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# Reactive Interdiffusion in the Binary System Ni-Si: Morphology of the $Ni_3Si_2$ Phase

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**In binary multiphase diffusion, it is generally admitted that interfaces between phases are necessarily plane. However, a few cases exist, as the binary diffusion couples Ni-Si, Mo-Si, and Fe-Al, for which an intermediate phase of each system grows with an irregular needlelike morphology. To characterize the nonplanar growth of $Ni_3Si_2$ in bulk samples, the authors studied the behavior of intermetallic compound formation by optical microscopy and x-ray microtomography, for different annealing times. They show that both the average height and the tip radius of curvature grow as the square root of time with two diffusion coefficients separated by orders of magnitude. Moreover, x-ray diffraction indicates that the needles are aligned along the crystallographic *c*-axis. These results could be consistently explained by an anisotropic diffusion model.**

**Keywords** interdiffusion, morphology, nonplanar growth, reactive diffusion

## 1. Introduction

The formation of intermediate compounds during interaction of silicon with metals has been the subject of numerous investigations,[1-4] which is explained by the importance of silicides in advanced technologies. Such phase formation by reactive diffusion remains of great practical interest for classic metallurgy[5] as well as for microelectronics.[6]

It is established that the growth of intermediate phases can be governed by chemical reactions at the interfaces (linear kinetics) and/or by interdiffusion of the reacting species through the different phases (parabolic kinetics).[7,8]

In the case of reactive interdiffusion of a binary system, interfaces relax toward plane fronts.[3,9] However, in the system Ni/Si, the $Ni_3Si_2$ phase grows with an irregular needlelike morphology[10,11] close to that of $Fe_2Al_5$ in the Fe/Al couple[12] and $Mo_5Si_3$ in Mo/Si.[13] The origin of this highly irregular morphology is still not understood.

This is particularly troublesome since nickel silicides grown by reactive diffusion are used as ohmic contacts in integrated circuits. When dimensions are reduced, interfacial planarity obviously becomes a matter of concern.

It is clear that the types of intermetallic layers formed and their thicknesses play an important part in obtaining materials with optimum performances. Thus, it is essential to understand the phase formation at the interfaces, the interface morphology, and the growth mechanisms to provide guidelines for the prediction and control of interface reactions.

In the work presented here, experiments were carried out with nickel and silicon. The $Ni_3Si_2$ phase was identified as forming at the interface at various temperatures and for different annealing times. In the absence of a theoretical model of morphological instability, the authors aimed at experimentally characterizing the $Ni_3Si_2$ microstructure by examining its shape to understand the instability.

## 2. Experimental Procedure

The authors processed samples starting from pure nickel and silicon rods. After polishing, cleansing in trichloroethylene, and etching of silicon parts in HF, these assemblies were loaded into a vacuum furnace, with an external load of 1.25 MPa, sufficient to ensure good interfacial contact.

Two series of experiments were performed, aiming at investigating the morphology of the $Ni_3Si_2$ phase in two and three dimensions.

In the first series, couples of 1 mm thickness and 10 mm diameter were annealed at 700 °C for 6, 12, 18, and 24 h. Following annealing, cross sections were made, perpendicular to the interface, through the reaction zone. After a standard metallographic procedure, samples were examined by optical microscopy.

In the second series of experiments, the couples were composed of 5 mm thick and 3 mm diameter rods. The annealing was performed at 750 °C for four different durations: 6, 13, 24, and 48 h. The morphology of the $Ni_3Si_2$ phase was characterized by in situ x-ray microtomography at the ID19 beamline of ESRF synchrotron (Grenoble). This nondestructive control method gave access to three-

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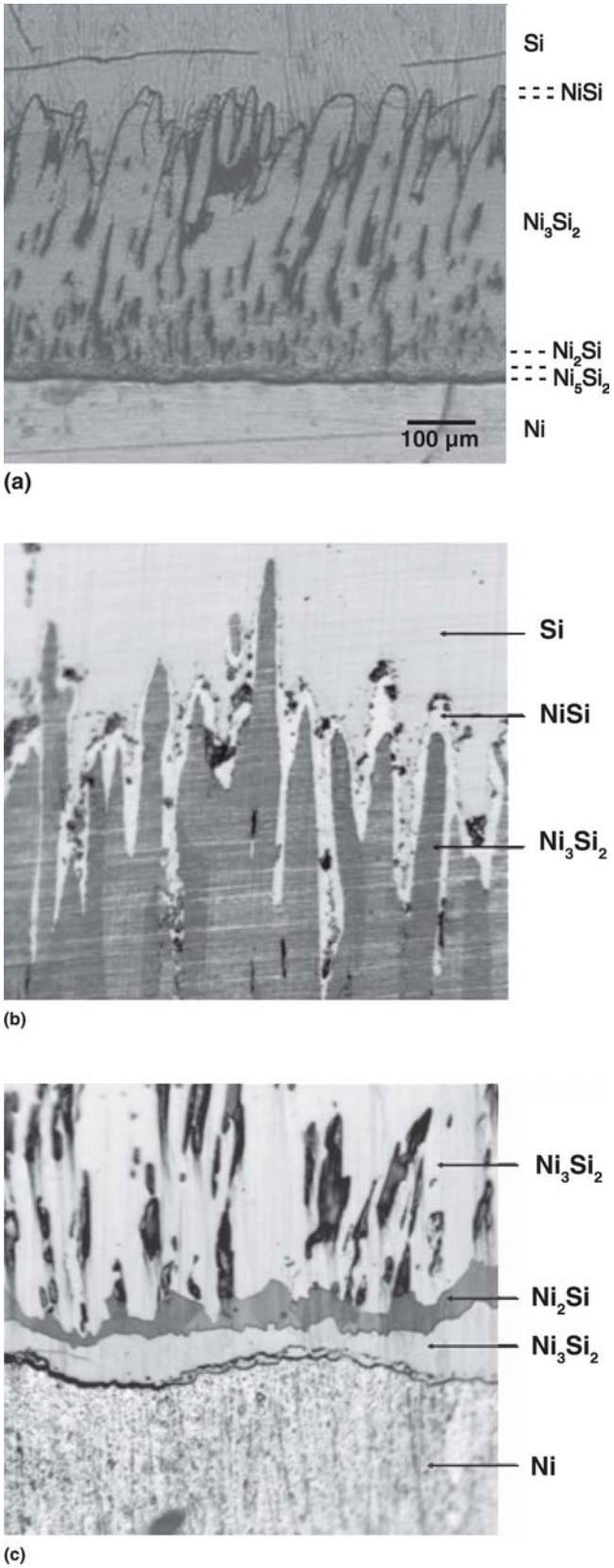


**Fig. 1** Intermetallic compounds observed between solid nickel and silicon using optical microscopy. Experiments performed at 700 °C for 12 h.

dimensional (3-D) representations of the $Ni_3Si_2$ microstructure by image reconstruction.

Indeed, microtomography by x-ray absorption enables calculation of local absorption coefficients [$\mu(x, y, z)$] from reconstructed numerical images and thus reveals the internal microstructure of the sample.[14] The x-ray emergent flux $I(x, y)$ and the x-ray incident flux ($I_0$) are linked according to the law:

$$I(x, y) = I_0 e^{-\int \mu(x,y,z)dz}$$

Absorption depends on the chemical nature of the samples. More precisely, one has $\mu \alpha Z^3$, where $Z$ is the average atomic number of the species present at location $x$, $y$, $z$. The high contrast between nickel ($Z = 28$) and silicon ($Z = 14$) allowed the authors to capture the boundary between the Ni-rich compounds and unreacted silicon.

## 3. Results

### 3.1 Phase Identification and Average Growth

Figures 1(a) to (c) show a typical longitudinal section of a bulk Ni/Si sample, as observed with optical microscopy after polishing.

One observes a needle microstructure growing from nickel toward silicon perpendicularly to the Ni/Si interface. As in Ref 10 and 11, four phases are clearly identified in the experiments: $Ni_5Si_2$ and $Ni_2Si$ (thin layers adjacent to nickel), $Ni_3Si_2$ (the largest layer), and NiSi (thin layer coating the last one). Only the $Ni_3Si_2$ phase is not planar, it appears to be formed as a collection of needles separated by valleys. The needle sizes appear to be distributed moderately around a well-defined mean value, with a dispersion of about 10%.

Figure 2 shows the evolution with time of the square of needle average height ($\langle h \rangle^2$), for experiments performed at the fixed temperature of 700 °C. The experimental data are represented with a linear fit that makes clear that $\langle h \rangle^2$ evolves linearly with time.

One can thus conclude that the growth of $Ni_3Si_2$ is diffusion controlled and introduce the evolution equation:

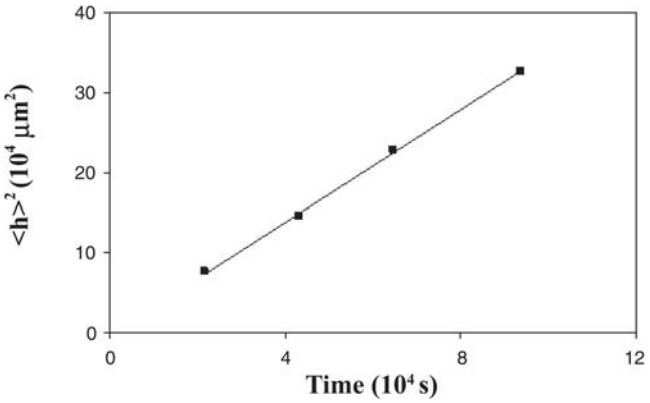


**Fig. 2** Evolution of the square of needle average height with the annealing time at $T = 700$ °C

$\langle h \rangle^2 = K_{700}t$, where $K_{700}$ is a parabolic rate constant proportional to the interdiffusion coefficient $\tilde{D}$ in the $Ni_3Si_2$ phase. A best fit to the experimental data gives: $K_{700} = 3.49 \times 10^{-12}$ $m^2s^{-1}$ at 700 °C.

Measurements of the height of $Ni_3Si_2$ needles at other temperatures enabled one to determine the temperature dependency of the parabolic rate constant and to extrapolate it at $T = 750$ °C. One obtains the estimation: $K_{750} = 7.5 \times 10^{-12}$ $m^2s^{-1}$.

### 3.2 Characterization of Needles

The second series of experiments is examined in this section. Figure 3 shows three-dimensional visualizations of the $Ni_3Si_2$ compound obtained by x-ray microtomography.

For all experiments carried out at 750 °C, the $Ni_3Si_2$ phase appears highly irregular. One can see that the number of needles decreases while their average size grows, signaling a coarsening process. To characterize quantitatively these microstructures and better understand their growth, various measurements were made.

**3.2.1 Needle Distribution.** The authors first determined the distribution of needle height (Fig. 4). The distribution is peaked around a typical value albeit with a statistically significant dispersion (~20%). Further analysis focused on a subgroup of the needles corresponding to a height close to the most probable one.

**3.2.2 Needle Shape.** Binary images (Fig. 5) enabled the authors to measure needle cross-section areas in the tip region to study more precisely the needle shape.

Figure 6 displays the evolution of these cross-section areas as a function of altitude.

One can see that each needle yields an almost linear graph $S = a(z_0 - z)$, where $z_0$ is the altitude of the tip of the needle. The slopes of these graphs fluctuate around a well-defined mean value. Paraboloidal needles [$\pi r^2 = a(z_0 - z)$] would give straight lines, but deviation from axisymmetry introduces fluctuations (Fig. 7).

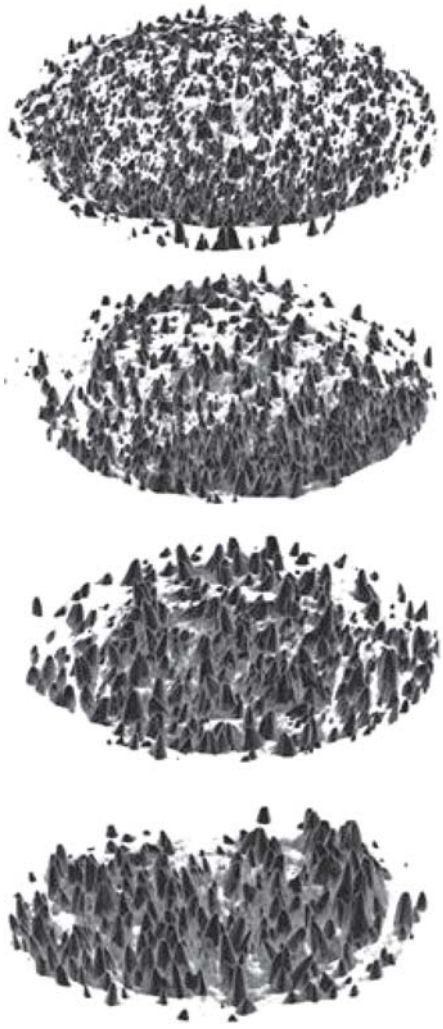

**Fig. 3** Needle microstructure of the $Ni_3Si_2$ phase. Experiments performed at 750 °C. From top to bottom: $t = 6$, 13, 24, 48 h. Diameter sample: 3 mm

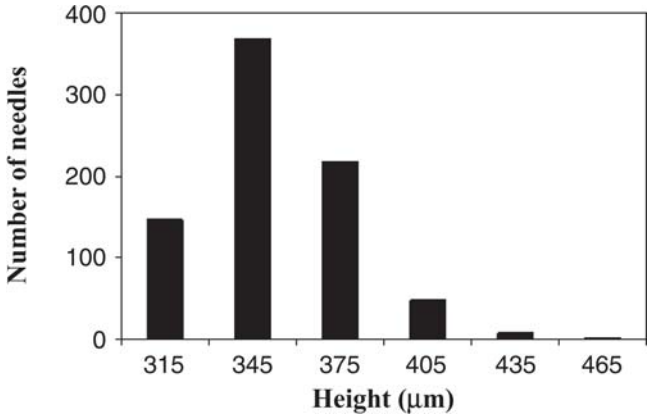


**Fig. 4** Distribution of needle height for a sample annealed at 750 °C for 6 h

**Fig. 5** Horizontal slice binary image. Dark regions correspond to the $Ni_3Si_2$ phase.

Because the needle tips appear to be very close to paraboloids in shape, one can extract from the equation $\pi r^2 = a(z_0 - z)$ an expression for the radius of curvature ρ at the tip of the needle. One gets: $\rho = -a/2\pi$.

The authors examined the square of mean radius of curvature as a function of time, for experiments performed at the fixed temperature of 750 °C (Fig. 8). The experimental data are represented with a linear fit that shows that the time and the radius of curvature are related according to a parabolic law, suggesting that the evolution of the morphology of the $Ni_3Si_2$ phase is also governed by diffusion. One gets: $\rho^2 = K'_{750}t$ where $K'_{750} = 4.10^{-16}$ $m^2s^{-1}$. Comparing these results with those found in the first series of experiments, one obtains: $K_{750}/K'_{750} \approx 1.9 \times 10^4$, showing the existence of two separated diffusion coefficients in this problem.

### 3.3 Crystallographic Texture

To supplement the geometrical data with crystallographic information, the authors performed an x-ray diffraction (XRD) analysis of a transverse section cut deep into the microstructure, at a level where needles are closely packed and thus correspond to pure $Ni_3Si_2$. The XRD spectrum (Fig. 9) is composed of two main peaks, which correspond to (004) and (006) orientations of the $Ni_3Si_2$ phase. This shows that the microstructure is strongly textured, the *c*-axis of the $Ni_3Si_2$ grains being aligned with the growth direction. As a color contrast between individual needles is made apparent by the metallographic procedure (Fig. 1b), one may suspect that each needle corresponds to an individual grain, the *c*-axis of which is identified with the needle major axis.

## 4. Discussion

The authors studied the growth properties of nickel silicides during isothermal interdiffusion. The morphology of the $Ni_3Si_2$ phase was characterized by optical microscopy and in situ x-ray microtomography. Slices and 3-D images were used to yield qualitative and quantitative observations of the microstructure.

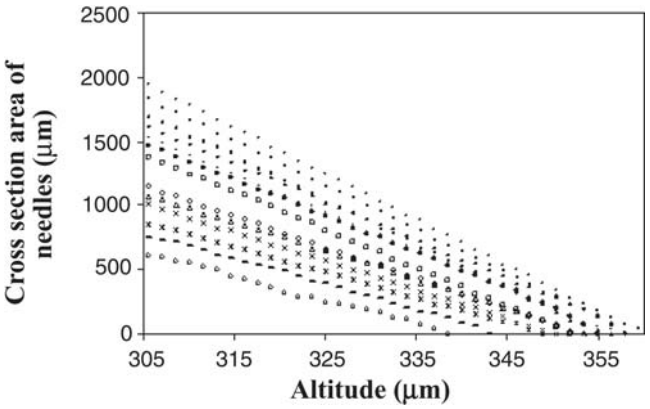


**Fig. 6** Evolution of the cross-section area of needles with the altitude for an annealing time of 6 h

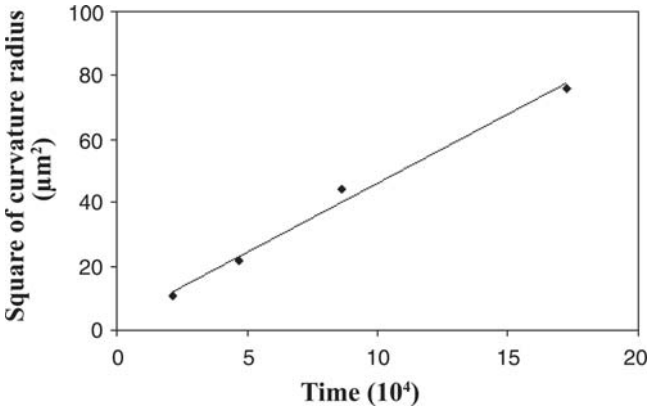


**Fig. 8** Evolution of the square of needle radius of curvature with the annealing time at $T = 750$ °C, according to three-dimensional tomographic data.

**Fig. 7** Tomographic image showing asymmetric morphology. Experiments performed at 750 °C during 6 h.

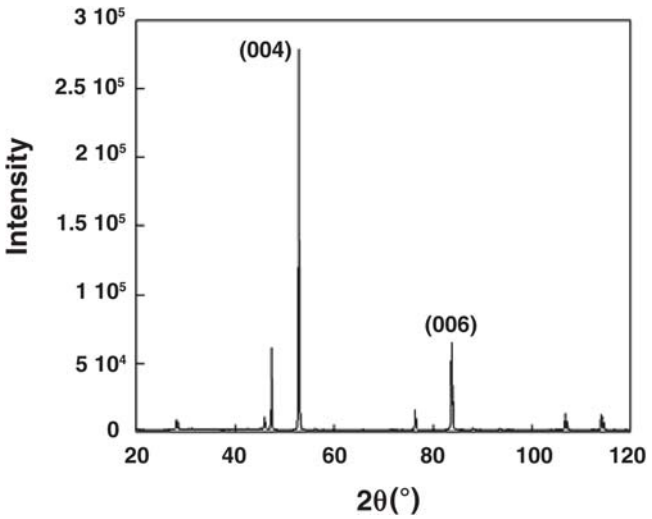


**Fig. 9** X-ray diffraction spectrum of a transverse section cut deep into the microstructure.

The $Ni_3Si_2$ phase boundaries were found to be highly irregular. It is demonstrated that the evolution with time of needle average height is parabolic. This shows that the growth of $Ni_3Si_2$ is controlled by diffusion. The analysis of the evolution of the square of needle curvature radius with time shows that the latter is controlled by a characteristic diffusion coefficient several orders of magnitude smaller than the average layer height.

Supposing that needles are indeed very close to ellipsoids, with the long semiaxis $L$ and the short semiaxis $l$, their aspect ratio $L/l$ would be given by $\sqrt{\langle L\rangle/\langle\rho\rangle}$. Observations show that $L/l = (K_{750}/K'_{750})^{1/4} \approx 10$. This ratio is constant in time, and thus the microstructure persists whatever the duration of an experiment.

XRD analyses have shown that needles are oriented toward the crystallographic *c*-axis, and thus one could suspect that the existence of these diffusion coefficients is due to anisotropy of diffusion within the $Ni_3Si_2$ compound. Indeed, one could assume that diffusions perpendicular and parallel to the *c*-axis are distinct, with separated diffusion coefficients $D_{\parallel}$, $D_{\perp}$. One would have $L^2 = D_{\perp}t$, $l^2 = D_{\parallel}t$, and the radius of curvature at the tip could be expressed by: $\rho = \sqrt{D_{\parallel}^2 t/D_{\perp}}$. Using the experimental results presented here, they would give a diffusion coefficient ratio at 750 °C of: $D_{\perp}/D_{\parallel} \approx 10^2$.

A series of experiments are in progress to confirm the quantitative concordance of this model.

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