear, e.g. the ratio of diffusing flux of metal atoms to Si atoms during an epitaxial growth might differ greatly from that during a non-epitaxial growth. To resolve some of the subtleties it seems that a careful study comparing the well-established epitaxial growth of Pd<sub>2</sub>Si on {111} Si and the non-epitaxial growth of Pd<sub>2</sub>Si on {100} Si at low temperatures will be quite useful.

The large ( $\sim 3$  nm) separation between the NiSi and the Ni<sub>2</sub>Si layer in some cases is not fully understood at present. It may be related to the agglomeration of excess vacancies generated by unbalanced diffusion fluxes of Ni and Si, i.e. by the Kirkendall effect. However, whereas the Kirkendall effect is certainly present in many thin-film diffusion couples, it is not clear whether it has to manifest itself in void formation. If a vacancy supersaturation is built up on one side of the interface, it might anneal out at the film surface or at dislocations and grain boundaries in the film. An alternative explanation for the NiSi-Ni<sub>2</sub>Si interfacial layer can be found by invoking remainders of the original native oxide layer present on the Si substrate (Föll and Ho 1981). The interfacial layer is interesting since it might effect the sharpness of the Ni<sub>2</sub>Si/NiSi interface in terms of composition.

The last point to be discussed is the observation of NiSi<sub>2</sub> twinned with respect to the substrate. This has not been reported in previous work (Ishiwara *et al.* 1978, Chiu *et al.* 1980), although channelling studies can in principle reveal this. Since in our study the NiSi<sub>2</sub> was developed from a rather perfect epitaxial layer of NiSi, this might have increased the chance of the twin formation. The twinned interface is probably the interface with the lowest energy ( $\sim 20 \text{ mJ/m}^2$  as suggested by the extended dislocation nodes in fig. 15). However, it is conceivable that small differences in specimen preparation could have affected the balance between the twinned and untwinned (but epitaxial) regions ( $\sim 4 : 1$  in our case).

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