Ion beam modification of the Ni-Si solid-phase reaction: The influence of substrate damage and nitrogen impurities introduced by ion implantation

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We report on the growth of thin NiSi films via the thermal reaction of Ni layers (13 - 35 nm) with Si(100) substrates modified by ion implantation. By introducing substrate damage or nitrogen impurities prior to the solid-phase reaction, several properties of the NiSi films can be modified: the formation temperature, texture, diffusion-limited growth rate and morphological stability. As some of the modifications to the NiSi films are rooted in the early silicide phases preceding the NiSi phase, particularly its formation temperature, special attention is devoted to the growth of the amorphous Ni-Si alloy and the crystalline δ -Ni₂Si and θ -Ni₂Si phases.

We employed a number of experimental techniques, including *in situ* synchrotron X-ray diffraction (XRD), *in situ* Rutherford backscattering spectrometry (RBS), *in situ* sheet resistance measurements, *ex situ* ion beam channelling and *ex situ* pole figure measurements. We show that both the formation temperature of the NiSi films and the intensity of epitaxial and axiotaxial components of the NiSi texture can be either lowered or raised by selecting appropriate implantation conditions. Agglomeration of the NiSi films at high temperature ($> 700^{\circ}\text{C}$) can be slowed down, either by slowing down the mobility of the Ni and Si atoms, or by removing the morphologically destabilizing axiotaxial texture. Our results emphasize the strong interwoven nature of phase formation, texture and morphological degradation. We illustrate that the kinetics of the early stages of thin film reactions consist of more than just diffusion, i.e. nucleation can also play a crucial role.

I. Introduction

Thin film reactions have been studied extensively in the past.¹ Such reactions are generally a complex interplay of thermodynamics and kinetics. Silicide formation is often used as model system. One of the most prominent examples is the Ni-Si thin film reaction.²⁻⁴ In recent decades, a number of discoveries sparked further scientific curiosity in this reaction: its early stages feature transient, metastable phases (see below); the preferred orientation of the silicide grains (texture) is complex and interwoven with the phase sequence; the final phase, NiSi₂, is an interesting case of nucleation-limited growth of a silicide phase. Moreover, due to the use of thermally-grown Ni_{1-x}(Pt_x)Si films as contact material in Si-based CMOS technology,⁵ interest in the solid-phase reaction is also driven by technological applications.

The reaction of a thin Ni film on Si(100) consists approximately of a sequence of crystalline Ni silicide phases. The metal-rich δ -Ni₂Si phase forms first, which is converted into the NiSi phase at higher temperature, which in turn is converted into the final NiSi₂ phase upon further annealing.⁴ Extensive research, however, has revealed the appearance of two metastable phases during the reaction. The first is an amorphous interlayer, preceding the crystalline phases. It forms upon deposition and grows slightly upon subsequent annealing. Nucleation barriers initially prevent the formation of crystalline phases;⁶ during this time the amorphous phase can grow up to a few nm.⁷ For most films (≥ 10 nm), the amorphous phase crystallizes long before the metal supply is consumed. The second metastable phase observed in the reaction is the θ -Ni₂Si phase, which appears in the film during the growth of the δ -Ni₂Si phase; both phases grow simultaneously for a brief temperature window before the θ -Ni₂Si phase is consumed. Not only is the concurrent growth of multiple phases in thin film reactions uncommon, the appearance of the θ -Ni₂Si phase is remarkable in itself, since the phase is thermodynamically unstable below 825°C.⁸ Nevertheless, it has been observed in Ni-Si reaction at relatively low temperature under a variety of experimental conditions.⁹

It has been found that both metastable phases mentioned above, the θ -Ni₂Si phase and the amorphous interlayer, can be stabilized (i.e., their temperature window extended) by various methods. For the θ -Ni₂Si phase, two properties are crucial in its stabilization: it can form low-energy interfaces with the Si substrate, and it is a non-stoichiometric phase.

Indeed, previous research has shown that the θ -Ni₂Si temperature window can be extended both by means of strong epitaxial texture,¹⁰ and by addition of a third element, such as Pt.¹¹ Similarly, the amorphous phase can be stabilized as well, even to the point that the entire film is converted to an amorphous alloy, i.e. an *impurity-enhanced solid-state amorphization* (IESSA) reaction.¹² Upon implanting nitrogen above a critical threshold, the typical metal-rich, crystalline silicides (δ -Ni₂Si and θ -Ni₂Si) no longer appear. Instead, an amorphous phase a-Ni-Si, growing at the interface, consumes the entire (35 nm) Ni supply. This change in reaction path is caused by the introduction of an impurity that is immobile in Si; insoluble in any stable, crystalline silicide; and binds strongly to Si atoms. As both species in the reaction (Ni, Si) require a minimum of mobility to atomically rearrange into crystals, nucleation of crystalline phases is limited by the slowest-moving element (Si), which is slowed down even further due to its strong bonds with the immobile nitrogen impurities. Consequently, nitrogen increases the kinetic nucleation barriers of crystalline silicides, hindering the formation of crystalline phases and stabilizing the amorphous phase. At temperatures high enough to overcome these barriers, the NiSi phase forms at the a-Ni-Si/Si interface. Throughout this paper, we will refer to the phenomenon of IESEA as the “*amorphous reaction path*”, as a means to distinguish it from the contrasting case in which the crystalline, metal-rich silicides do form before the entire metal supply is consumed (e.g. for samples without any implantation); we will refer to this latter scenario as the “*crystalline reaction path*”.

The initial conditions of the thin film system before annealing are essential in determining the reaction path taken. This is true for both thin film reactions in general¹ and for the Ni/Si system specifically.² Indeed, all examples given above of changes to the Ni-Si reaction rely on some way of modifying those initial conditions. Different methods have been used to achieve this change. One such method is altering the deposition of the films: it was reported that if a Ni:Si intermixed layer with a specific composition and thickness forms during Ni deposition, silicide films with *transrotational* texture can grow during annealing,¹³ which were not observed when depositing thicker Ni films.¹⁴ Another household method is ion implantation. Indeed, the starting conditions of thin film reactions can be influenced by the creation of substrate damage, the introduction of a foreign element, or other implan-

tation effects. For example, it has been shown that the amorphization of the Si substrate by ion implantation causes the final Ni silicide phase (NiSi_2) to nucleate at significantly lower temperatures.¹⁵ Additionally, the introduction of an impurity via implantation, such as carbon or nitrogen, has been shown to increase the morphological stability of the NiSi films.¹⁶

Despite earlier works, many aspects of the influence of ion implantation on the Ni-Si thin film reaction have not been explored, such as the role of (partial) substrate damage and nitrogen impurities on the stability of the θ - Ni_2Si phase, the growth kinetics of the various silicide phases (δ - Ni_2Si , NiSi and the amorphous Ni-Si alloy), the NiSi film texture and the cause of the increased NiSi morphological stability. In this paper, we investigate the effects of implantation damage and nitrogen impurities, introduced prior to annealing, on the Ni-Si thin film reaction and on the properties of the resulting NiSi films. As will be shown, the phase sequence, diffusion kinetics, texture and agglomeration of the silicide films are strongly interwoven.

II. Experimental

Samples were prepared by evaporating Ni layers (13 and 35 nm) onto Si(100) substrates at 0.2 Å/s, using molecular beam epitaxy (MBE) at the Ion and Molecular Beam Laboratory (IMBL) of the KU Leuven. All substrates were Radio Corporation of America (RCA) cleaned and HF(2%) dipped before loading into the ultra-high vacuum chamber ($\leq 10^{-9}$ mbar). To investigate the influence of damage on the reaction, Ar^+ was implanted at 60 keV/atom prior to film deposition, minimizing the amount of Ar atoms in the silicide films. For experiments focusing on the influence of impurities, N_2^+ was implanted after film deposition at 20 keV/atom for the 13 nm Ni sample and 40 keV/atom for 35 nm Ni films. As a result, nitrogen is distributed throughout the Ni film and the near-surface part of the Si. The current density was always kept below $0.6 \mu\text{A}/\text{cm}^2$ to minimize heating of the samples. More details concerning the implantation processes can be found in a previous report.¹²

In situ X-ray diffraction (XRD) experiments on the 13 nm Ni films were performed at the DiffAbs beamline (SOLEIL synchrotron, France), using X-rays with wavelengths of λ

$\lambda = 1.54 \text{ \AA}$. Samples were kept in vacuum ($\leq 10^{-4}$ mbar), and annealed at 0.333°C/s , up to 440°C . Diffraction was recorded using an area detector (XPAD), probing a 2θ range of 10° . For the 35 nm Ni films, the same experiments were performed at the facilities of the Conformal Coating of Nanomaterials (CoCoon) research group of Ghent university, using conventional $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$), an inert $\text{He} + 5\% \text{ H}_2$ as ambient and a linear detector spanning 20° in 2θ . *Ex situ* pole figures were recorded at the DiffAbs beamline as well for the 13 nm Ni films. The XPAD was placed close to the sample, covering a 2θ range of 30° . Samples were rotated 90° around their normal (azimuth ϕ), and 90° around an axis in the sample plane (elevation χ). The area detector allows a large region in reciprocal space to be probed simultaneously, resulting in fast acquisition of pole figures.¹⁷

In situ Rutherford backscattering spectrometry (RBS) measurements were performed at the facilities of the Materials Research Group (MRG) of iThemba LABS, South Africa. Samples were kept in vacuum ($\leq 10^{-7}$ mbar), and annealed at 2°C/min . Spectra were recorded with two detectors, positioned at scattering angles 170° and 135° , respectively. The recorded data were compiled into a single spectrum every two minutes. The beam used was 2 MeV He^+ , with a current of around 50 nA.

Assessing the substrate damage caused by implantation was done using ion channelling at the IMBL. By aligning the 1.57 MeV He^+ beam to the crystal axis of the substrate, the Si yield decreases drastically (i.e., *ion channelling*). Substrate disorder gradually negates this decrease in yield, allowing the backscattering spectrum to be converted to a depth profile of the implantation damage, using an iterative procedure outlined by Schmid.¹⁸

In situ sheet resistance measurements using the four-point probe method were performed at Ghent university. Samples were kept in an inert $\text{He} + 5\% \text{ H}_2$ ambient and annealed at 1°C/s .

A. Implantation damage and nitrogen distribution

Before discussing the thin film reactions, we show the effects of the implantation on the crystallinity of the substrate, prior to annealing. A number of samples were implanted

FIG. 1. The disorder depth profile in the Si substrate, resulting from 60 keV Ar⁺ implantation, as deduced from ion channeling experiments, as described in section II. The dashed, vertical line indicates the Si depth that will be consumed by the Ni layer when fully converted to the δ -Ni₂Si phase.

with 60 keV Ar⁺ ions to different fluences (0.3 , 0.8 and 5×10^{14} Ar/cm²). The substrate disorder caused by this implantation was investigated by ion channeling measurements, and converted to a depth profile of substrate disorder (figure 1). The three fluences result in three different levels of substrate damage: slightly damaged (0.3×10^{14} Ar/cm²), heavily damaged but not without crystallinity (0.8×10^{14} Ar/cm²) and amorphous (5×10^{14} Ar/cm²). In the case of the highest Ar implantation fluence, no ion channeling is observed in the near-surface Si substrate signal, meaning the Si crystal near the interface has become 100% disordered, i.e. amorphous.

Upon implanting nitrogen, at 20 and 40 keV/atom for 13 and 35 nm Ni films, respectively, the ions are distributed throughout the Ni layer and deeper into the Si. Using SRIM simulations, the nitrogen distribution was calculated (figure 2). Additionally, the Si which

FIG. 2. The depth profile of (a) 1×10^{15} nitrogen ions/cm² implanted in 13 nm Ni on Si at 20 keV/atom, and (b) 1×10^{16} nitrogen ions/cm² implanted in 35 nm Ni on Si at 40 keV/atom, as calculated by SRIM simulations. The solid, vertical lines indicate the Ni/Si interface. The dashed, vertical lines indicate the Si depth that will be consumed by the Ni layer when fully converted to the δ -Ni₂Si phase.

will be consumed by the δ -Ni₂Si phase is indicated. These simulations show that the interface will contain nitrogen throughout the entire reaction.

In all depth profiles (figures 1 and 2), the position of the δ -Ni₂Si/Si interface after full consumption of the metal supply is indicated. We will refer throughout this paper to this position when talking about the amount of damage or nitrogen concentration in the Si substrate, even though these values vary within the substrate. Around this depth, the NiSi phase forms. Hence, the concentration of substrate disorder and nitrogen is most relevant at this specific depth for the NiSi formation.

All depth profiles presented here describe the initial sample conditions, before annealing. Nitrogen or argon were not directly observed in our experiments (e.g. during TEM/EDX

measurements), due to their low concentration. Additional experimental information on the possible clustering of these atoms, either upon implantation or during annealing, could provide more insight in the interfacial free energies, relevant for phenomena such as texture formation (see section III C).

III. Results and discussion

Here, we present our experimental results on the early phase formation after Ar^+ or N_2^+ implantation (subsection III A), the diffusion of Ni in the silicide films containing nitrogen (subsection III B) and the impact of damage and impurities on the texture of the NiSi film (subsection III C) and the NiSi morphological stability (subsection III D). The reaction path for the two thicknesses studied (13 and 35 nm) is roughly identical; the only difference in phase sequence is highlighted in subsection III A.

A. Solid-phase reaction and phase sequence

Reaction without implantation: The phase sequence of an unimplanted 13 nm Ni film with Si(100), recorded by *in situ* XRD, is shown in figure 3(a). Initially, no other diffraction peaks are seen besides those from the pure Ni layer. The reaction begins roughly around 250°C, indicated by the appearance of the δ -Ni₂Si diffraction peaks. An additional diffraction peak appears around 315°C, originating from the θ -Ni₂Si grains growing at the δ -Ni₂Si/Si interface.⁴ At around 360°C, this phase disappears, and NiSi diffraction peaks appear. The entire film is subsequently converted to the NiSi phase, which converts to the NiSi₂ phase at 800°C when the film is in contact with crystalline silicon, 500°C if it is in contact with amorphous Si (not shown).¹⁵

For 35 nm Ni films, a similar reaction takes place (not shown). The only significant difference between the reaction of a 13 nm and a 35 nm film is that the consumption of the θ -Ni₂Si phase does not coincide with the formation of the NiSi phase for the 35 nm films. Rather, the θ -Ni₂Si grains are converted back to δ -Ni₂Si grains around 375°C,⁴ whereas the NiSi phase forms at a higher temperature of around 410°C.

FIG. 3. *In situ* XRD measurements of the reaction of a 13 nm Ni film on Si(100), for (a) an unimplanted sample, (b) a sample implanted with 0.8×10^{14} and (c) 5×10^{14} Ar/cm² implanted at 60 keV/atom. The samples were annealed at a rate of 0.333°C/s. The silicide phases, as evidenced by their diffraction peaks, are indicated in (a). The dashed lines indicate the appearance of the NiSi phase.

FIG. 4. Overview of the formation (and consumption) temperature of the θ -Ni $_2$ Si and NiSi phase in 13 nm Ni/Si samples, in terms of substrate disorder 13 nm below the Ni/Si interface (lower axis) or Ar implantation fluence (upper axes). The implantation was carried out prior to film deposition. The implantation energy was 60 keV/atom.

Argon implantation: The reaction of 13 nm Ni films with argon-implanted Si substrates is shown in figures 3(b-c). For fluences that do not completely amorphize the substrate (e.g. 0.8×10^{14} Ar/cm 2 , figure 1), little difference is seen between implanted and unimplanted samples. Once sufficient Ar is implanted to completely amorphize the substrate (5×10^{14} Ar/cm 2), the θ -Ni $_2$ Si phase appears only in a very small temperature window, and the NiSi phase forms at lower temperatures. An overview of the formation and consumption temperatures of the θ -Ni $_2$ Si and NiSi phase is shown in figure 4. Similar results for 35 nm Ni films were observed (not shown): initially, little difference is found for partially damaged substrates. Once the substrate is amorphized, the temperature window of the θ -Ni $_2$ Si phase decreases strongly. However, as was the case for the unimplanted samples, the NiSi formation is no longer concurrent with the θ -Ni $_2$ Si consumption. Despite an earlier consumption of the θ -Ni $_2$ Si phase by the δ -Ni $_2$ Si phase, substrate amorphization causes no significant difference in NiSi formation temperature for the 35 nm Ni films.

FIG. 5. *In situ* XRD measurements of the reaction of a 13 nm Ni film on Si(100), for (a) an unimplanted sample, (b) a sample implanted with 1×10^{15} and (c) $2 \times 10^{15} \text{ N/cm}^2$ implanted at 20 keV/atom. The samples were annealed at a rate of 0.333°C/s . The silicide phases, as evidenced by their diffraction peaks, are indicated in (a). The dashed lines indicate the appearance of the NiSi phase. The implantation was carried out after film deposition, i.e. nitrogen is dispersed throughout the film and near-surface part of the substrate.

FIG. 6. Overview of the formation (and consumption) temperature of the θ -Ni₂Si and NiSi phase in (a) 13 nm Ni/Si samples and (b) 35 nm Ni/Si, as a function of nitrogen implantation fluence (lower axis) or nitrogen concentration in the consumed Si layer 13 or 35 nm, respectively (upper axes). Implantation energy was (a) 20 keV/atom and (b) 40 keV/atom. The different causes for the shifting NiSi formation temperature are indicated as well.

Nitrogen implantation: The reactions of 13 nm films with Si, implanted with nitrogen at 20 keV/atom are shown in figures 5(b-c). At low fluence, nitrogen implantation increases the temperature window of the θ -Ni₂Si phase and delays the formation of the NiSi phase. At higher fluences however, the system follows the “amorphous reaction path” as described in the introduction: an amorphous phase grows at the interface, consumes the entire Ni film and directly converts to the NiSi phase. The formation of the metal-rich crystalline silicides is circumvented entirely. Upon increasing the nitrogen fluence, the formation of the NiSi phase is delayed to higher temperatures.

A full overview of the formation and consumption temperatures, for both 13 and 35 nm Ni films, is shown in figure 6. From these figures, it is also clear that thicker films require higher concentrations of nitrogen to undergo the “amorphous reaction path”. For 13 nm Ni films, the threshold is estimated between 0.2 and 0.4% of nitrogen in the near-surface part of the Si substrate, whereas for 35 nm, it is estimated between 0.65 and 1.3%.

A.1 θ -Ni₂Si stability

As mentioned in the introduction, the temperature window of the θ -Ni₂Si phase is typically determined by two factors: its interface with the substrate¹⁰ and its stoichiometry.¹⁹ This is reflected in our experiments as well. When introducing substrate damage (figure 4), the disorder at the interface of the θ -Ni₂Si phase increases, raising its energy. Consequently, the θ -Ni₂Si phase will become less energetically advantageous, which decreases the temperature window in which the phase appears. The difference between partial and complete amorphization is, however, striking. As will be discussed below (subsection III C), silicide texture is remarkably robust against partial loss of substrate template; partial substrate amorphization does not prevent the silicide film from forming low-energy interfaces. The extended stability of the θ -Ni₂Si phase (due to its texture on crystalline substrates) disappears only when the interface is entirely disordered.

The other factor that determines the θ -Ni₂Si stability, its stoichiometry, becomes dominant when introducing nitrogen impurities. For samples implanted with a (relatively) low nitrogen fluence (i.e., the system still undergoes the “crystalline reaction path”), the θ -Ni₂Si phase is stabilized in a larger temperature window, despite the destabilizing substrate damage induced by the implantation. Hence, this is an impurity effect of nitrogen, not consequence of the defects cause by implantation. Here, the non-stoichiometric nature of this metastable phase comes into play. Nitrogen is known to be insoluble in all stable Ni silicides.²⁰ Although no experimental data are known for the metastable θ -Ni₂Si phase, it is likely that there is some solubility of nitrogen in this phase. Indeed, the energetic cost of nitrogen incorporation in a phase with variable composition can be expected to be lower, compared to line phases with a fixed Ni:Si ratio (e.g. the δ -Ni₂Si or NiSi phase). Moreover, experiments have shown that As impurities, which are also insoluble in stable crystalline silicides, are incorporated into the θ -Ni₂Si crystal lattice.⁴ Hence, the θ -Ni₂Si silicide will likely incorporate the nitrogen impurities. This raises the energetic cost of its consumption. Indeed, nitrogen must be redistributed to the grain boundaries, the interface or the surface of the δ -Ni₂Si or NiSi grains. This redistribution requires a higher thermal budget, and as a result the θ -Ni₂Si phase is stabilized, proportional to the amount of nitrogen in the films (figure 6).

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2 Once a threshold of nitrogen is reached, the system undergoes the “amorphous reaction
3 path”. In these samples, no diffraction peaks of the θ -Ni₂Si phase are unambiguously ob-
4 served. Here, the amorphous Ni-Si phase consumes the entire Ni supply and the NiSi phase
5 grows directly from this amorphous film,¹² whereas the metal-rich, crystalline silicides are
6 not formed at all.

7 *A.2 NiSi formation temperature*

8 The temperature at which the NiSi forms varies significantly under different implantation
9 conditions, as shown in figure 4 and 6. This seemingly erratic variation crucially depends
10 on the reaction path of the system. In the “crystalline reaction path”, the NiSi phase is pre-
11 ceded by the metal-rich silicides (δ -Ni₂Si and θ -Ni₂Si). Hence, the growth of these metal-rich
12 phases determines the formation temperature of the NiSi phase. This is no longer the case
13 for samples which follow the “amorphous reaction path”. The NiSi formation temperature
14 in both reaction paths is discussed below.

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17 For samples implanted with argon or nitrogen at low fluences, the reaction proceeds
18 according to the “crystalline reaction path”. As described above, NiSi nucleation is con-
19 current with the consumption of the θ -Ni₂Si phase for 13 nm Ni samples, and the NiSi
20 formation temperature varies accordingly: when the substrate is fully amorphized by argon
21 implantation and the θ -Ni₂Si phase is destabilized, the NiSi phase forms at lower temper-
22 ature; when the θ -Ni₂Si phase is stabilized by nitrogen, the NiSi formation is delayed to
23 higher temperatures. The situation is slightly different for the 35 nm Ni films, where the
24 NiSi formation temperature is no longer coupled to the consumption of the θ -Ni₂Si phase.
25 Instead, the NiSi phase can form only when the δ -Ni₂Si phase has completely consumed the
26 metal supply.²¹ As the growth rate of the δ -Ni₂Si phase is insensitive to the crystallinity of
27 the Si substrate,²² no difference in formation temperature is seen for the NiSi phase when
28 implanting argon for 35 nm Ni films, even if the amorphization threshold is exceeded. For
29 the nitrogen implanted samples however, the NiSi formation is still delayed. Rather than
30 a more stable θ -Ni₂Si phase (as was the case for 13 nm Ni samples), this delay is due the

1 slower growth of the δ -Ni₂Si phase. Similar to the case for unimplanted samples, the NiSi
 2 phase was found to form only once the δ -Ni₂Si phase has consumed the full metal supply,
 3 even after nitrogen implantation. As will be shown below (subsection III B), nitrogen slows
 4 down diffusion of Ni through the growing δ -Ni₂Si layer. Hence, the slower growth of the
 5 preceding δ -Ni₂Si phase results in a higher formation temperature of the NiSi phase.

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 8 When sufficient nitrogen is implanted for the system to switch to the “amorphous reaction
 9 path”, the NiSi phase formation is no longer delayed by the growth of the crystalline, metal-
 10 rich silicides. Rather, the NiSi phase can form directly at the a-Ni-Si/Si interface, without
 11 the film converting to another crystalline phase first. Hence, the limiting factor in this
 12 reaction path is the direct nucleation of the NiSi phase itself, resulting in a lower NiSi
 13 formation temperature than for the unimplanted samples. Upon increasing the nitrogen
 14 content however, the formation temperature still increases. As was shown earlier,¹² the
 15 crystallization temperature of the NiSi phase is proportional to the nitrogen content of the
 16 (amorphous) film. A higher nitrogen content increases the need for local rearrangement
 17 to form crystalline nuclei and NiSi nucleation is suppressed until a higher temperature.
 18 Note that in the case of “amorphous reaction path”, the underlying Si has been completely
 19 amorphized, and the texture of the grown NiSi films is random (see section III C). If in some
 20 way, the system could be made to follow the “amorphous reaction path” without entirely
 21 removing the substrate template, the NiSi might very well form with non-random texture
 22 (e.g. axiotaxial, epitaxial, rotational). Such texture would lower the interfacial free energy of
 23 the film with the substrate, and in turn lower the thermodynamic nucleation barrier. Indeed,
 24 it can be shown that nitrogen can have a strong effect on the NiSi texture, if the Si substrate
 25 is not damaged (see section III C). A more pronounced NiSi texture would counteract the
 26 increased kinetic nucleation barriers caused by the immobile nitrogen, yielding perhaps even
 27 lower formation temperatures than observed here.

28 A.3 *amorphous reaction path and T-T-T diagram*

29 The nitrogen threshold required for the system to switch from the “crystalline reaction
 30 path” to the “amorphous reaction path” is thickness dependent (figure 6). This can be un-

derstood as follows: the film can only be fully converted to an amorphous phase if nucleation of crystalline phases is suppressed during the full growth of the amorphous phase. As the amorphous phase takes longer to consume a 35 nm than a 13 nm Ni film, the crystalline phases need to be suppressed for longer, which in turn requires more nitrogen, resulting in a higher nitrogen threshold for the change in reaction path.

As described earlier,¹² time-temperature-transformation (T-T-T) diagrams are useful for illustrating and quantifying the impurity-enhanced solid-state amorphization (IESSA) reaction (figure 7). In this diagram, two kinetic processes are shown. On the one hand, crystallization curves are drawn, i.e. the time needed to nucleate a very thin, crystalline layer. This time, $t_{nucl}(T)$, is proportional to:²³

$$t_{nucl}(T) \propto \exp\left(-\frac{\Delta G^*}{k_b T}\right) \exp\left(-\frac{Q}{k_b T}\right), \quad (1)$$

with ΔG^* and Q the thermodynamic and kinetic nucleation barriers, respectively. On the other hand, the diagram also indicates the thickness of the growing amorphous layer. The thickness x of a diffusion-limited $A_m B_n$ layer during a ramped anneal evolves as:²⁴

$$x^2 - x_0^2 = 2 \frac{(m+n)^2}{mn} \frac{|\Delta H_{A_m B_n}^0|}{E_a \rho} \times T \times D \Big|_{T_0}^T, \quad (2)$$

with $D = D_0 \exp\left(\frac{-E_a}{k_b T}\right)$ (see subsection III B), E_a the (effective) activation energy for diffusion, ρ the ramping rate and $\Delta H_{A_m B_n}^0$ the heat of formation.

By plotting both temperature-time dependences of these two kinetic processes in one diagram, their competition can be understood visually. In case the system crosses the nucleation curve before the amorphous alloy can reach its maximum thickness (roughly twice the initial Ni thickness, i.e. around 26 nm and 70 nm if the initial Ni film was 13 nm or 35 nm, respectively), the system follows the conventional “crystalline reaction path”. For example, this is the case for unimplanted samples with > 6 nm Ni layers deposited onto Si. The amorphous phase can reach 10 nm at most before crystallizing.⁷ As there is still unreacted Ni present once crystallization sets in, the conventional reaction path is followed, with the first crystalline phase being the δ -Ni₂Si phase. For ultrathin Ni films (≤ 6 nm Ni), the film is converted entirely to the amorphous phase before crystalline phases nucleate; this already occurs during the deposition of the Ni film.²⁵ Similar to our reported alteration

FIG. 7. Schematic time-temperature-transition (T-T-T) diagram, representing the evolution of a Ni film on Si upon annealing, for two annealing rates (solid lines). Along the lines, several thicknesses of the amorphous interlayer are indicated, assuming no crystallization sets in and sufficient Ni is available (equation 2). The dashed curves represent the nucleation of a thin crystalline layer (equation 1), for different nitrogen concentrations. Nitrogen increases the kinetic barrier Q in equation 1, allowing the amorphous phase to grow thicker before crystallizing. The inset shows a close-up of the 1°C/s line crossing the nucleation curves. If the amorphous phase reaches its highest thickness for the available Ni supply (roughly twice the thickness of the Ni layer, i.e. 26 and 70 nm for a 13 and 35 nm Ni layer, respectively) before crossing the nucleation line, the system follows the “amorphous reaction path”. The thickness of the amorphous layer was calculated using the experimental values in Sect. III B. The nucleation curves shown here are only approximate, a dedicated study would be required for an accurate assessment of the activation energies Q and ΔG^* in equation 1.

of the reaction path using nitrogen implantation (see below), the reaction path is altered when the amorphous phase is able to consume all unreacted Ni before crystallizing.²⁶ These phenomena, related to ultrathin films, can also be illustrated using T-T-T diagrams. This emphasizes that these figures are not limited to discussions about e.g. the addition of impurities, but represent the overall competition between diffusion and nucleation in (early) thin film silicide formation.

Adding nitrogen to the Si substrate increases the kinetic nucleation barrier Q (equation 1),¹² displacing the nucleation curves. Consequently, the amorphous layer can grow thicker before these crystallization curves are reached. Upon implanting sufficient nitrogen, the initial (13 or 35 nm) Ni supply is completely consumed before the system reaches the crystallization curves, i.e. the amorphous phase reaches its maximum thickness (roughly 26 or 70 nm, respectively), and the system follows the “amorphous reaction path”. From this figure, it is easy to see why the nitrogen threshold for IESSA in the Ni-Si system is thickness dependent.

The T-T-T diagram shows that whether the system goes through the “amorphous reaction path” is not just dependent on the nitrogen content, it is also dependent on the ramp rate. Indeed, at very high annealing rates, the amorphous Ni-Si alloy can reach a higher thickness before crystallizing, both with and without nitrogen implantation, as illustrated by the red solid line (figure 7). This is not mere conjecture, it was reported²⁷ that annealing a Ni film at 8×10^4 K/s allows the amorphous Ni-Si alloy to reach a thickness of roughly 28 nm without crystallizing, even without nitrogen impurities. Similar to the IESSA case, the entire film is converted to the amorphous phase and the metal-rich crystalline silicide phases are skipped in favor of the NiSi phase.

B. Ni diffusion in silicide films after nitrogen implantation

As shown in the previous section, nitrogen implantation has a very strong effect on the Ni-Si solid-phase reaction. It is therefore likely that the nitrogen also influences the diffusion

FIG. 8. (a) *In situ* RBS measurement of a 35 nm Ni film on Si, implanted with 4×10^{15} N/cm². The sample was annealed at 2°C/min. (b) Analysis of the elemental depth profile, indicating the amount of Ni atoms in the different layers, as a function of temperature.

processes during this reaction. By recording phase formation using *in situ* RBS, we have deduced the kinetics for both the crystalline silicide films (δ -Ni₂Si or NiSi layers) and the amorphous layer. Two 35 nm Ni samples were implanted with nitrogen at 40 keV/atom to a fluence of 4×10^{15} N/cm² and 1×10^{16} N/cm², respectively. The spectra were individually analyzed using neural networks and the IBA DataFurnace software.²⁸

The raw data and the analysis of layer thicknesses of a sample implanted with 4×10^{15} N/cm² and 1×10^{16} N/cm², are shown in figure 8 and figure 9, respectively. Due to experimental limits, the ramp rate driving these experiments was lower than those for the XRD measurements. Hence, the formation temperatures do not correspond to those obtained from XRD (figure 6). For the sample implanted with 4×10^{15} N/cm², the reaction proceeds according to the “crystalline reaction path”. A layer with a Ni:Si stoichiometry 2:1 forms first (corresponding to the crystalline δ -Ni₂Si phase); after it has consumed all of the Ni supply, a layer with a 1:1 stoichiometry (the NiSi phase) forms, similar to unimplanted samples. However, the growth of both phases proceeds more slowly than for unimplanted samples, as will be shown below. For the sample implanted with 1×10^{16} N/cm², the reaction switches to the “amorphous reaction path”. A Ni-Si mixture with an average stoichiometry of 46% Si grows between the Ni layer and the Si substrate. No evidence of the δ -Ni₂Si (33%) or θ -Ni₂Si (33 - 40%) phase is seen.

FIG. 9. (a) *In situ* RBS measurement of a 35 nm Ni film on Si, implanted with 1×10^{16} N/cm². The sample was annealed at 2°C/min. (b) Analysis of the elemental depth profile, indicating the amount of Ni atoms in the different layers, as a function of temperature.

B.1 Kinetic analysis

From the temperature-dependent growth of the silicide layers (figures 8(b) and 9(b)), the kinetic parameters can be extracted.²⁴ Once these Ni silicides have grown thicker than a few nm, their growth rate is limited by diffusion of atoms through the layer;²¹ when fitting the kinetic parameters, only data points were used at which the layer growth was indeed diffusion-limited. Moreover, it has been shown that Ni is the dominant diffusing element, both in the crystalline and in the amorphous phases.²⁹ Consequently, the growth rate is dictated by the diffusion coefficient $D = D_0 e^{\frac{-E_a}{k_b T}}$ of Ni through the silicide layer. The resulting kinetic parameters for the different phases can be found in table I. A direct visual comparison between the unimplanted and implanted samples can be made by plotting the diffusion coefficients in the relevant temperature windows (figure 10). It is clear that nitrogen implantation slows down diffusion through the crystalline silicide layers. Moreover, the diffusion coefficient in the amorphous phase is comparable to those of the crystalline silicides, and very close to the diffusion coefficient of Ni in amorphous Si.³⁰

TABLE I. Overview of the kinetic parameters D_0 and E_a , obtained from the *in situ* RBS measurements shown in figures 8 and 9. The kinetic analysis of an unimplanted (80 nm Ni) sample was taken from Demeulemeester *et al.*²⁸

	δ -Ni ₂ Si		a-Ni-Si		NiSi	
	$\log_{10} D_0$ (nm ² /s)	E_a (eV)	$\log_{10} D_0$ (nm ² /s)	E_a (eV)	$\log_{10} D_0$ (nm ² /s)	E_a (eV)
Unimplanted	13.7 ± 0.3	1.25 ± 0.05	-	-	14.4 ± 0.2	1.34 ± 0.06
4×10^{15} N/cm ²	13 ± 1	1.6 ± 0.2	-	-	12 ± 1	1.7 ± 0.2
10×10^{15} N/cm ²	-	-	12 ± 1	1.3 ± 0.2	13 ± 1	1.8 ± 0.2

FIG. 10. The diffusion coefficients $D = D_0 e^{\frac{-E_a}{k_b T}}$ of Ni atoms in different silicide phases, with and without nitrogen implantation, obtained from *in situ* RBS measurements (table I) in the relevant temperature window. The error bars are denoted with a shaded area. (a) The diffusion coefficients of Ni in the the first silicide phases of the reaction (δ -Ni₂Si or amorphous phase). The diffusion coefficient of Ni in amorphous Si³⁰ is plotted for comparison. (b) The diffusion coefficient of Ni in the NiSi phase.

B.2 Ni diffusion in crystalline silicides

The decrease of diffusivity in crystalline silicides after nitrogen implantation can be understood by considering the two main diffusion mechanisms that make up the effective diffusion

coefficient in thin films reactions, i.e. lattice and grain boundary (GB) diffusion.³¹ Due to its insolubility in the δ -Ni₂Si and NiSi lattice,²⁰ nitrogen is confined to the grain boundaries. Hence, nitrogen affects the contribution of the GB diffusion, either by decreasing the GB volume (i.e. by increasing grain sizes of the film) or by blocking the GB diffusion paths. As no noticeable difference in grain sizes after implantation was observed in *ex situ* synchrotron XRD experiments (not shown), the slower diffusion is attributed to nitrogen decorating the grain boundaries.³² This explains why Ni diffusion in both the δ -Ni₂Si and the NiSi phase is significantly slowed down upon implantation of 4×10^{15} N/cm², yet further increasing the fluence to 1×10^{16} N/cm² has no influence on the diffusion coefficient in the NiSi phase (figure 10). Indeed, once the contribution of GB diffusion in the NiSi film is reduced to negligible amounts, all Ni diffusion is forced to occur via lattice diffusion; any further increase in nitrogen content of the grain boundaries does not influence the diffusion coefficient.

B.3 *Ni diffusion in amorphous Ni-Si phase*

The growth of the amorphous Ni-Si phase is not only remarkable because of its thermodynamic metastability, but also due to its fast growth. Diffusion through amorphous phases is typically very slow compared to crystalline phases, since it often involves collective motion of many matrix elements.³³ Our experiments, however, show that the diffusion coefficient of Ni in the amorphous phase is comparable to that in its crystalline counterparts: its value lies between that of the δ -Ni₂Si phase with and without nitrogen implantation (figure 10(a)). Indeed, high diffusivity in an amorphous phase is not uncommon for binary systems undergoing a solid-state amorphization reaction. In such systems, the mobile element A often has an anomalously high mobility in both the other element B, as well as the amorphous alloy A-B.³⁴ Indeed, whereas Si diffuses slowly in Ni,³⁵ Ni is a fast diffuser in both crystalline³⁶ and amorphous³⁰ Si, and estimates of the diffusion coefficient from a previous report³⁵ suggest Ni diffuses rapidly in the amorphous Ni-Si phase as well, in line with our findings.

One could speculate about the diffusion mechanism(s) of Ni in the amorphous Ni-Si phase. The low activation energy found in this work suggests that the Ni diffusion mechanism involves one or a limited number of atoms (e.g. an interstitial migration, similar to Ni

diffusion in crystalline³⁶ and amorphous³⁰ Si), rather than the collective movement of many atoms typically found for amorphous layers or metallic glasses. Moreover, the remarkable similarity between the Ni diffusion coefficients in the amorphous Ni-Si phase and in amorphous Si (figure 10(a)), implies that the diffusion mechanisms in both matrices may be closely related. However, further research is needed to clarify the exact mechanisms of Ni diffusion in the amorphous Ni-Si matrix.

C. NiSi film texture

Previous research has shown that the NiSi texture is strongly influenced by the substrate orientation, the preceding silicide phases and alloying elements/impurities.³⁷ Implantation, introducing both substrate damage and impurities, can therefore be expected to change the texture as well. To assess these changes, the texture of NiSi films with different implantation parameters was recorded using *ex situ* pole figures (figure 11). All samples were annealed to 440°C, their texture measured at room temperature after cooling down. These pole figures show the diffraction recorded for a *d*-spacing of 1.98 ± 0.02 Å, i.e. the diffraction originating from the NiSi(211) and NiSi(202) planes. The four Si(220) substrate peaks are present in all pole figures as well.

In figure 11(a), a pole figure of a NiSi film is shown, formed by annealing an unimplanted 13 nm Ni sample to 440°C. The texture of a NiSi film is a complex mixture of *axiotaxial* and *epitaxial* components.³⁸ In axiotaxy, specific planes of film grains align with specific, off-normal planes of the substrate in one dimension; whereas the grain can still be rotated around the normal axis to these planes. Consequently, axiotaxial components can be recognized in pole figures by off-center, circular features. Epitaxy is characterized by the in-plane alignment of film grains with a fixed orientation to the substrate. All grains of a particular epitaxy have a single orientation; consequently, epitaxial components lead to well-defined spots on the pole figure.³⁷ The axiotaxial lines of the NiSi(211) and (202) planes are clearly visible as circular arcs, centred around the Si(220) peaks. Along these axiotaxial lines, brighter spots can be seen, indicating epitaxial components of the texture.

When substrate damage is gradually introduced by Ar implantations (figures 11(b-d)),

FIG. 11. Pole figures for d -spacing $1.98 \pm 0.02 \text{ \AA}$, obtained from 13 nm Ni layers annealed to 440°C and cooled down to room temperature. All films were (fully) converted to the NiSi phase. These measurements show diffraction from the NiSi(211) and (202) planes, as well as the fourfold Si(220) planes. For each pole figure, the implantation fluence is indicated. (a) An unimplanted sample, (b-d) 60 keV Ar^+ implanted samples, representing an increasing amount of substrate damage from left to right (figure 1) (e) 7.5 keV/atom nitrogen implanted sample. For this energy, substrate damage is mostly avoided. (f-h) 20 keV/atom nitrogen implanted samples. For this energy, increasing the fluence leads to higher substrate damage.

the intensity of axiotaxial lines decreases, but remains visible even when the NiSi phase forms on Si substrate with around 70% disorder (figure 11(c)). When the Si underneath the film is fully amorphized however (figure 11(d)), no NiSi texture components can be distinguished, i.e. the film texture is random.

Pole figures of the NiSi texture were also measured for nitrogen-implanted samples, shown in figures 11(e-h). These figures are again sorted by increasing substrate damage, reaching full substrate amorphization upon implanting $2 \times 10^{15} \text{ N/cm}^2$. One sample (figure 11(e)) was

implanted with nitrogen at 7.5 keV/atom, at an angle of 40° . Due to the low implantation energy, nearly all nitrogen ($>90\%$) is confined to the Ni film and a few nm beneath it. The Si crystal at the depth at which the NiSi phase nucleates, remains nearly pristine. Compared to the unimplanted NiSi film (figure 11(a)), the axiotaxial and epitaxial features in the pole figure are much more intense. As there is very little substrate damage, it is clear this is due to an impurity effect of nitrogen. A similar effect might very well be observed when the nitrogen was introduced by co-evaporation, rather than implantation. In figures 11(f-h), the NiSi texture is shown for samples implanted with nitrogen at 20 keV/atom, at different fluences. At this implantation energy, most nitrogen penetrates the Ni film and is stopped deeper in the Si substrate (figure 2(a)). Consequently, the nitrogen implantation at this energy will cause substrate damage as well. For these samples, two opposite effects are at play: a more textured film as more nitrogen is introduced (as in figure 11(e)), yet a less texture film as substrate damage is increased (as in figures 11(a-d)). Indeed, this is what is seen in figures 11(f-h): initially, the texture is more pronounced than for the unimplanted sample due to nitrogen in the film (figure 11(f)); as more nitrogen is implanted, however, the texture begins to fade away due to higher substrate damage (figure 11(g)). At the highest nitrogen fluences, the Si is entirely amorphized, and the NiSi film exhibits a random texture (figure 11(h)). In summary, implantation can either decrease (substrate damage) or increase (nitrogen impurities) the axiotaxial and epitaxial texture components of the NiSi film. Both effects are discussed below.

C.1 Influence of substrate damage

The loss of non-random texture as the substrate template is removed is not very surprising, since film grains no longer have a substrate template to which they can orient. Although texture can arise via other mechanisms (such as lateral grain growth or diffusion anisotropy),^{37,39} the pole figures of Ar implanted samples (figures 11(b-d)) and other experiments involving amorphous Si interlayers of varying thickness (not shown) show that the crystallinity of the Si substrate at the interface where NiSi nucleation takes place is the sole determining factor of the film texture (for temperature $\leq 440^\circ\text{C}$). Indeed, our RBS results (section III B) show a layer-by-layer growth, meaning that the initial crystalline layer

grows in two planar dimensions at the interface first, and subsequently thickens in the third dimension. This initial very thin layer determines the texture of the films, as no qualitative change in NiSi texture was observed between samples annealed to 350°C and 440°C. Hence, if the NiSi grains form at a completely disordered interface, the final film texture is random. However, it is remarkable that even at high levels of substrate disorder (70%, figure 11(c)), axiotaxial lines are still visible in the pole figure. Texture selection during the solid-phase reaction is driven by the creation of low-energy interfaces, and the nucleation barrier to ‘textured’ silicide grains is lower than that of randomly oriented grains. However, quantitatively, little is known on the thermodynamics of silicide interfaces;^{11,40} even less when the crystalline phases deviate from a perfect, bulk crystal structure.

The observation that axiotaxial texture decreases rather slowly as substrate damage is increased, implies that the low-energy interfaces formed are rather insensitive to defects. If their energy was raised significantly by e.g. 15% of disordered atoms (figure 11(a)), the energetic advantage of aligned grains over randomly oriented grains would decrease and axiotaxial texture would rapidly disappear with increasing implantation damage. These measurements corroborate the stability of the θ -Ni₂Si phase during the solid-phase reaction after introducing partial amorphization (figure 4). They indicate the interfacial energy of textured silicide grains is relatively insensitive to substrate disorder.

These results shed a first insight into how the texture of silicide films changes as substrate damage is gradually introduced. However, many more types of texture can be explored. The texture of these NiSi films grown from a 13 nm Ni film in direct contact with Si is mainly characterized by 1D alignment of film planes with planes in the substrate, i.e. axiotaxy. Indeed, the epitaxial components of the NiSi texture are strongly linked to the 1D axiotaxial alignment.⁴¹ However, other types of texture can be achieved by altering the initial conditions, such as epitaxial films (by e.g. introducing Pt)⁴² or pseudo-epitaxial transrotational films (by having a Ni-rich intermixed layer at the interface)⁴³, which are characterized by 3D alignment with the substrate. This higher order of substrate coupling will influence how the film texture evolves as the substrate template is gradually removed. Further exploration of different types of texture will be crucial in obtaining a better understanding of interfacial free energy in thin film systems.

C.2 Influence of nitrogen impurities

When implanting nitrogen at low fluence, the increase in axiotaxial and epitaxial texture can be attributed to the more difficult nucleation of the NiSi phase: for 13 nm Ni films, the NiSi phase nucleates from the θ -Ni₂Si grains,⁹ which are stabilized by nitrogen (figure 6(a)). The overall increase in nucleation barrier due to the incorporation of nitrogen in the film implies a stronger selection of nuclei with a particularly advantageous orientation. The favorable interfacial energy that axiotaxial or epitaxial orientations provide, partly counteracts the higher nucleation barrier. As a result, the film has more intense axiotaxial and epitaxial components. It emphasizes that both the kinetic and thermodynamic sides of nucleation determine many aspects of the early stages of the solid-phase reaction, ranging from the reaction path, the formation temperature of phases (see section III A) to the texture of the resulting films.

At high fluence, however (figure 11(h)), the process of implantation removes the substrate crystallinity and the non-random film texture disappears, as was the case for samples amorphized by Ar implantation (figure 11(d)).

D. NiSi film agglomeration

The morphological stability of NiSi-based films has been studied extensively,⁴⁴ as it has important consequences for technological applications.⁴⁵ A crucial factor is the NiSi texture.⁴⁶ Indeed, axiotaxy has been shown to facilitate agglomeration.⁴⁷ Consequently, the change in texture described above is expected to influence the morphological evolution of the NiSi films. Indeed, we found that both the use of an amorphous Si interlayer, as well as nitrogen implantation, result in a delayed agglomeration of the film. However, the enhanced stability has two different origins, as discussed below.

To assess the influence of substrate amorphization, texture changes and nitrogen impurities on the morphological stability of NiSi films, the sheet resistance evolution of 13 nm Ni films on Si(100) upon annealing was recorded *in situ*. One such sheet resistance measurement of a Ni film in contact with pristine Si(100) is shown in figure 12(a). During

FIG. 12. Sheet resistance measurements of 13 nm Ni films on Silicon-on-insulator (SOI) substrates. The samples were annealed at 1°C/s up to 750°C, and kept at this temperature for 10 minutes. The texture of the corresponding NiSi films, annealed to 440°C and cooled down, is also shown in the insets (figure 11). (a) A Ni film on Si(100), with and without an amorphous Si interlayer. (b) Ni films on Si(100), implanted with 20 keV/atom nitrogen.

the complex early stages, the sheet resistance fluctuates strongly. Indeed, many different phases (Ni, amorphous Ni-Si, δ -Ni₂Si, θ -Ni₂Si) grow and disappear in different quantities during these stages. Each of these phases has a distinct resistivity, and each is accompanied by growth-induced stress, which in turn affects the film morphology and consequently the sheet resistance. This results in an erratic evolution of the sheet resistance at low temperature. Around 330°C however, the resistance of the film decreases significantly, signaling the conversion to the low-resistivity NiSi phase. At higher temperature, the sheet resistance of the unimplanted Ni/Si sample (“no interlayer”) increases rapidly around 650°C. This indicates agglomeration: the film is breaking up into isolated, large grains, increasing its sheet resistance.

As different implantation conditions lead to very different film evolution at low temperature (section III A), the evolution of sheet resistance during the first stages also changes drastically with different implantation conditions. To fully explain these changes in sheet

resistance below 330°C, further research is needed. We will focus in the following section on the evolution of the sheet resistance at high temperature, where film agglomeration causes it to increase rapidly.

D.1 Influence of substrate amorphization

As axiotaxial texture facilitates agglomeration, and substrate amorphization removes this type of texture (figure 11(d)), a higher morphological stability is expected when the NiSi is formed by annealing a Ni film on amorphous Si. However, a fully formed NiSi film in contact with amorphous Si will convert into the NiSi₂ phase at around 500°C.⁴⁰ To avoid this transformation, a sample with an 18 nm amorphous Si interlayer between the 13 nm Ni layer and the pristine Si(100) was grown. This amorphous interlayer is consumed entirely during the growth of the NiSi phase, resulting in an NiSi layer in contact with pristine Si(100), but whose texture is entirely random at 440°C, as evidenced by pole figure measurements. The sheet resistance measurement of this sample is shown in figure 12(a). The increase in sheet resistance - indicating film agglomeration - occurs at a higher temperature for the sample with the amorphous interlayer, indicating that the NiSi film with random texture is indeed morphologically more stable than the NiSi film with axiotaxial texture.

D.2 Influence of nitrogen impurities

Nitrogen implantation also affects the agglomeration behaviour of the NiSi films, as shown in figure 12(b). With increasing nitrogen content, the NiSi films remain increasingly more morphologically stable, regardless of NiSi texture. This indifference to NiSi texture is surprising at first: for a sample implanted with 0.75×10^{15} N/cm², the NiSi axiotaxial components become more pronounced in the film texture (figure 11(f)), yet the film agglomerates slower than the film without implantation. Clearly, this enhanced stability cannot be explained by a change in texture, since stronger axiotaxy is expected to facilitate agglomeration. Rather, it is the nitrogen present in the film that delays agglomeration. Agglomeration of Ni silicide films is accomplished through grain boundary grooving,⁴⁸ i.e. material diffuses away from the grain boundaries to the interface, deepening the groove. Hence, the speed of agglomeration

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eration is proportional to the diffusivity of atoms along the grain boundaries and interface, especially that of the slowest-moving element Si.⁴⁵ Nitrogen slows down the mobility of both elements. Indeed, the mobility of Ni in NiSi films is lowered several orders of magnitude due to nitrogen stuffing the grain boundaries (subsection III B). Moreover, the strong Si-N bonds formed by the nitrogen impurities slow down the already rate-limiting Si atoms even further, similar to the underlying cause of the IESSA reaction.¹² Although their relative contributions are not known, both effects will hinder the kinetic process of grain boundary grooving. Consequently, the agglomeration of the films is delayed by nitrogen, even despite the stronger axiotaxial texture.

IV. Conclusion

By modifying the initial thin film conditions using ion implantation, the early stages of the Ni-Si reaction and the resulting NiSi films can be tailored. Introducing substrate damage results in a slow, gradual loss of axiotaxial and epitaxial film texture. When full amorphization is reached, the θ -Ni₂Si phase is present during a much shorter temperature window. Introducing nitrogen impurities slows down two kinetic processes: nucleation of crystalline phases and diffusion of Ni in those phases. This results in an erratic dependence of the NiSi formation temperature on the nitrogen concentration. Finally, it is demonstrated that the NiSi morphology can be made to remain intact up to higher temperature, either due to the removal of destabilizing texture components or due to nitrogen slowing down diffusion in the grain boundaries.

The interplay between substrate damage and impurity effects changes the reaction path in surprising and occasionally opposite ways. As outlook, one could further explore the dynamics between impurity effects and substrate crystallinity, by investigating the reaction of Ni films with Si_{1-x}C_x layers. Unlike nitrogen, carbon is miscible in Si, and larger amounts of impurities could be introduced without destroying the Si crystal structure. Indeed, carbon is also expected to enhance the solid-state amorphization reaction,¹² and is known to alter the texture of the silicide phases.⁴⁹

Our results offer new insight into the complex first stages of thin film reactions. Typically,

the “kinetics” of early phase formation are considered synonymous with the one-dimensional, *diffusion-limited* growth of the phase, dominated by the long-range diffusion coefficients and interfacial reaction rates.⁵⁰ In our experiments, a more nuanced picture involving two different kinetic processes emerges, i.e. early phase formation as an interplay between nucleation and (long-range) diffusion. Indeed, the growth of a new phase (the NiSi phase) can be limited by either diffusion through the preceding layers (the δ -Ni₂Si phase) or by nucleation, depending on the amount of implanted nitrogen. Historically, nearly all phase transformations were strictly classified as either *diffusion-limited* or *nucleation-limited*.⁵¹ Our research shows that in early phase formation, the distinction is not always as clear cut.

Acknowledgments

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