Cross-sectional transmission electron microscopy of silicon-silicide interfaces

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(Received 27 May 1980; accepted for publication 6 August 1980)

The epitaxial interfaces of Si/Pd_2Si, $Si/NiSi_2$, and, to a lesser extent, Si/PtSi have been investigated by transmission electron microscopy using cross-sectional specimens. Direct lattice imaging was used to image the Si/Pd_2Si and the $Si/NiSi_2$ interfaces. The Si/Pd_2Si interface was found to be rather smooth on a macroscopic scale but rough on a atomic scale, whereas the opposite is true for the $Si/NiSi_2$ interface. A twinning relationship between $NiSi_2$ and {111} Si has been observed. The Si/PtSi interface is very rough on a macroscopic scale. Interface dislocations are present in the Pd- and Ni-silicide cases. No evidence for an amorphous interfacial layer has been obtained.

PACS numbers: 68.55. + b, 61.16.Di, 81.10.Jt, 61.70. — r

I. INTRODUCTION

Thin films of silicides find increasing use as Ohmic or Schottky contacts in Si devices. This is not only because the silicide/Si interface has electrical properties suitable for contacts to very small junctions but also because the silicide layer can improve junction reliability by providing an effective barrier against Al penetration into the junction.[1] Silicides are commonly formed by a solid-state reaction between the Si substrate and an evaporated metal film. During the reaction the silicide/Si interface moves into the Si, thus providing a relatively clean interface which is not much affected by the native oxide or any contamination on the original Si surface. For optimal junction characteristics, a uniform and relatively flat interface is requried; therefore, the knowledge of the interface morphology is important. Moreover, there exists a considerable basic interest in the atomic structure of the silicide/Si interface. For example, the formation of the first phase and the electronic properties of the contact might be controlled by the atomic structure of the interface.[1] The existence of a thin amorphous metallic glass at the interface has been proposed in order to predict the formation of the first silicide phase in transition-metal/Si systems.[2] A direct observation of the atomic structure of silicide/Si interfaces, however, has not been reported so far. This is because the methods commonly used to study silicides, e.g., ion backscattering and glancing-angle x-ray diffraction, cannot provide detailed information about interface properties on an atomic scale. A more suitable method for studying these properties is transmission electron microscopy (TEM), particularly with specimens prepared for a cross-sectional examination. This paper gives the first results of such a TEM investigation. The silicides chosen for this study were near-noble-metal silicides: Pd_2Si, $NiSi_2$, and PtSi, which can grow epitaxially on Si, thus facilitating a detailed structural observation by TEM lattice-imaging techniques.

II. EXPERIMENTAL

The silicides studied were as follows: Pd_2Si on chemically cleaned {111} surfaces, $NiSi_2$ on chemically cleaned {100} and {111} surfaces, and, to a lesser extent, PtSi on chemically cleaned {111} surfaces. All silicides were formed by electron-beam evaporation of the metals at room temperature followed by an annealing treatment either in vacuum or in He atmosphere.

After the silicides were formed, specimens with dimensions of approximately $2\times2\times5$ mm were cut from the wafers. Several of these specimens were then glued together using Araldite or Epon epoxy, following the procedure outlined by Sheng and Chang.[3] During the curing of the epoxy the specimen block was kept under pressure in a small Teflon-lined press to ensure a thin and uniform epoxy layer between the specimens. From this specimen block, thin slices were cut with a wire saw and subsequently ground and polished to a final thickness of $\sim 50\,\mu$m. These slices were then glued on a supporting Cu grid with one large hole and finally ion milled at ~ 5 kV from both sides until a hole was formed in the sample center. In order to obtain good specimens it is important to start with a rather thin specimen ($\sim 50\,\mu$m) and to keep the epoxy layer as thin as possible ($< 1\,\mu$m). Ion milling at low voltages (~ 1 kV) introduces damage (visible black dots) into the Si, whereas at higher voltages (~ 5 kV) no directly visible damage was observed. Specimens for investigations of the silicide "flat-on" were made by chemical thinning of the Si from the back side. TEM was performed in a Siemens Elmiskop 102 operating at 125 kV, or in a Jeol 200 B operating at 200 kV.

III. RESULTS AND DISCUSSION

A. Palladium silicide

The first case to be discussed is Pd_2Si, which was made by evaporating 50 nm of Pd on a {111} Si wafer; no subsequent annealing treatment was performed. Cross-sectional specimens were made, and during the specimen preparation its temperature may have reached ~ 100 °C for ~ 20 h during ion milling. TEM showed that the Pd had partially reacted with Si, forming a Pd_2Si layer ~ 31 nm thick; the remaining Pd layer had a thickness of ~ 37 nm. Figure 1 shows a cross-sectional view of this sample and illustrates very clearly some of the artifacts and difficulties encountered in cross-sectional TEM. Due to the stresses in the sample, thin areas

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of the specimen around the interface region are severely bent; frequently, the silicide is even partially peeled off. In this case the Si and the silicide are separated by a groove which appears as a bright band in Fig. 1. Different ion-milling rates between Pd, Pd_2Si, and Si may also contribute to such artifacts. This makes it exceedingly difficult to ascertain whether some observations reflect intrinsic properties of the sample or are due to artifacts and/or a mixture of both. The presence of voids in the interface, for example, would facilitate a peeling off of the silicide layer; this was observed for metal layers of GaAs [4] and may also play a role in the Pd_2Si case. Despite all these difficulties, Fig. 1 shows that the Pd_2Si is basically single crystalline and has an epitaxial relationship to the Si matrix (this was deduced from the diffraction pattern); the unreacted Pd is polycrystalline with a grain size of $\sim$10–20 nm. More importantly, it is clearly visible that the Si/Pd_2Si and the Pd_2Si/Pd interfaces are rather flat, with an estimated roughness of $\sim$2 nm.

The bending of the specimen in the interface region makes direct lattice imaging of the interfacial region very difficult. For carrying out so-called structural imaging,[5,6] which under favorable conditions can give direct information about the positions of atoms, the specimen has to be oriented very precisely into a high-symmetry orientation[7] (in this case $\{110\}$ for the Si and $\{1\bar{1}00\}$ for the Pd_2Si). This so-called axial diffraction condition can be easily achieved in the thicker parts of the Si by using Kikuchi lines, but in interface regions thin enough for lattice imaging (<40 nm for Si, <10 nm for Pd_2Si) the unavoidable bending of the specimen makes almost certain that the diffraction conditions are no longer axial. Consequently, lattice images, if obtained at all, are no longer structural images (i.e., they cannot be interpreted in terms of absolute atom positions). Nevertheless, they still contain valuable information not obtainable otherwise. Figure 2 shows a lattice image in the Si-Pd_2Si interface of the sample shown in Fig. 1. On the Si side, the contrast is similar to a structural image (i.e., the white dots may be interpreted as the open channels of the Si lattice viewed in the $\langle 110\rangle$ direction[8]), whereas only the $\{22\bar{4}0\}$ fringes of the hexagonal Pd_2Si lattice are visible in the Pd_2Si.

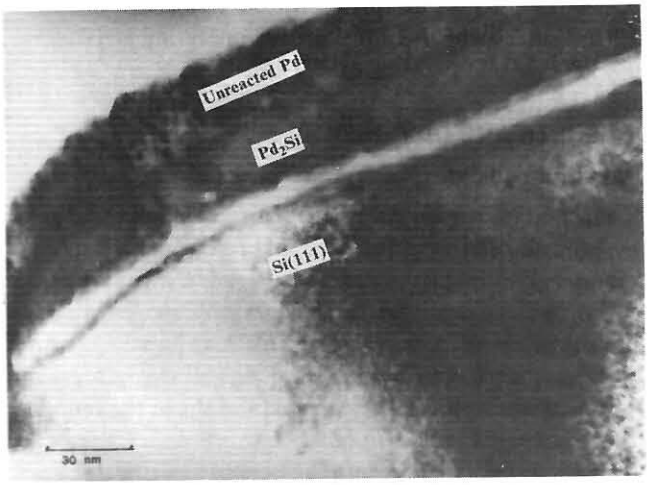

FIG. 1. Thin layer of Pd_2Si and Pd on Si. The layer is severely bent (coming out of the paper plane in the left-hand corner).

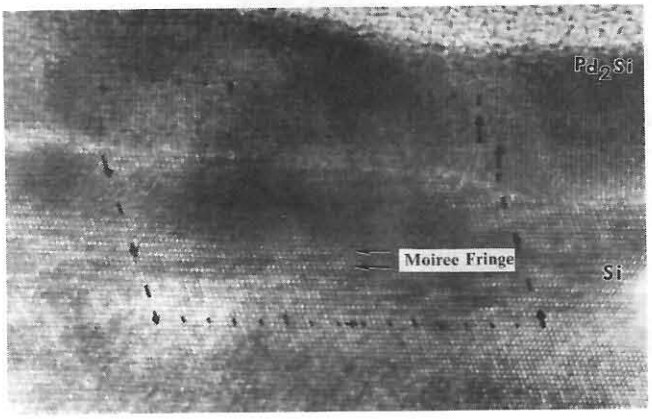

FIG. 2. Lattice image of the Pd_2Si-Si interface. The spacing of the Si $\{111\}$ fringes (e.g., parallel to the interface) is 0.31 nm. A Burgers-like circuit is drawn in, showing 79 Pd_2Si $\{22\bar{4}0\}$ fringes for 75 Si $\{111\}$ fringes.

The interface is rough on an atomic scale, with an average amplitude of $\sim$1.5 nm and an average wavelength of $\sim$4 nm. A circuit (analogous to a Burgers circuit) going from a well-resolved point at the interface on the Si side to another well-resolved point at the interface and then back to the starting point in the Pd_2Si side (cf. Fig. 2) reveals the presence of excess $\{22\bar{4}0\}$ fringes in the Pd_2Si side. That is, there are more Pd_2Si $\{22\bar{4}0\}$ fringes than corresponding Si $\{111\}$ fringes (counted along the interface) within a certain distance along the interface. This indicates that dislocations are present within the circuit, and since these dislocations are neither in the Si nor in the Pd_2Si (as verified by looking along the Pd_2Si $\{22\bar{4}0\}$ fringes or the Si $\{111\}$ frignes), they must be in the interface and therefore are interface dislocatios. On the average, there is one additional Pd_2Si $\{22\bar{4}0\}$ fringe for about 23 Si $\{111\}$ fringes. The additional $\{22\bar{4}0\}$ fringes cannot simply be identified as partial dislocations having a Burgers vectro $\mathbf{b} = \frac{1}{6}a\langle 11\bar{2}0\rangle$ (the distance between $\{22\bar{4}0\}$ planes) because lattice imaging reveals only the component of the Burgers vector in the image plane[9] (therefore, a dislocation with an inclined Burgers vector $\mathbf{b} = \frac{1}{3}a\langle 11\bar{2}0\rangle$ would give the same image as $\mathbf{b} = \frac{1}{6}\langle 11\bar{2}0\rangle$). Moreover, the concept of dislocation in the interface between a hexagonal and a cubic material needs more detailed considerations than intended in this paper, especially if the interface is not flat but has steps, as is the case with the Pd_2Si-Si interface. Nevertheless, the presence of dislocations, whatever detailed characteristics they might have, is a strong argument for an ordered interface, i.e., no amorphous layer is present. This is already indicated by the absence of such a layer in the lattice image in Fig. 2, although in some places a very thin (1 nm) amorphous like layer might be obscured in this picture because the whole interface cannot be expected to be exactly end-on, due to its roughness.

Measuring the spacing of a large number of $\{22\bar{4}0\}$ fringes in the silicide and comparing it to the spacing of the Si $\{111\}$ fringes allows one to obtain a fairly accurate measurement of the Pd_2Si lattice constant. If the lattice constant of the Si is taken to be $a = 0.543$ nm (measured 8 nm away from the interface), the Pd_2Si lattice constant is determined to be $a = 0.642$ nm ($\sim$1.5 nm away from the interface), which is

~1.5% smaller than the nominal (x-ray) value of 0.652 nm. This indicates the presence of elastic stresses and possibly also a change in the lattice constant of the silicide due to stoichiometry variation. A Pd-rich silicide, for example, has been shown to lead to smaller lattice constants compared to a stoichiometric silicide,[10] and this may also be true for Si-rich silicides. This interpretation is supported by the presence of more misfit dislocations than would have been needed to compensate for the differences in the lattice constants of Si and stoichiometric Pd_2Si, which would have been one ending $\{22\bar{4}0\}$ fringe for every 50 Si $\{111\}$ fringes. With the measured lattice constant of Pd_2Si ($a = 0.642$ nm), one additional fringe for every 29 $\{111\}$ fringes of Si would be expected, which agrees fairly well with the observed value of ~23–25.

The Si image close to the interface shows an intensity modulation of the lattice fringes which appears to be a Moiré contrast effect. On the average, every third Si $\{111\}$ fringe parallel to the interface is somewhat brighter than its neighbors. A contrast like this could result from overlapping crystals with similar lattice geometry but different lattice constants, e.g., at an interface inclined with respect to the electron beam. The roughness of the Pd_2Si-Si interface, however, cannot account for the rather broad zone of the Moiré contrast (~8 nm) since at the most a region ~1 nm in width can be expected to show this effect. While it is possible that the lattice constant of Si could be locally changed by incorporating Pd atoms, this change would have to be of the order of 50% to explain the observed contrast; this is too high to be reasonable and the remaining possibilities to account for this contrast are as follows: (i) Some form of platelet-like Pd-rich regions (possibly small monolayers of Pd_2Si) or a thin surface of Pd_2Si which may have formed during specimen preparation; (ii) some Pd might have reached the Si surface by surface migration (possibly assisted by the ion-milling process) and may have reacted to form Pd_2Si. At present, it is not possible to distinguish between these two possibilities.

B. Nickel silicide

$NiSi_2$ was formed on both $\{100\}$ and $\{111\}$ Si by evaporating 50 nm of Ni at room temperature and subsequent annealing at 800 °C in He atmosphere. In order to form different phases of Ni silicides, part of the sample was directly annealed at 800 °C for 1 h, and another part was first annealed at 300 °C for 20 min (which forms Ni_2Si [11]), then at 400 °C for 20 min (which forms NiSi [11]), and finally at 800 °C for 1 h to form $NiSi_2$.

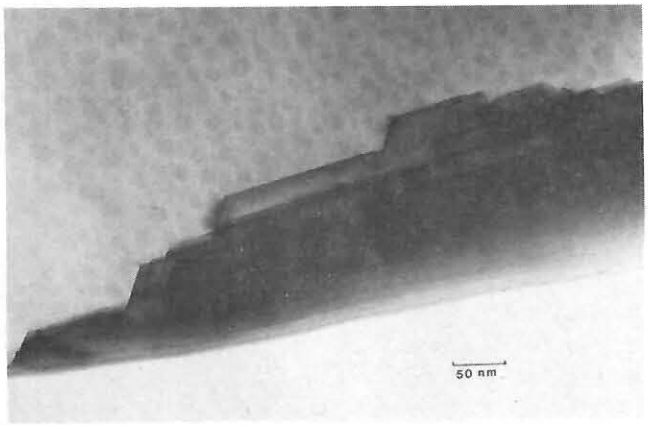

FIG. 3. Heavily faceted $NiSi_2$ on $\{100\}$ Si. Parts of the silicide have been removed during ion milling; the surface of the silicide therefore is not the original silicide surface.

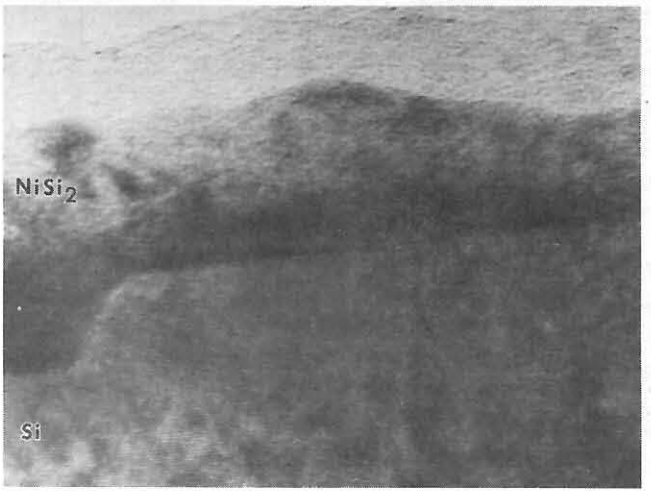

FIG. 4. Lattice image of the Si-$NiSi_2$ interface for silicide formed on $\{100\}$ Si. A large facet on a $\{100\}$ plane and on a small facet on a $\{111\}$ plane are visible.

C. $NiSi_2$ on $\{100\}$ Si

The $NiSi_2$ on $\{100\}$ Si forms a heavily faceted interface with the Si substrate (Fig. 3). The facets are on $\{111\}$ and $\{100\}$ planes, with the former more frequently observed. The interface is very rough on a large scale, and the thickness of the $NiSi_2$ layer may vary by more than 100 nm (the average thickness is 170 nm). The $NiSi_2$ formed by stepwise annealing appears to be somewhat less faceted than the $NiSi_2$ formed by direct annealing, but the overall difference is not significant.

On an atomic scale the interface is perfectly flat within a

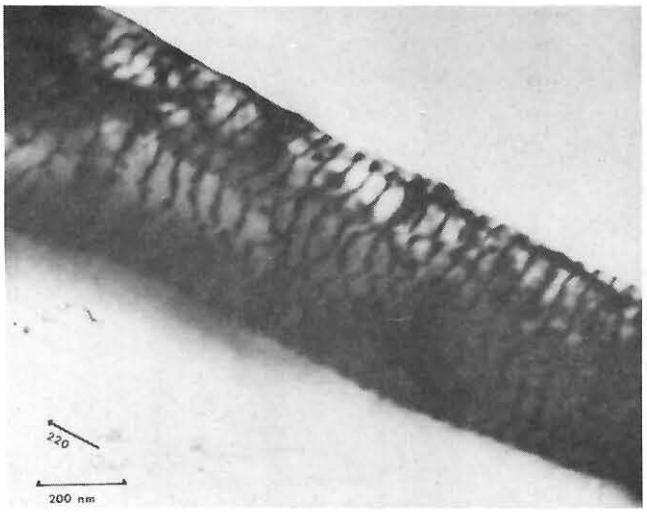

FIG. 5. Misfit dislocations in the Si-$NiSi_2$ $\{100\}$ interface and dislocations in the silicide.

facet; Fig. 4 shows an example. A facet on a {100} plane and on a {111} plane can be seen, and the interface was found to be confined to one lattice plane for a lateral dimension of more than 60 nm (the largest distance measurable on the original negative). An offset of the {111} fringes crossing the interface, e.g., from $NiSi_2$ into Si, is visible in Fig. 4, but this could be a contrast artifact; however, it may also reflect a true property of the interface. A Burgers circuit similar to the one described for Pd_2Si does not reveal interface dislocations in Fig. 4, but this cannot be taken as evidence for the absence of misfit dislocations since the area sampled might have been too small. In fact, if a cross-sectional sample is tilted about an axis not perpendicular to the interface (so the interface is no longer end-on), interfacial dislocations and internal dislocations in the silicide are visible (Fig. 5). These dislocations can be better revealed using conventional TEM techniques with the electron beam normal to the sample surface. Figure 6 gives such an example. Due to the stresses present in the sample, the specimen starts to bend severely as soon as it become thin enough for TEM; this practically prevents the imaging using a well-defined diffraction condition. Despite this difficulty, three basic types of dislocation networks have been distinguished: (1) a square network of edge dislocations with $\mathbf{b} = \frac{1}{2}a\langle 110\rangle$ and a spacing of ~ 57 nm, (2) a hexagonal network with a spacing similar to that given above and probably also containing edge dislocations with $\mathbf{b} = \frac{1}{2}a\langle 110\rangle$, and (3) a rather irregular rectangular network with a spacing from 50 to 200 nm. These networks can be accounted for simply by assuming that in the first case the dislocation network is one a rather large {100} facet, in the second case on a large {111} facet, and in the third case on an area with many small facets. The observed spacing of ~ 57 nm is considerably smaller than the theoretically expected value of ~ 97 nm taking the lattice constant of $NiSi_2$ to be

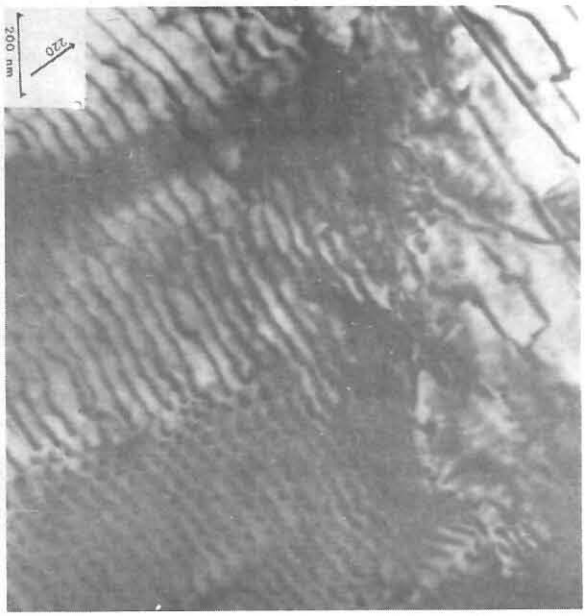

FIG. 6. Misfit dislocations in the Ni-$NiSi_2$ interface viewed flat-on. A hexagonal network (lower right-hand corner; one set of dislocations not in contrast), a square network (left-hand corner; one set of dislocations not in contrast), and one irregular rectangular network can be seen.

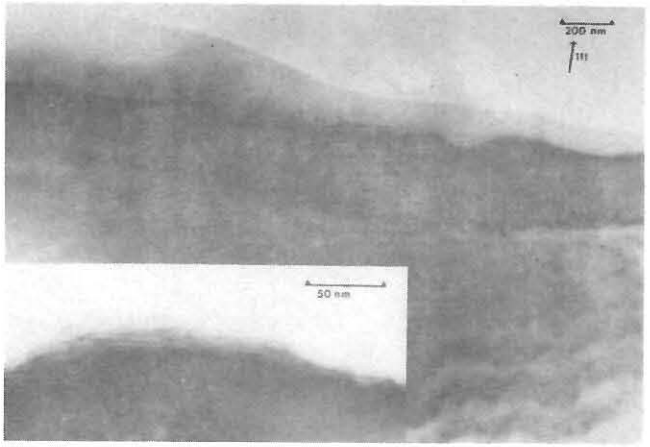

FIG. 7. Interface between $NiSi_2$ and {111} Si. The inset shows the $NiSi_2$ surface at a higher magnification.

$a = 0.5406$ nm.[11] This indicates that the difference in lattice constants is larger at 800 °C so that more misfit dislocations are needed to relieve the stresses. During cooling down of the wafers the dislocations were frozen-in, thus creating the high stresses observed at room temperatures.

D. $NiSi_2$ on {111} Si

The interface between {111} Si and $NiSi_2$ is also faceted, but much less so than on {100} Si. Figure 7 shows a typical example where it can be seen that very large facets are formed on the {111} plane parallel to the original wafer surface and only small facets are found on the inclined {111} planes. The amplitude of interface roughness is ~ 20 nm, with a rather large modulation period in the order of several μm. In this case it was also found that the surface of the $NiSi_2$ was faceted; see inset in Fig. 7. Direct lattice imaging again showed a perfectly straight interface which can be defined within one {111} plane; see Fig. 8. However, as can be seen in Fig. 8, the $NiSi_2$ is not epitaxial to the Si matrix but rather in a twin orientation relative to the Si; this is also shown by

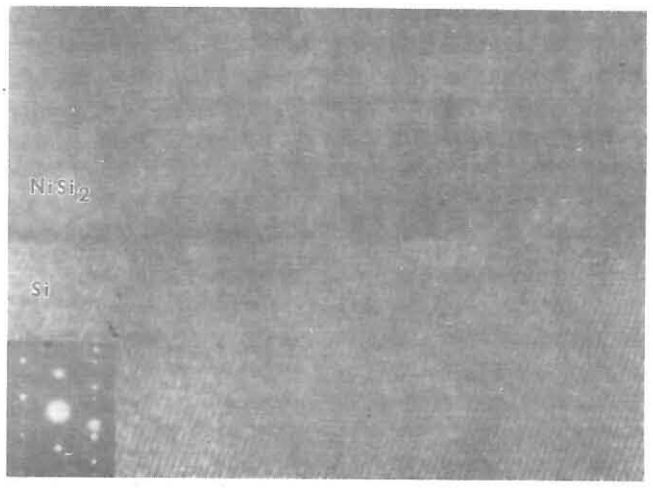

FIG. 8. Lattice image of the Si-$NiSi_2$ interface on a {111} plane. The $NiSi_2$ is twinned with respect to the Si matrix; this also can be seen from the typical twin-diffraction pattern. The interface contains a dislocation at the dark spot.

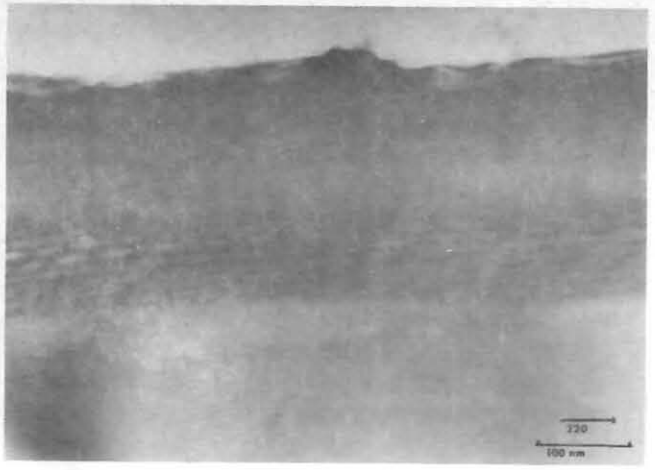

FIG. 9. Misfit dislocations in the interface between $NiSi_2$ and {111} Si.

the twin spots in the diffraction pattern. The direct lattice image, however, has the advantage of demonstrating that the entire silicide is twinned and that the twin spots do not come from microtwins within an epitaxial silicide. Burgers circuits in some direct lattice images as well as the images of tilted specimen, Fig. 9, show the presence of dislocations at the interface. Again, conventional (flat-on) specimens are better suited for studies of such networks. (Figure 10 gives an example.) It should be mentioned, however, that images observed on strongly tilted cross-sectional specimens show directly that the network is at, or very close to, the interface

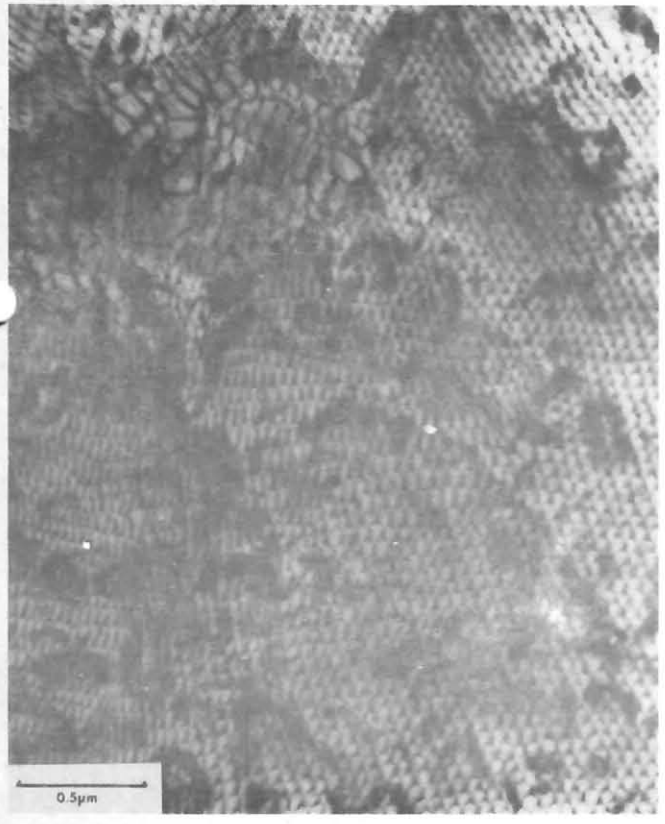

FIG. 10. Flat-on view of misfit dislocations in the Si-$NiSi_2$ {111} interface. The micrograph was taken with multibeam diffraction conditions close to the {111} pole.

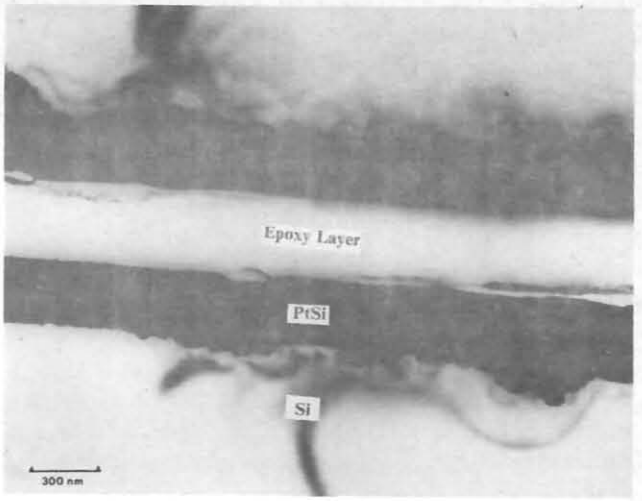

FIG. 11. Interface between Si and PtSi (two samples with the silicide side glued together).

(Figs. 5 and 9), information not easily obtainable with conventional techniques. A rather regular hexagonal network with a spacing of ~50 nm can be seen in Fig. 10, which is interrupted in some places by patches of a less regular hexagonal network with a spacing of ~85 nm. Contrast anslysis showed that the network with the smaller spacing consists of edge dislocations with $\mathbf{b} = \frac{1}{6}a\langle 112\rangle$, whereas the larger network is formed by edge dislocations with $\mathbf{b} = \frac{1}{2}a\langle 110\rangle$. The latter marks the areas where $NiSi_2$ has grown in a direct epitaxial relationship to the matrix, whereas the former is formed in the twin boundary between the Si and the $NiSi_2$. The spacing of the dislocations in these cases is closer to the theoretically expected value (~97 nm) for $\mathbf{b} = \frac{1}{2}a\langle 110\rangle$ dislocations and ~60 nm for $\mathbf{b} = \frac{1}{6}a\langle 112\rangle$), indicating a better fit at 800 °C between $NiSi_2$ and {111} Si than between $NiSi_2$ and {100} Si. The dislocation nodes in the network of the perfect dislocations may be somewhat extended, but no clearcut statement can be made at present. About 80% of the total area showed the twin-related network, indicating that a twinned interface is strongly preferred. The misfit dislocations with $\mathbf{b} = \frac{1}{6}a\langle 112\rangle$ are the grain-boundary dislocations expected for a twin boundary, which for topological reasons can only exist exactly in the twin boundary,[12] i.e., in the interface. Again, this is clear evidence for an ordered interface without an amorphous interface layer, in contrast to recent predictions.[2,13]

E. Platinum silicide

Only one specimen has been investigated. PtSi was formed by deposition of 500 nm Pt at room temperature on {111} Si and by a subsequent heat treatment at 400 °C for 2 h. This specimen was of particular interest because the PtSi layer showed fine lines concentric to the center of the wafer. Conventional TEM showed that the PtSi grains in these lines (width ~1 μm) were almost randomly oriented with respect to the matrix, whereas between the lines they were in pseudoepitaxial relationship with respect to the Si.[14] It is possible that the circular lines in the silicide reflect areas of the Si wafer where some residual damage or contamination from

the last polishing step was present. Cross-sectional specimens showed that the Si-PtSi pseudoepitaxial interface is exceedingly rough, with amplitudes of 200 nm (thickness ~350 nm) and a wavelength of ~700 nm (Fig. 11). In contrast, the PtSi surface is rather flat. This example serves to demonstrate that epitaxial interfaces are not necessarily flat.

IV. CONCLUSIONS

Transmission electron microscopy of silicon-silicide interfaces with cross-sectional specimens is a powerful technique for studying interfacial properties at high spatial resolution. Interfacial parameters such as flatness, preferred interfacial planes, and interfacial defects are easily observable and can be measured almost at an atomic level. It was found that the Si/Pd_2Si interface is rough on an atomic scale and that it contains interfacial dislocations. The $NiSi_2$/Si interface is faceted but perfectly flat on an atomic scale. $NiSi_2$ grows epitaxial on {100} Si but has a twin relation to {111}-oriented Si. No evidence for an amorphous interface layer was found in either case.

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