

Origin of *A*- or *B*-Type NiSi₂ Determined by *In Situ* Transmission Electron Microscopy and Diffraction during Growth

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In situ transmission electron microscopy during the growth of NiSi₂ on Si by molecular beam epitaxy shows that the metastable phase θ -Ni₂Si grows at $\approx 300^\circ\text{C}$ upon the reaction of certain deposited Ni films on (111) but never on (100) Si. Its existence correlates with the subsequent growth of type-*A* NiSi₂ at 450°C . The low energy of epitaxial interfaces can influence phase formation in very thin films, leading to unusual thickness-dependent behavior such as the type-*B*-type-*A* NiSi₂ enigma.

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The deposition and reaction of Ni on clean Si surfaces has been quite widely studied by a variety of surface-science techniques including photoemission,^{1,2} LEED,^{3,4} reflection high-energy electron diffraction (RHEED),^{5,6} Rutherford ion channeling and backscattering (RBS),^{7,8} and surface extended x-ray adsorption fine structure (SEXAFS).⁹ Much of this work was stimulated by the novel observation that after reaction of deposited Ni films, high-quality epitaxial NiSi₂ layers with one of two orientations (type *A* or type *B*) could be grown on (111) Si, the orientation dependent on the initial Ni thickness.¹⁰ The type-*A* orientation represents coincidence of crystallographic axes in the NiSi₂ and Si lattices and type *B* involves a 180° mutual rotation about the [111] growth direction. On annealing at 450°C of a 10-\AA Ni film on (111) Si the type-*B* orientation is observed, whereas 20-\AA deposits result in the type-*A* orientation. This has the important consequences that the physical properties of the type-*A* and type-*B* interfaces can be independently studied and their Schottky barrier heights have been found to be significantly different.¹¹⁻¹⁴

The phenomena which dominate the growth of NiSi₂ from deposited Ni layers occur at thickness of order 10 ML (monolayers) and are thus not readily amenable to conventional surface-limited techniques. The studies of Ni on Si (111) referenced above have been able to shed only a little light on the *A-B* enigma. One can find evidence from such studies for the existence of Ni₂Si,⁸ NiSi,² and NiSi₂ (Ref. 9) in nominally similar deposited Ni films at room temperature. In this paper we report *in situ* studies of NiSi₂ growth in an ultrahigh-vacuum (UHV) transmission electron microscope (TEM) with both imaging and diffraction (TED) which provide a considerable amount of new information and in particular allow a straightforward explanation of the *A-B* enigma. Our data show that an intermediate phase, hexagonal θ -Ni₂Si,¹⁵ which is metastable in bulk Ni-Si alloys, grows in deposited Ni films at $\approx 300^\circ\text{C}$ and is correlated with the subsequent formation of type-*A* NiSi₂. This observation and studies of the as-deposited structure lead to our explanation of the *A-B* enigma and can be recon-

ciled with most of the previous data. Previous studies on the related CoSi₂/Si system have already been reported with this technique.¹⁶ The combination of diffraction and imaging from the entire volume of thin films was key to the success of the experiments. The use of TEM and TED in surface science has been admirably demonstrated by Takayanagi *et al.* through the solution of the (111) 7×7 structure,¹⁷ for which penetration and kinematical diffraction information were also the key features.

The UHV high-resolution TEM instrument has been described in a separate publication¹⁸ and was operated at 100 kV. Specimens of (111) Si with resistivity $10\ \Omega\ \text{cm}$ were prethinned in HF/2HNO₃ and directly resistively heated to 1200°C *in situ* to produce thin flat 7×7 reconstructed surfaces of typical area $1\ \mu\text{m}^2$. Specimens were examined in the "plan-view" mode, i.e., with the electron beam parallel to the surface normal. Specimen thickness was of order $2000\ \text{\AA}$ and two surfaces are seen in projection, although Ni was deposited only on the electron-beam-entrance surface. Ambient vacuum was $\approx 1\times 10^{-9}$ Torr. Ni was deposited from resistively heated Ni-coated Ta filaments at rates $\approx 10\ \text{\AA}\ \text{sec}^{-1}$. Deposited thickness was measured *ex situ* by RBS, and specimen temperature to $\pm 50^\circ\text{C}$ by pyrometry combined with resistivity/power extrapolation. Specimens were examined in another 100-kV TEM with tilting facilities, after growth, to identify *A* and *B* NiSi₂ regions. The results reported below are only a small fraction, picked to emphasize the origin of *A*- or *B*-type growth, of a large number of systematic experiments which will be described in a more extensive publication.

Figure 1 shows a composite of 60° sections from transmission electron diffraction patterns of deposited Ni films on Si (111) of various thicknesses at room temperature. (All patterns exhibit sixfold symmetry). At zero coverage a 7×7 reconstruction is observed. The 7×7 is removed at all coverages of Ni (although a faint 7×7 from the second uncovered surface can sometimes be seen). Dark-field imaging reveals that additional contributions from the as-deposited film occur in the Si 220

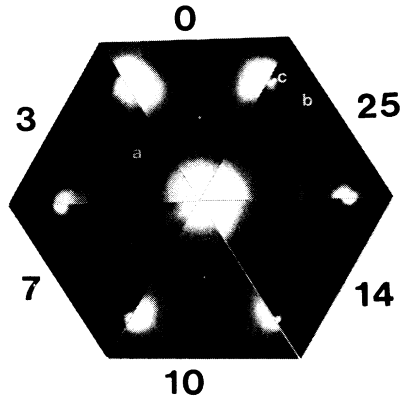


FIG. 1. Composite of 100-kV transmission electron diffraction patterns for different coverages of Ni on (111) Si at room temperature. 1 \AA of Ni is defined as 5.4×10^{14} atoms cm^{-2} . The lettered diffraction spots *a* and *c* and ring *b* are referred to in the text. Diffraction spots also arise from occasional SiC particles remaining from incomplete surface cleaning.

diffracted beams. For films with $t \leq 10 \text{ \AA}$, a very faint diffuse ring occurs at $2.0 \pm 0.05 \text{ \AA}$ (grain size $< 30 \text{ \AA}$) which could be attributed to $\approx 1\text{--}2$ ML of polycrystalline Ni. In excess of 10-\AA coverage, unreacted fcc Ni appears with grain size increasing with coverage (e.g., *b* in Fig. 1 corresponds to the 111 diffraction ring from 70-\AA grains). At high coverages ($\geq 20 \text{ \AA}$) there is evidence for the growth of noncoherent orthorhombic $\delta\text{-Ni}_2\text{Si}$ (e.g., *c* in Fig. 1) at room temperature as reported by Bennett after mild annealing⁵ [with orientation (010) $\text{Ni}_2\text{Si} \parallel (111) \text{Si}$].

Figure 2 shows a composite from an annealing sequence of a single Ni film of thickness 7 \AA . Two features of this sequence are common to most films: all unreacted Ni disappears at $\approx 300^\circ\text{C}$ and a strong spot occurs at the $\frac{1}{3} 422$ position (*a* in Fig. 2). This intense diffraction spot arises from a new phase with hexagonal symmetry which has consumed a significant fraction of the film. It is readily indexed as¹⁵ $\theta\text{-Ni}_2\text{Si}$ (*a* in Fig. 2 is the 100 spot) which is the only hexagonally symmetric silicide with an acceptable lattice match (within 1%) to Si. This silicide is stable when cooled to room temperature without further annealing. From dark-field imaging and tilting experiments on films removed from the UHV TEM, at this stage we confirm the hexagonal symmetry and the lattice parameters within 1% of bulk values.¹⁵ The possibility that this is a hexagonally distorted form of orthorhombic $\delta\text{-Ni}_2\text{Si}$ (Ref. 5) is ruled out from three-dimensional diffraction studies. Hexagonally distorted NiSi has also been seen in thicker, less clean films¹⁹ but it has a mismatch of 13%. Although the $\theta\text{-Ni}_2\text{Si}$ structure is the best fit to our diffraction data, there are some minor discrepancies from the published bulk data¹⁵: The structure factor of the 100 diffraction spot appears significantly larger than previously reported

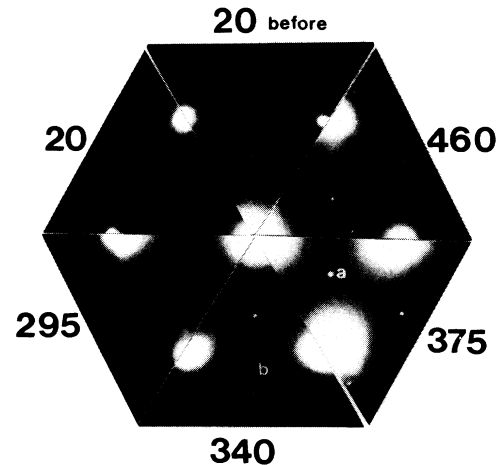


FIG. 2. Composite of 100-kV transmission electron diffraction patterns for a 7-\AA Ni film on Si (111) as a function of annealing temperature in degrees Celsius. The uppermost section shows the 7×7 diffraction pattern prior to deposition. The diffraction spot marked *a* is the 100 spot of $\theta\text{-Ni}_2\text{Si}$.

and we also observe a double-period diffraction spot $\frac{1}{2} 100$, suggesting either superlattice ordering or surface reconstruction.

Our diffraction and microscopic studies reveal that where the $\theta\text{-Ni}_2\text{Si}$ phase occurs, it comprises the full thickness of the silicide film, and that its existence correlates with the subsequent growth of type-*A* NiSi_2 at higher temperatures. Figure 3 shows the correlation between the existence of $\theta\text{-Ni}_2\text{Si}$ during annealing and the subsequent growth of type-*A* NiSi_2 . In Fig. 3(a), which is a dark-field image from the 100 diffraction spot at 400°C during *in situ* annealing of a 9-\AA -thick Ni film, we see bright regions corresponding to islands of $\theta\text{-Ni}_2\text{Si}$. Figure 3(b) is a dark-field image from the same specimen area after annealing to 500°C and cooling to room temperature, taken with a 111 reflection arising from type-*B* NiSi_2 . Bright regions in Fig. 3(b) are type-*B* NiSi_2 and dark areas are predominantly type *A* (with some small fraction equivalent to holes in the silicide). The correlation between $\theta\text{-Ni}_2\text{Si}$ and type-*A* NiSi_2 is quite evident from the arrowed pattern.

It should be noted that other ordered phases are occasionally observed during the annealing of Ni films on Si. For example, the weak diffraction spot marked *b* in Fig. 2 at $d = 2.02 \pm 0.04 \text{ \AA}$ is commonly seen on mild annealing of films $\leq 10 \text{ \AA}$ thick. It is possibly attributed to texturing in the thin Ni film, or the [101] projection of $\delta\text{-Ni}_2\text{Si}$, but its intensity belies its representing a major fraction of the deposited film.

A simple explanation for the *A-B* enigma occurs from these data. At room temperature intimate reaction of the first $\approx 10 \text{ \AA}$ of deposited Ni occurs, consistent with previous studies. The surface is covered with $1\text{--}2$ ML of

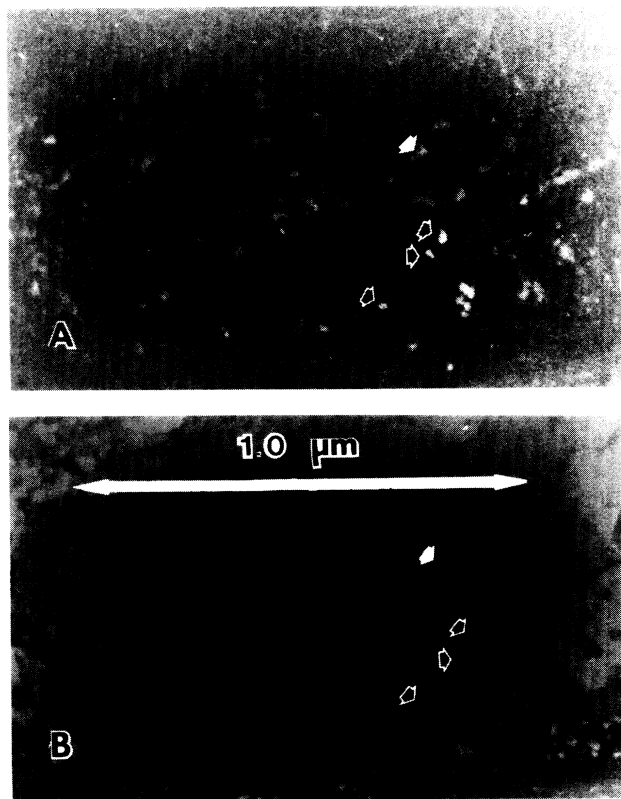


FIG. 3. (a) Dark-field image of a 9-Å-thick Ni film deposited *in situ* on Si (111) and annealed to 400° C, showing the areas contributing to the θ -Ni₂Si 100 diffraction spot. (b) A 111 dark-field image of the same area after NiSi₂ formation at \approx 500° C, which reveals the type-B NiSi₂ regions as bright and the type-A regions as dark. A clear correlation exists between θ -Ni₂Si and subsequent growth of type-A NiSi₂.

disordered Ni which explains why LEED and RHEED studies generally reveal no diffraction from flat layers below 300° C. However, our data show that the majority of the as-deposited layer below 10 Å is an ordered structure with a diffraction pattern equivalent to bulk Si. It is therefore most simply explained as NiSi₂—no other known or likely silicide structure could fit. This is consistent with the interpretation of SEXAFS data⁹ and with other evidence which confirms²⁰ that the CaF₂ silicide structure can be formed extremely deficient in Si which occurs as the layer thickens. This is also consistent with the general observation that stoichiometrically this as-deposited silicide appears to be more Ni rich than NiSi₂. It is difficult in our *in situ* experiments to identify the orientation of the NiSi₂ layer (because of the lack of *in situ* tilting); however, it seems most likely that it is type B.

Other data can be reconciled with this picture. For example, the medium-energy RBS analysis⁸ decided the composition of Ni₂Si on the necessary assumption of dis-

order. Yet it is not clear that the channeling data presented to support this assumption would clearly reveal the presences of a defective type-B layer. We do not observe a disordered phase comprising as much as 10 Å Ni at room temperature, as suggested by van Loenen, van der Veen, and LeGoues,⁸ although we see evidence for one or two monolayers of distorted material, which is most likely unreacted Ni, on the surface of an ordered layer. If 10 Å of disordered material were present, it would be invisible to us only if it contained almost no short-range order, which is inconsistent with SEXAFS experiments.⁹ There may of course be significant differences in the growth conditions between experiments—e.g., van Loenen, van der Veen, and LeGoues employed an extremely low rate of Ni deposition—however, in our experiments we have been able to reproduce in detail the original *A-B* versus thickness observations,¹⁰ and so our conclusions are directly pertinent to the *A-B* enigma. Photoemission data have given conflicting evidence for the stoichiometry of as-deposited silicides, although most data have been on (100) Si. Our data show that the as-deposited structure depends on orientation. Yet recent photoemission² on (111) Si reveals that on very mild annealing of \approx 10-Å-thick Ni layers, NiSi₂ forms, and this is consistent with our observations of grain growth and stoichiometry improvement, but no phase change, on mild annealing < 250° C.

The θ -Ni₂Si phase is stable in bulk Ni-Si alloys only above \approx 850° C. (θ -Ni₂Si has been seen in rapidly quenched thin films at room temperature.²¹) However, we speculate that its excellent lattice match to Si (111) allows minimum free energy to be achieved at lower temperatures in these very thin films because a significant fraction of atoms are at the interface. In thicker films (> 20 Å) the stable orthorhombic δ -Ni₂Si phase is observed as might be expected. θ -Ni₂Si forms in large quantities only where sufficient unreacted Ni occurs, i.e., at coverages in excess of 10 Å. Because of nonuniformity in the coverage of the *B*-NiSi₂ layer below 5 Å, some θ -Ni₂Si grows at very low coverages also. The NiSi₂ phase presumably forms at first because of its low interface energy with Si (Ref. 10) and the type-B orientation because it involves least displacement of Si atoms.⁹ At higher coverages, where Si-rich compounds are unfavorable because of a limited supply of Si, the formation of θ -Ni₂Si on annealing to 300° C eradicates the *B*-NiSi₂ layer and when NiSi₂ forms at higher temperatures (> 400° C) the type-A orientation, which presumably grows more readily, dominates. The sixfold symmetry of θ -Ni₂Si prevents memory of the type-B as-deposited layer. At higher coverages δ -Ni₂Si begins to grow, even at room temperature, and the subsequent growth of NiSi₂ is possibly affected by misfit strain which may cause the *B* orientation to become common again (i.e., *A+B*) as it does in¹⁶ CoSi₂ and the alkaline-earth fluorides.²²

Preliminary experiments on (100) Si indicate that the

θ -Ni₂Si phase does not occur. This is to be expected because of the absence of fourfold symmetry in the hexagonal structure, prohibiting good epitaxial match. The phases observed on reaction of very thin Ni films therefore depend on both thickness and orientation and are predominantly epitaxial. The observation of metastable phases occurring because of epitaxy was first made by Schulz²³ for CsCl on NaCl. Jesser²⁴ reported such phenomena for elemental metals, and Farrow *et al.*²⁵ found that α -Sn on InSb could be stabilized in this manner. In this paper, we present evidence for influence on the chemical composition of binary phases because of this phenomenon, with a clear thickness and substrate orientation dependence to the "phase diagram." We speculate that the free energy of very thin films can be significantly affected by the interface energy. Not only does this favor epitaxial phases, but it can influence the apparent "phase diagram" with a resulting dependence on film thickness and substrate orientation. Interface effects may influence first-phase formation even in quite thick films. As in the Ni-Si system, this phenomenon can affect the subsequent growth of thicker films.¹⁰ The thickness at which these phenomena dominate can be expected to be less than that at which elastic strain effects are important.

In conclusion, *in situ* TEM and TED studies of NiSi₂ formation by MBE show that a metastable intermediate phase θ -Ni₂Si occurs at $\approx 300^\circ\text{C}$ and correlates with the subsequent growth of NiSi₂ type *A*. The as-deposited structure of Ni on Si (111) likely comprises a layer of type-*B* NiSi₂ for $t < 10 \text{ \AA}$ Ni coverage, which is covered with unreacted Ni for higher coverages. The data provide a simple explanation for the dependence of orientation on thickness in this system. New phases may occur in other binary because of the influence of epitaxy on thin-film free energy, and *in situ* monitoring by a penetrating diffraction-imaging technique is invaluable in the understanding of such phenomena.

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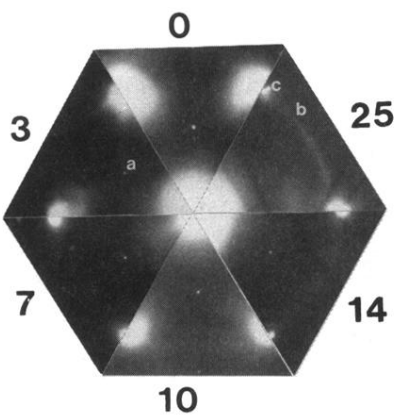


FIG. 1. Composite of 100-kV transmission electron diffraction patterns for different coverages of Ni on (111) Si at room temperature. 1 Å of Ni is defined as 5.4×10^{14} atoms cm^{-2} . The lettered diffraction spots *a* and *c* and ring *b* are referred to in the text. Diffraction spots also arise from occasional SiC particles remaining from incomplete surface cleaning.

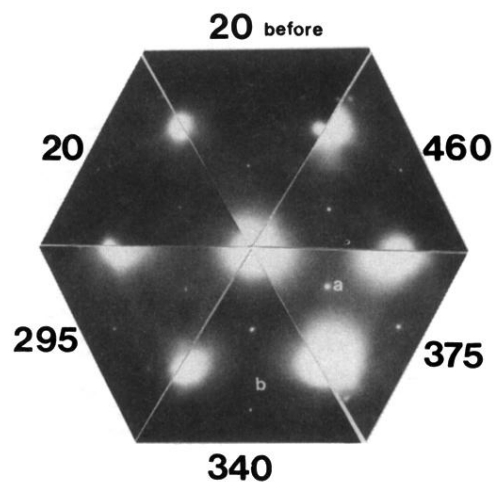


FIG. 2. Composite of 100-kV transmission electron diffraction patterns for a 7-Å Ni film on Si (111) as a function of annealing temperature in degrees Celsius. The uppermost section shows the 7×7 diffraction pattern prior to deposition. The diffraction spot marked *a* is the 100 spot of θ -Ni₂Si.

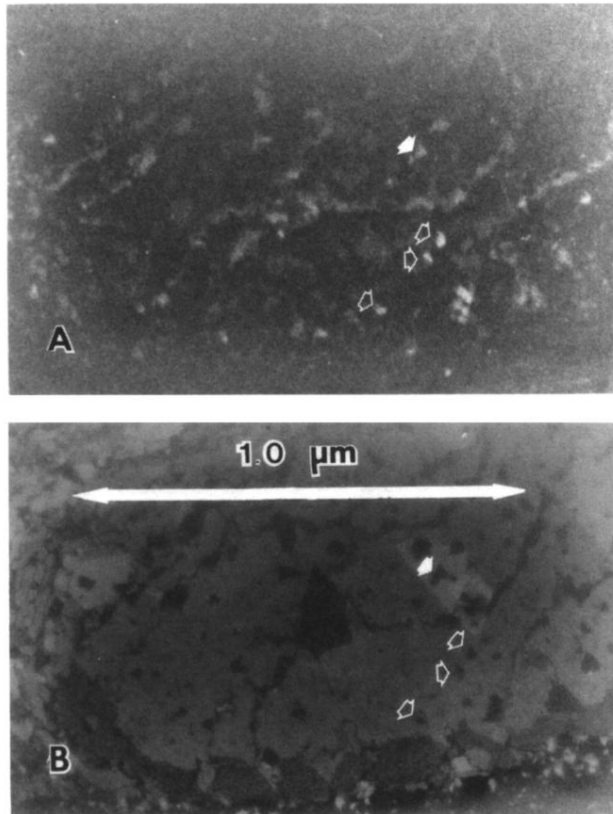


FIG. 3. (a) Dark-field image of a 9-Å-thick Ni film deposited *in situ* on Si (111) and annealed to 400° C, showing the areas contributing to the θ -Ni₂Si 100 diffraction spot. (b) A 111 dark-field image of the same area after NiSi₂ formation at \approx 500° C, which reveals the type-*B* NiSi₂ regions as bright and the type-*A* regions as dark. A clear correlation exists between θ -Ni₂Si and subsequent growth of type-*A* NiSi₂.