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**Impurity-enhanced solid-state amorphization: the Ni-Si thin film reaction altered by nitrogen**

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Solid-state amorphization, the growth of an amorphous phase during annealing, has been studied in a wide variety of thin film structures. Whereas research on the remarkable growth of such a metastable phase has mostly focused on strictly binary systems, far less is known about the influence of impurities on such reactions. In this paper, the influence of nitrogen, introduced via ion implantation, is studied on the solid-state amorphization reaction of thin (35 nm) Ni films with Si, using *in situ* XRD, *ex situ* RBS, XTEM, and synchrotron XRD. It is shown that due to small amounts of nitrogen ( $< 2$  at.%), an amorphous Ni-Si phase grows almost an order of magnitude thicker during annealing than for unimplanted samples. Nitrogen hinders the nucleation of the first crystalline phases, leading to a new reaction path: the formation of the metal-rich crystalline silicides is suppressed in favour of an amorphous Ni-Si alloy; during a brief temperature window between 330 and 350°C, the entire film is converted to an amorphous phase. The first crystalline structure to grow is the orthorhombic NiSi phase. We demonstrate that this phenomenon occurs only under specific implantation conditions. In particular, the initial distribution of nitrogen upon implantation is crucial: sufficient nitrogen impurities must be present at the interface throughout the reaction. Introducing implantation damage without nitrogen impurities (e.g. by implanting a noble gas) does not cause the enhanced solid-state reaction. Moreover, we show that the stabilizing effect of nitrogen on amorphous Ni-Si films (with a composition ranging from 40% to 50% Si) is not restricted to thin film reactions, but is a general feature of the Ni-Si system.

## I. INTRODUCTION

Thin film growth has been studied extensively for several decades.<sup>1-3</sup> One particular way of growing thin films is to anneal two elemental films (or a film and a substrate) which are in contact with each other, creating compounds at the interface during the solid-state reaction. Special attention was given to reactions between a metal layer and Si substrates, due to the role of metal silicide growth as model system for solid-state reactions. Many studies and models<sup>2,4,5</sup> focus on the reaction path of binary systems during annealing, from the initial deposition of the metal layer to the system reaching thermal equilibrium, e.g. the evolution of a Co-Ti bilayer to an epitaxial CoSi<sub>2</sub> film.<sup>6</sup> This path is bound by thermodynamic and kinetic constraints and as a result, the first phase formed at the interface is often not the phase which would be expected in thermal equilibrium. Solid-state reactions are typically a succession of several phases, until a phase is reached which is stable in contact with the substrate. Moreover, due to the aforementioned constraints, the growth of metastable phases has been observed in many metal/Si reactions: phases which have a larger Gibbs free energy than another phase (or a combination of phases) of identical composition, such as the  $\epsilon$ -FeSi phase<sup>7</sup> or the hexagonal  $\theta$ -Ni<sub>2</sub>Si phase (sometimes also referred to as the *the  $\theta$  phase*).<sup>8</sup> Another example of a binary reaction involving metastable phases is a solid-state amorphization (SSA) reaction: upon annealing, the first interlayer formed is an amorphous phase, even when one or both parent phases are (poly)crystalline.<sup>9</sup> Since its discovery in the early 1980's,<sup>10,11</sup> several binary metal/Si and metal/metal systems undergoing this type of reaction have been identified.

As binary reactions of elemental thin films have become better understood, attention is turning to ternary systems. In these systems, a third element is introduced, e.g. during deposition or via ion implantation. When the concentration of the third element constitutes only a few atomic percent, the system is typically considered a binary system containing impurities. It has been shown<sup>12</sup> that reactions can be modified by impurities, with respect to the reaction *path*, the reaction *rate* or the *stability* of metastable states. Efforts to understand the effects of impurities on metal silicide formation are ongoing.<sup>3,13,14</sup>

Surprisingly, very little is known about the effect of impurities on the SSA reaction. J.J.



Hauser<sup>15</sup> showed that impurities, originating from residual gas present in the vacuum system, play an important role in the nucleation of an amorphous phase in the Ni-Zr system. Other reports, focusing on the growth of the amorphous phase following its nucleation, show that impurities can either enhance<sup>16</sup> or diminish<sup>17</sup> the growth of the amorphous phase in metal/metal or metal/Si couples. However, few cases have been studied, and a general understanding of the impurity effect on SSA reactions is lacking.

One binary reaction that has been studied extensively, is that of thin Ni films with silicon.<sup>18,19</sup> This reaction has proven scientifically interesting, with the appearance of metastable phases,<sup>8</sup> a strong interplay between texture and film evolution,<sup>20</sup> and a nucleation-limited growth of the final phase.<sup>21</sup> Additionally, investigation of this reaction is partly driven by the use of NiSi films as contact material in CMOS architecture.<sup>3,22</sup> The Ni-Si reaction is also a promising test case for the effect of impurities on the SSA reaction: it has been reported<sup>23</sup> that the reaction of the Ni-Si system starts off with the growth of an amorphous phase (see below). Moreover, it has been shown that the Ni-Si reaction can be strongly affected by impurities,<sup>24</sup> such as nitrogen,<sup>25</sup> carbon<sup>26</sup> and oxygen.<sup>27</sup>

Below, we briefly discuss the most prominent (general) models of solid-state amorphization reactions, nucleation in thin film reaction and the growth of an amorphous interlayer in the Ni-Si system specifically.

## A. General considerations on SSA

Solid-state amorphization has been studied in many binary systems, both in metal/metal and metal/Si couples. Based on experimental evidence, two required conditions for a SSA reaction have been identified:<sup>9</sup>

1. The formation of an amorphous interlayer must have a negative enthalpy of mixing.
2. The diffusivity of one element in the other must be asymmetrically high.

These conditions represent the thermodynamic and kinetic prerequisites for a SSA reaction, respectively. It is often found that when the diffusivity of element A in element B is very high, the diffusivity of A in the amorphous alloy  $A_xB_y$  is high as well.<sup>9</sup> Hence, a likely consequence of the second condition is an anomalously fast diffusion of the mobile element

through the amorphous phase, which in turn results in a fast growth of the amorphous phase. These conditions can also be generalized to include ternary systems (or systems with even more elements), by requiring that one element is a fast diffuser in the other two (or more) elements, e.g. the fast diffusion of hydrogen in Rh-Zr compounds.<sup>28</sup>

The first condition provides a driving force for the amorphous phase growth. The interpretation of the second, kinetic condition is less obvious, and has led to two (related) schools of thought as to why an amorphous phase is the first to grow at the metal/Si interface in these systems. The first school<sup>9,29</sup> considers that the amorphous phase grows at temperatures too low for crystalline phases to nucleate. Consequently, it implies that nucleation barriers to the formation of the first crystalline phase exist, whose origin will be discussed below. The second school<sup>30,31</sup> makes no assumption concerning these barriers; it considers scenarios in which the nucleation of a crystalline phase is not necessarily an issue. Rather, this school focuses on the kinetic competition between phases. It assesses that the first phase to grow is that which has the highest *rate* of lowering the system's Gibbs free energy ( $-\mathrm{d}\Delta G/\mathrm{d}t$ ). Other phases, even if they can overcome nucleation barriers, are consumed by the first (fast-growing) phase. In other words, the formation of other phases is suppressed due to a *growth instability*, until the growth of the first phase (inversely proportional to its thickness) sufficiently slows down.<sup>4,30</sup> For systems in which the second condition is met, the amorphous phase wins against any other (crystalline) phase that might nucleate: despite a lower driving force, it has the highest lowering rate due to its rapid growth. Consequently, the amorphous phase grows first and crystalline phases are suppressed until the amorphous phase has reached a certain *critical thickness*.

These two interpretations are not mutually exclusive,<sup>30</sup> e.g. in a system in which crystalline phases are initially unable to nucleate, the rate at which a growing amorphous phase lowers the free energy  $\Delta G$  is (trivially) higher than that of the crystalline phases (which cannot grow). In this respect, the first interpretation (i.e. nucleation barriers cause the SSA reaction) can be thought of as a specific case of the more general second interpretation of growth instability. Other models for SSA<sup>32,33</sup> often hold an intermediate view, comparing the thickening rate of the amorphous phase to the nucleation rate of the crystalline phases.

## B. Nucleation barriers

In thin film reactions, converting the film to a new phase requires that small nuclei of this phase first form, i.e. the new phase must nucleate. As noted above, nucleation barriers can be responsible for the solid-state amorphization in a number of systems. However, such barriers could be thermodynamic or kinetic in nature. Nucleation and its role in metal/Si systems, has been discussed most notably by d'Heurle.<sup>34</sup> The rate of nucleation,  $\dot{N}$ , is proportional to

$$\dot{N} \propto \exp\left(-\frac{\Delta G^*}{k_B T}\right) \exp\left(-\frac{Q}{k_B T}\right), \quad (1)$$

$$\text{with } \Delta G^* = \frac{\Delta \sigma^3}{(\Delta H - T \Delta S)^2}. \quad (2)$$

$\Delta \sigma$ ,  $\Delta H$  and  $\Delta S$  denote the respective change in interface energy, enthalpy and entropy due to the phase transition. These factors determine  $\Delta G^*$ , the energetic barrier imposed by the creation of new interfaces.  $Q$  represents the activation energy for the (short-range) diffusion needed to form the nuclei. Indeed, the atoms must rearrange themselves into the particular microstructure of the new phase, e.g. atoms hopping into their substitutional positions in the new crystal lattice. Each exponent represents a different barrier to nucleation: the first is thermodynamic in nature ( $\Delta G^*$ ), the second kinetic ( $Q$ ). Typically, thermodynamic nucleation barriers are only significant during the later stages of the reaction, when the enthalpy of formation  $\Delta H$  is low.<sup>34</sup> In contrast, the kinetics barrier  $Q$  play a role at the very beginning of the reaction. Indeed, at low temperatures, atoms have low thermal energy and are slow to rearrange themselves into the crystal lattice.

Although all silicide formation requires some form of atomic rearrangement, the low-temperature nucleation barrier  $Q$  can be a crucial factor in systems which undergo SSA. Indeed, a significant discrepancy in mobility between the different elements (the second condition for SSA, section I A) means that the diffusion-limited growth of the amorphous phase (proportional to the long-range mobility of the fast element) can occur at lower temperature than the nucleation of crystalline phases (proportional to the short-range mobility of all elements, including the slow ones).

### C. SSA reaction in Ni-Si system

The Ni-Si system meets both criteria for SSA noted above: the estimated heat of formation for an amorphous Ni-Si phase is  $-12 \pm 5$  kJ/mol,<sup>35</sup> and Ni is indeed a fast diffuser in Si<sup>36</sup> and in the amorphous phase,<sup>37</sup> whereas diffusion of Si in Ni and Si self-diffusion is significantly slower.<sup>37,38</sup> With both conditions met, one can expect this system to undergo SSA. Indeed, an amorphous Ni-Si interlayer forms at the interface during deposition and thickens upon annealing, both on amorphous<sup>39</sup> and single-crystalline<sup>40</sup> substrates. Depending on the experimental conditions, this amorphous layer can reach a thickness of several nm (thicknesses up to 10 nm have been reported)<sup>23</sup> before crystallizing and has a composition close to 1:1.<sup>41</sup> Once the nucleation of the first crystalline phase occurs ( $\delta$ -Ni<sub>2</sub>Si), both phases grow side by side at the expense of the Ni film. When the temperature is raised by a few tens of degrees, the amorphous phase crystallizes,<sup>23</sup> and the reaction proceeds via a succession of crystalline phases, ending with the NiSi<sub>2</sub> phase.<sup>21</sup>

The existence of nucleation barriers to the first crystalline phase  $\delta$ -Ni<sub>2</sub>Si has been experimentally verified using differential calorimetry scanning.<sup>39,41</sup> Hence, for the Ni-Si system, the inability of crystalline phases to nucleate at low temperatures (rather than growth instability of the crystalline phases, cf. section IA) allows an amorphous phase to thicken up to several nm. Despite some controversy,<sup>42</sup> these barriers are kinetic in nature, i.e. the term  $Q$  in Eq. 1 is the dominant term. Indeed, d'Heurle<sup>34</sup> cites the Ni-Si system explicitly as illustration why the (thermodynamic) nucleation barrier  $\Delta G^*$  is almost completely negligible at the earliest stages of silicide formation.

It is well-documented that the addition of impurities can influence the reaction of a binary system of the Ni-Si system and the properties of the resulting films,<sup>12</sup> such as the morphological stability of the NiSi films<sup>24</sup> or the diffusion of the mobile element Ni through the silicide films.<sup>18</sup> However, little is known about the effect of impurities on the Ni-Si SSA reaction. In this paper, we investigate the effect of an impurity (specifically, nitrogen) on the solid-state amorphization during silicide formation (specifically, the reaction of thin Ni films with Si). We will show that the growth of the amorphous Ni-Si phase can be significantly

enhanced by the introduction of a few atomic % of nitrogen (via ion implantation), to the point that the *entire* Ni film is converted to an amorphous alloy. This alters the reaction path: the growth of metal-rich, crystalline silicides is entirely circumvented. We argue that higher kinetic nucleation barriers are responsible for the enhanced SSA reaction. Our results are reminiscent of those obtained by Ma *et al.*,<sup>16</sup> in which the authors reported a thick, planar amorphous phase growing between a crystalline  $\delta$ -Ni<sub>2</sub>Si layer and the substrate during the reaction of a Ni layer with amorphous Si, if the Si substrate contains 7 at.% C (introduced during deposition of the Si layer). Similarly, previous reports show that the addition of either nitrogen<sup>43</sup> or oxygen<sup>44</sup> contaminations to the Ni-Si system (introduced via ion implantation and during Si deposition, respectively) leads to the growth of Ni-Si layers which exhibit no clear diffraction peaks. However, our findings go beyond these results. We present a fundamentally different reaction path in the Ni-Si reaction, in which the first crystalline silicide formed is the NiSi phase, rather than the typical  $\delta$ -Ni<sub>2</sub>Si phase. Moreover, we demonstrate that the stabilizing effect of nitrogen on the amorphous phase is a general feature of the Ni-Si system. We explain that the (hitherto uncertain)<sup>16</sup> mechanism by which the SSA in the Ni-Si reaction is enhanced by the addition of nitrogen impurities, suggesting a similar mechanism is at play for all three aforementioned impurities: nitrogen, carbon and oxygen.

## II. EXPERIMENTAL

A number of sample batches were produced, for different purposes. For all samples, Si(100) substrates were cleaned using the standard Radio Corporation America (RCA) procedure, dipped in HF(2%), and immediately loaded into ultra-high vacuum ( $\leq 10^{-9}$  mbar). In **sections III A** and **III B**, all samples shown consisted of a 35 nm Ni film, evaporated onto a Si(100) substrate, except for the 80 nm Ni film evaporated onto a Si(100) substrate (details below). In **section III C**, a 30 nm amorphous Si layer was evaporated first, followed by co-deposition of Ni and Si to achieve a 35 nm mixture of Ni and Si with a specific stoichiometry, on amorphous Si. The purity, composition and thickness of the deposited films were checked using Rutherford backscattering spectrometry (RBS, see below), assuming bulk density of the Ni or Si, or a weighted average of Ni and Si in case of the Ni-Si mixtures. As the real density of the films might differ (particularly for the mixtures of Ni and Si), the

reported values could differ slightly from their real values.

Ion implantation was achieved using a high-current Danfysik implanter.<sup>45</sup> The ion beam was swept across the sample surface and four faraday cups positioned around the sample; these cups measured the implanted fluence. Moreover, charge collection and uniformity across the sample surface were checked prior by implanting  $\text{Fe}^+$  into a Si wafer and confirming the fluence (uniformity) using RBS.  $\text{N}_2^+$  was implanted at an energy of 30 or 40 keV/atom to a fluence ranging from  $1 \times 10^{15}$  to  $1.5 \times 10^{16}$  N/cm<sup>2</sup> (details below). The current density was kept below  $0.6 \mu\text{A}/\text{cm}^2$  to avoid excessive heating of the samples.  $\text{N}_2^+$  was implanted after the film deposition, unless mentioned otherwise. In other experiments (some of which are shown in the supplementary information, Fig. S2),  $\text{Ar}^+$  ions were implanted at an energy ranging from 25 to 80 keV, to a fluence ranging from  $0.3 \times 10^{13}$  to  $1 \times 10^{16}$  Ar/cm<sup>2</sup>, both before and after film deposition. During implantation, the samples were rotated  $7^\circ$  with respect to the ion beam, to minimize ion channelling. After implantation, nitrogen is spread throughout the Ni layer and the Si underneath. To illustrate the distribution of the impurity as-implanted, TRIM calculations (SRIM-2013)<sup>46</sup> were performed for a 35 nm Ni film on Si(100) (Fig. 1(a)) and a Ni-Si mixture on Si (Fig. 1(b)). At the interface, a small discontinuity in nitrogen concentration can be seen due to the difference in stopping power at either side of the interface.

*In situ* X-ray diffraction (XRD) was performed in a  $\text{He}(+ 5\% \text{H}_2)$  ambient, using a heating rate of  $0.5^\circ\text{C}/\text{s}$ , unless stated otherwise. Diffraction of the  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) was recorded with a linear detector (Vantec D8) spanning  $20^\circ$  in  $2\theta$ .<sup>47</sup> *Ex situ*, high-resolution XRD was performed at the DiffAbs beamline<sup>48</sup> at the Soleil synchrotron ( $\lambda = 1.54 \text{ \AA}$ ). Using a 6-circle goniometer and a X-ray pixel area detector (XPAD), a large section of reciprocal space can be probed in a short timeframe.<sup>48</sup> For direct comparison, the diffraction angles have been converted to d-spacing.

The sample for transmission electron microscopy (TEM) was prepared for cross-section observation using conventional dimple grinding and ion milling in order to achieve final electron transparency. The TEM micrographs were acquired using a Jeol 2100F operating at 200 kV. The lattice images were recorded with the sample aligned with the [011] zone

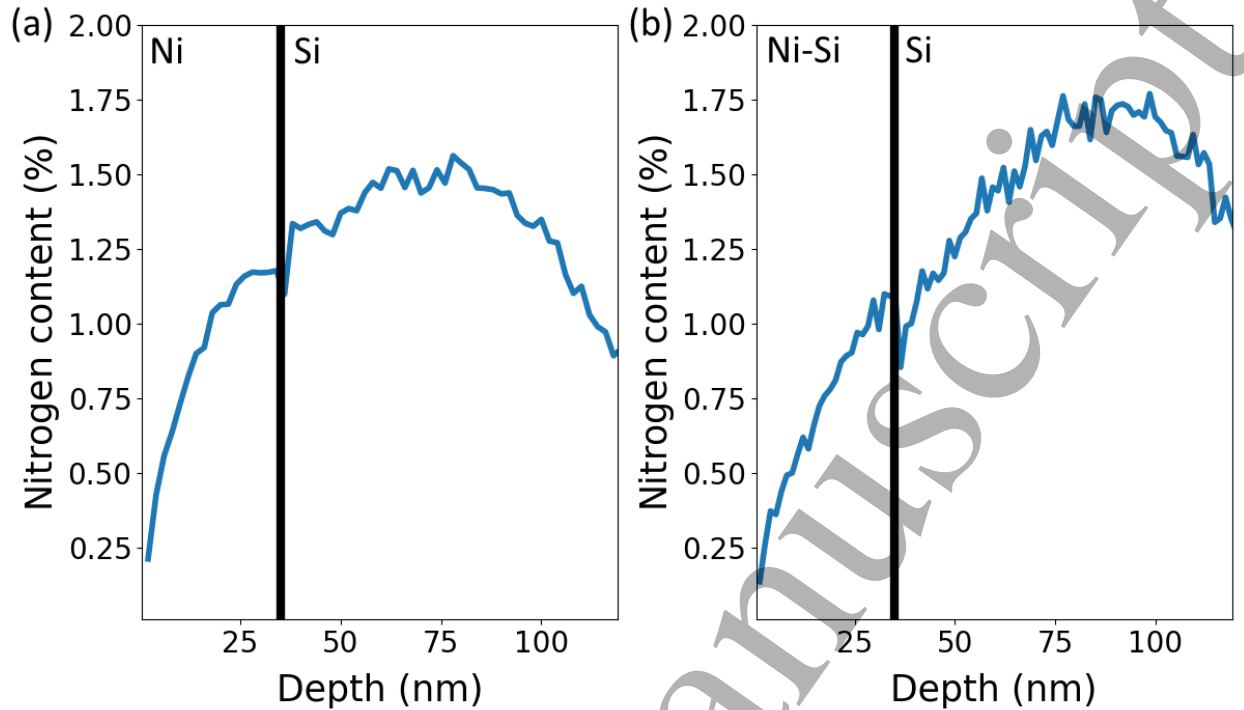


FIG. 1. TRIM calculations of the nitrogen distribution throughout the film and substrate, after implantation. (a)  $1 \times 10^{16}$  N/cm<sup>2</sup> implanted at 40 keV/atom into a 35 nm Ni film on Si. (b)  $1 \times 10^{16}$  N/cm<sup>2</sup> implanted at 40 keV/atom into a 35 nm Ni-Si film (46% Si) on Si.

axis of the silicon substrate.

Rutherford backscattering spectrometry (RBS) was performed using a He<sup>+</sup> beam with an energy of 1.57 MeV and a current of 20 nA. Spectra were recorded using a PIPS detector with an energy resolution of 15 keV. The ion beam, sample normal and detector were kept in the same plain. The incident angle of the ion beam onto the sample was 25° to the sample normal, the exit angle was 38° and the backscattering angle was 168°.

### III. RESULTS

Our results section is divided into three parts. First, we show that after nitrogen implantation, the entire 35 nm Ni film is converted to an amorphous Ni-Si layer upon annealing. Second, we demonstrate the implantation conditions (and consequently, the initial nitrogen distribution) required to induce the enhanced SSA reaction. Finally, we will explore the influence of nitrogen on the stability of amorphous Ni-Si films grown by (co)deposition rather

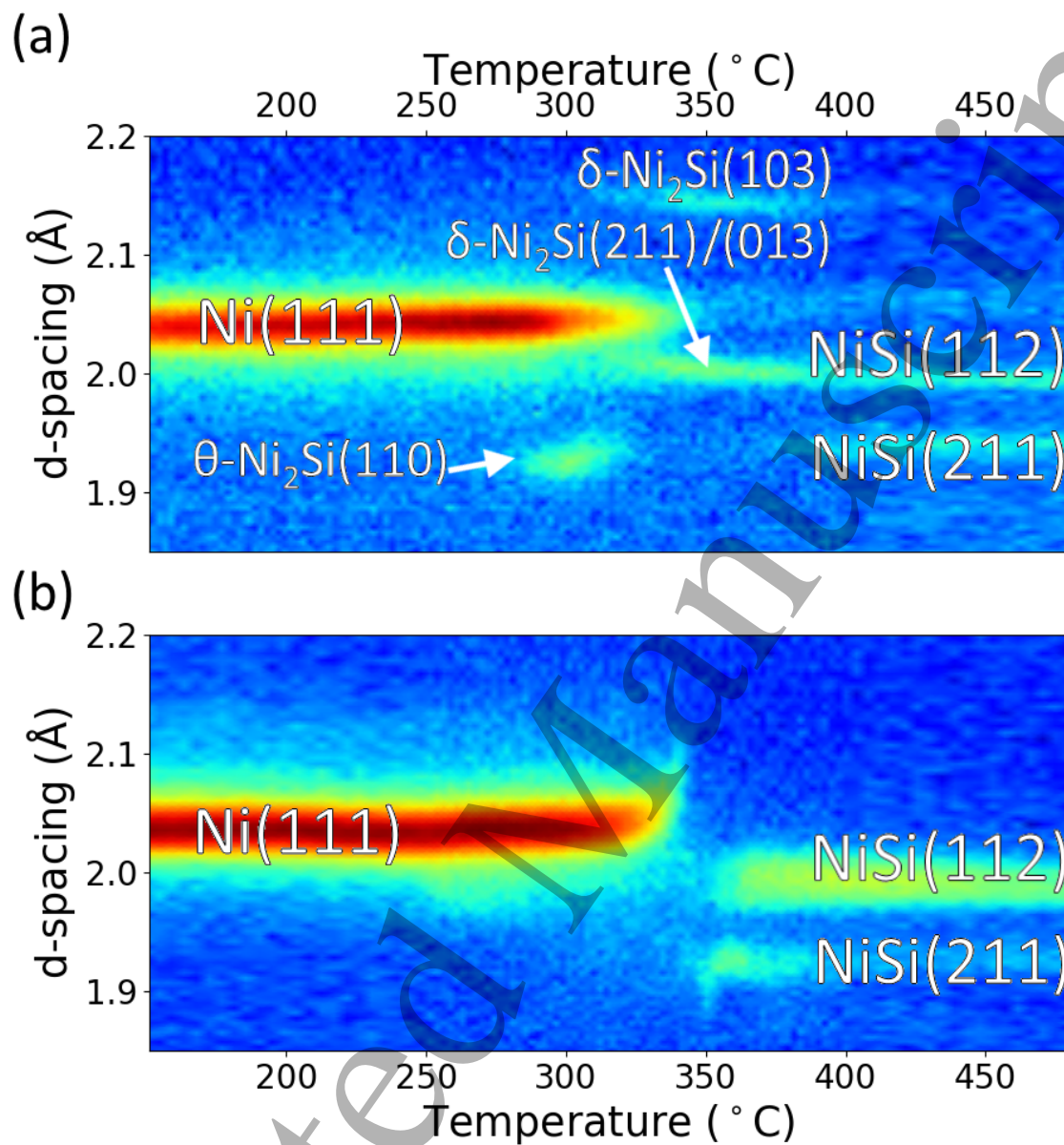


FIG. 2. *In situ* XRD measurements of the reaction of a 35 nm Ni film on Si(100) for (a) an unimplanted sample and (b) a sample implanted with  $1 \times 10^{16}$  N/cm<sup>2</sup> at 40 keV/atom.

than by thin film reaction.



## A. Extended growth of amorphous phase during thin film reaction

The solid-phase reaction of 35 nm Ni on Si substrates with and without N<sub>2</sub> implantation were recorded with *in situ* XRD (Fig. 2). Without implantation, the reaction starts with the growth of Ni-rich, crystalline silicides at the expense of the Ni layer, followed by a conversion to a NiSi film.<sup>19</sup> Implantation of  $1 \times 10^{16}$  N/cm<sup>2</sup> at 40 keV/atom alters the reaction significantly: upon annealing, the Ni diffraction peak disappears around 340°C, followed by a brief temperature window during which little or no diffraction is seen; none of the diffraction peaks of the typical metal-rich silicides ( $\delta$ -Ni<sub>2</sub>Si and  $\theta$ -Ni<sub>2</sub>Si) are unambiguously observed. At around 350°C, diffraction peaks originating from the NiSi phase emerge, which is the only silicide phase at 440°C, as further confirmed by *ex situ* XRD.

To understand which phase formed during the brief temperature window between the consumption of Ni and the growth of the NiSi phase (Fig. 2(b)), a number of samples, all implanted with  $1 \times 10^{16}$  N/cm<sup>2</sup> at 30 or 40 keV/atom, were quenched. These samples were subsequently investigated *ex situ* by TEM (Fig. 3, quenched at 330°C), synchrotron XRD (Fig. 4, quenched at 340°C) and RBS (Fig. 5, quenched at 340°C).

The TEM images (Fig. 3) show that the film is almost entirely converted to a thick amorphous Ni-Si alloy, as confirmed by selected area electron diffraction (SAED) measurements (see supplementary information, Fig. S3). At the surface, a few grains of unreacted Ni can still be seen, alongside some grains of a crystalline silicide whose crystal structure could not be identified (Fig. 3(a)). Most of the  $\sim 50$  nm film however, consists of an amorphous Ni-Si alloy, spanning from the surface to the interface (Fig. 3(b)). The interface of the amorphous layer with the substrate is very flat, a phenomenon typical of diffusion-limited phase growth. It is further evidenced that the layer grew by the (sole) rapid diffusion of Ni through the layer, rather than by any other process, e.g. ion beam mixing (see also the supplementary information, Fig. S4). This is contrasted by the a-Si/c-Si interface, at which end-of-range defects due to the nitrogen implantation are still present. At 340°C, (nitrogen-implanted) amorphous silicon does not recrystallize at laboratory time scales,<sup>50</sup> hence this interface did not move during annealing. Indeed, both ion channelling measurements (not shown) and

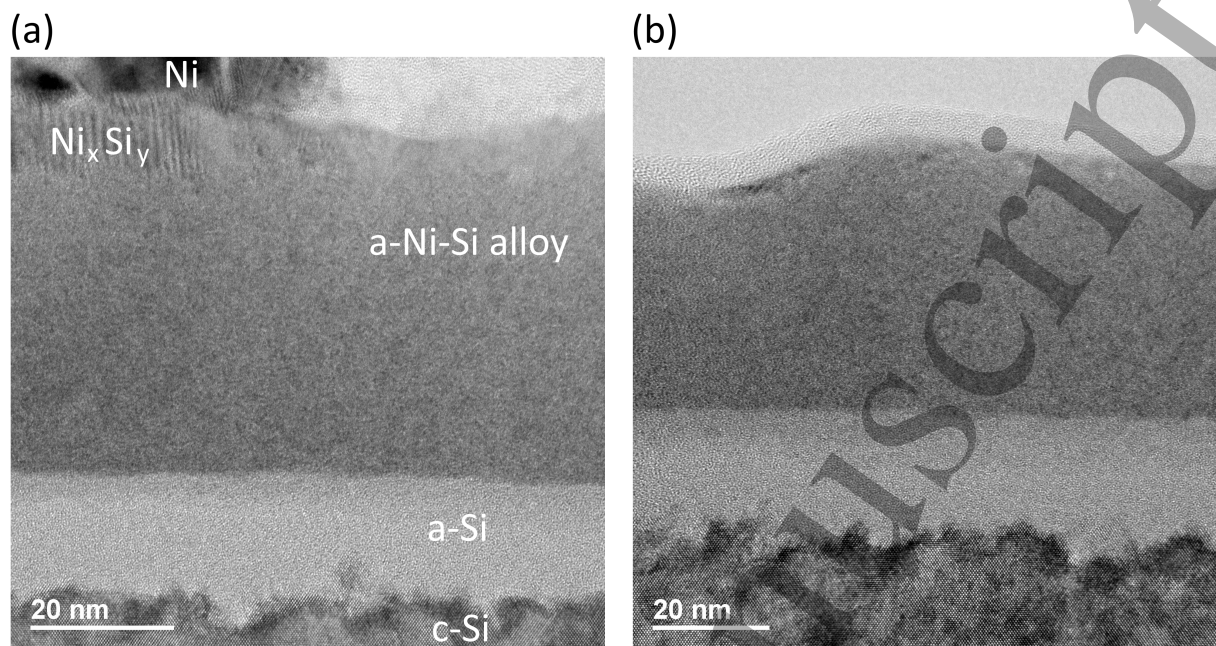


FIG. 3. TEM images of a 35 nm Ni film on Si(100) implanted with  $1 \times 10^{16}$  N/cm<sup>2</sup> at 30 keV/atom and annealed to 330°C, taken at two different regions of the same sample. During the reaction, a thick, amorphous mixture of Ni and Si has formed. In (a), some unreacted Ni grains are still present at the surface, as well as grains of an unidentified Ni silicide phase. In (b), the entire film consists of the amorphous alloy. Between the film and the pristine Si substrate at the bottom, there is a layer of amorphized Si due to the implantation process.

the TEM images (Fig. 3) confirm that, due to the implantation process, the Si just beneath the Ni film is entirely amorphous, both before and after annealing the sample to 340 °C.

The conversion of the film to an amorphous phase is also confirmed by the synchrotron XRD measurements, i.e. the film does not give rise to any intense, sharp diffraction peaks (Fig. 4). This XRD spectrum was obtained by probing a large range of orientations (one quarter of a full pole figure) for any given  $d$ -spacing. The Si substrate peaks were removed from the spectrum by subtracting a similar spectrum of a bare Si sample. The main feature of the spectrum is a very broad, faint peak. The few additional faint peaks might be due to some small crystalline grains that did form (e.g. as in Fig. 3(a)), or might be experimental artefacts due to the large background subtraction. For comparison, the same spectrum is

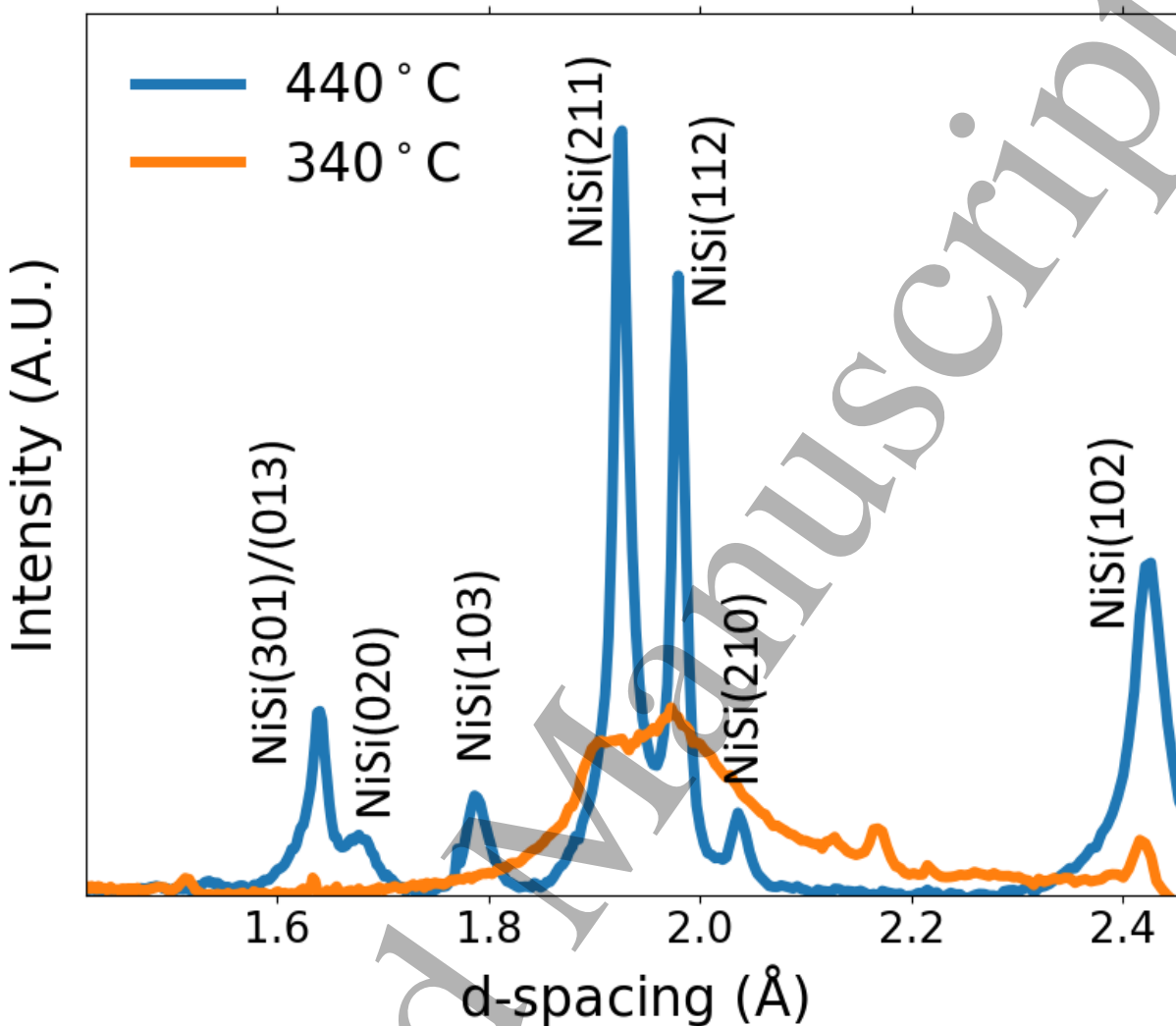


FIG. 4. Synchrotron X-ray diffraction of a 35 nm Ni film on Si(100) implanted with  $1 \times 10^{16}$  N/cm<sup>2</sup> at 40 keV/atom and annealed at 340 and 440°C.

shown for a similar sample quenched at 440°C, in which the film has fully converted to the orthorhombic NiSi phase. The lack of clear diffraction peaks after annealing to 340°C implies either that diffraction from the film coincides with that of the substrate (which was excluded in Fig. 4), or that the quenched film is indeed almost entirely amorphous, exhibiting no long-range periodic order. The former possibility could occur if the film was fully converted into an epitaxial, type A NiSi<sub>2</sub> structure. However, an RBS measurement (Fig. 5) reveals that the film contains (on average) 46% Si, which does not match the 1:2 stoichiometry of a film converted to the NiSi<sub>2</sub> phase. In fact, none of the crystalline silicides known from

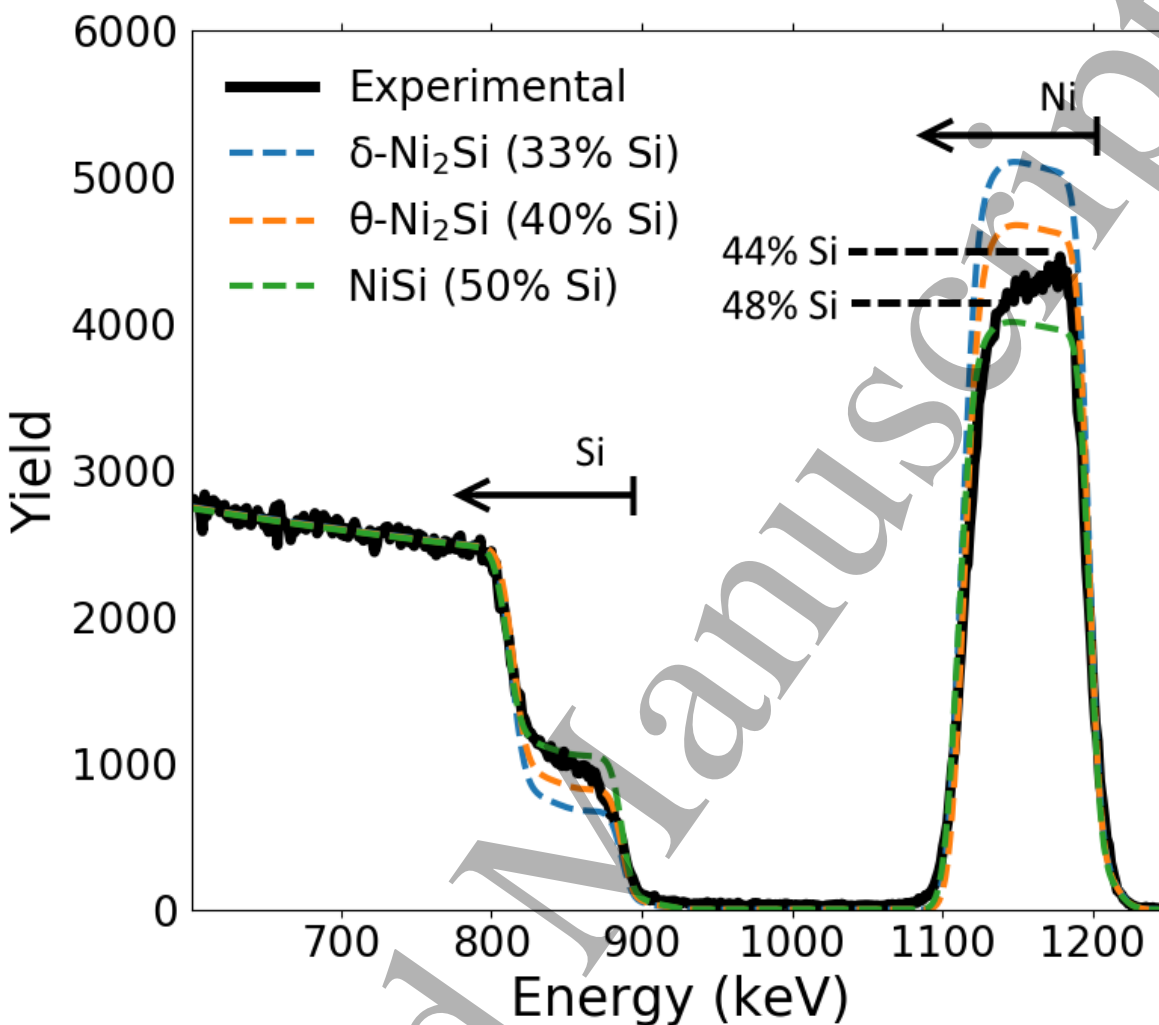


FIG. 5. RBS spectrum of a 35 nm Ni film on Si(100), implanted with  $1 \times 10^{16}$  N/cm<sup>2</sup> at 40 keV/atom and annealed at 340°C, along with simulations of three different film compositions corresponding to the respective stoichiometries of the  $\delta$ -Ni<sub>2</sub>Si,  $\theta$ -Ni<sub>2</sub>Si and NiSi phase. The  $\theta$ -Ni<sub>2</sub>Si phase<sup>1</sup> does not have a fixed stoichiometry; its most Si-rich composition (40% Si) was chosen.<sup>49</sup>

the Ni-Si phase diagram can account for the measured composition. Simulations of three different film compositions, corresponding to the respective stoichiometries of the  $\delta$ -Ni<sub>2</sub>Si,  $\theta$ -Ni<sub>2</sub>Si<sup>1</sup> and NiSi phase are shown (Fig. 5) as well; none of them fitting the experimental

<sup>1</sup> The  $\theta$ -Ni<sub>2</sub>Si phase can have different compositions, ranging from a 2:1 Ni:Si ratio (i.e. Ni<sub>2</sub>Si) up to a 3:2 Ni:Si ratio (i.e. Ni<sub>3</sub>Si<sub>2</sub>), prompting some authors to refer to the crystalline phase simple as *the  $\theta$  phase*, rather than the more commonly used  $\theta$ -Ni<sub>2</sub>Si or  $\theta$ -Ni<sub>3</sub>Si<sub>2</sub> name.<sup>8</sup> Here, the most Si-rich composition of

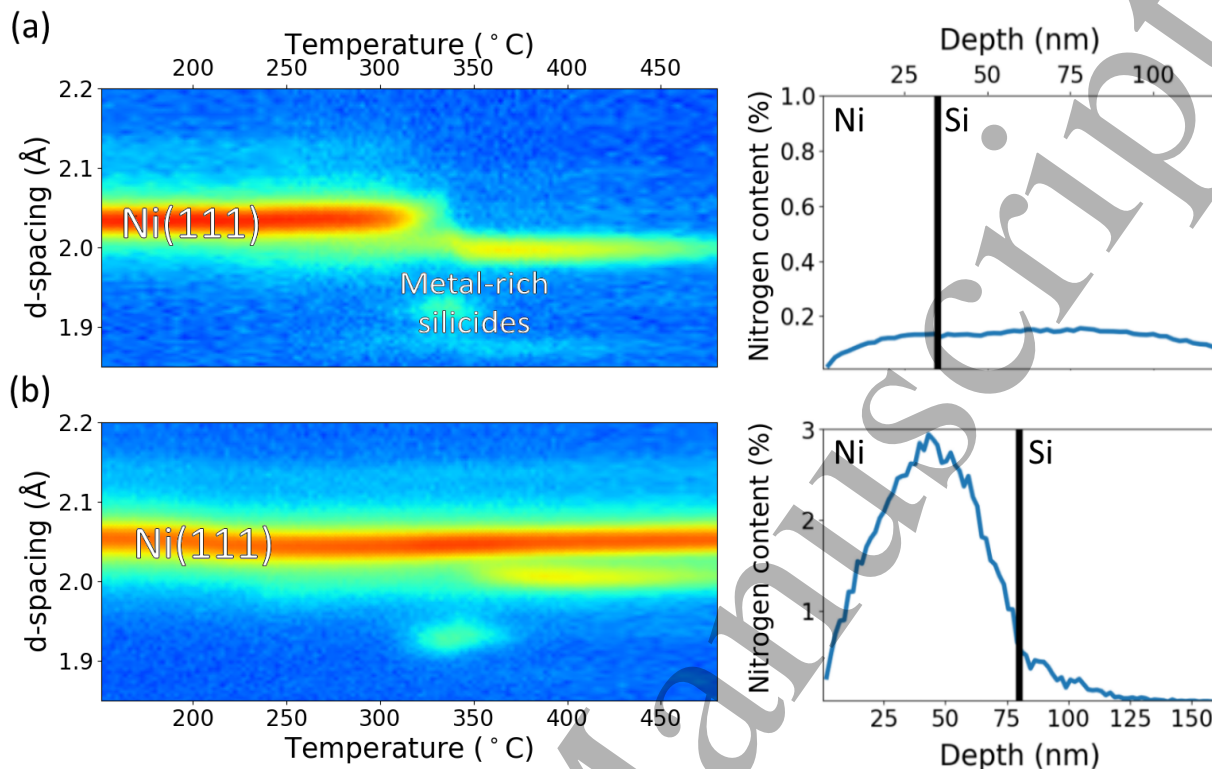


FIG. 6. *In situ* XRD measurements (left) and distribution of nitrogen throughout the film and substrate after implantation (calculated by TRIM, right) of (a) a 35 nm Ni film on Si, implanted with  $1 \times 10^{15}$  N/cm<sup>2</sup> at 40 keV/atom; (b) an 80 nm Ni film on Si, implanted with  $1.5 \times 10^{16}$  N/cm<sup>2</sup> at 40 keV/atom.

spectrum. However, the composition of the film is very close to the liquidus minimum of the Ni-Si phase diagram, at 46.5% Si.<sup>51</sup> Moreover, the film appears to have a compositional gradient, varying from Ni-rich (44% Si) at the surface to an almost 1:1 Ni-to-Si ratio (48% Si) at the interface with the Si substrate. Such a gradient implies that the amorphous phase has a very broad concentration range, unlike line phases such as the  $\delta$ -Ni<sub>2</sub>Si or NiSi phases.<sup>2</sup>

the phase is chosen (40% Si), to contrast it with the composition of the  $\delta$ -Ni<sub>2</sub>Si phase (33% Si).

## B. Implantation conditions

For the SSA reaction described above to occur, specific implantation conditions are required. It is important to note that the introduction of an impurity is crucial. The reaction path described above occurs due to the introduction of nitrogen into the system, rather than due to the ion implantation itself. Indeed, none of our experiments involving argon-implanted or evaporated (amorphous) silicon substrates reproduced such a reaction. By probing a large parameter space of Ar implantation, both before and after film deposition, we assessed the influence of the implantation process, the creation of substrate defects and amorphization, and ion beam mixing on the reaction. In all of these samples, the metal-rich, crystalline phases still form upon annealing. Hence, ion implantation and its concurrent effects (ion beam mixing, defect creation...) are in themselves not the cause of the enhanced SSA reaction. Similarly, evaporating amorphous Si interlayers or mixed Ni-Si layers onto Si substrates before depositing a Ni layer did not suppress the growth of the metal-rich phases. In the supplementary information (Figs. S1 and S2), some examples of these measurements are shown.

The only parameter which consistently determines whether the entire film is converted to an amorphous alloy (i.e. the metal-rich, crystalline phases do not form) is the total amount and depth profile of the implanted nitrogen (see below). In other words, ion implantation simply serves as a method of introducing the impurity; another way of introducing nitrogen into the system under the appropriate conditions would very likely yield similar results as described in this paper, e.g. introducing a few percent of nitrogen during evaporation of a silicon interlayer.

If insufficient nitrogen is present at the film/Si interface, the metal-rich, crystalline silicide phases still form upon annealing. This is the case when, for example, too little nitrogen is implanted (Fig. 6(a)) or when most of the nitrogen is implanted too deeply into the Si substrate. Based on our experiments, the threshold of nitrogen at the Ni/Si interface after implantation required for this reaction path lies somewhere between 0.65 and 1.3 at.% (based on TRIM calculations). It should be noted that nitrogen redistribution may occur during the reaction (on which we have no information). On the other hand, if too much

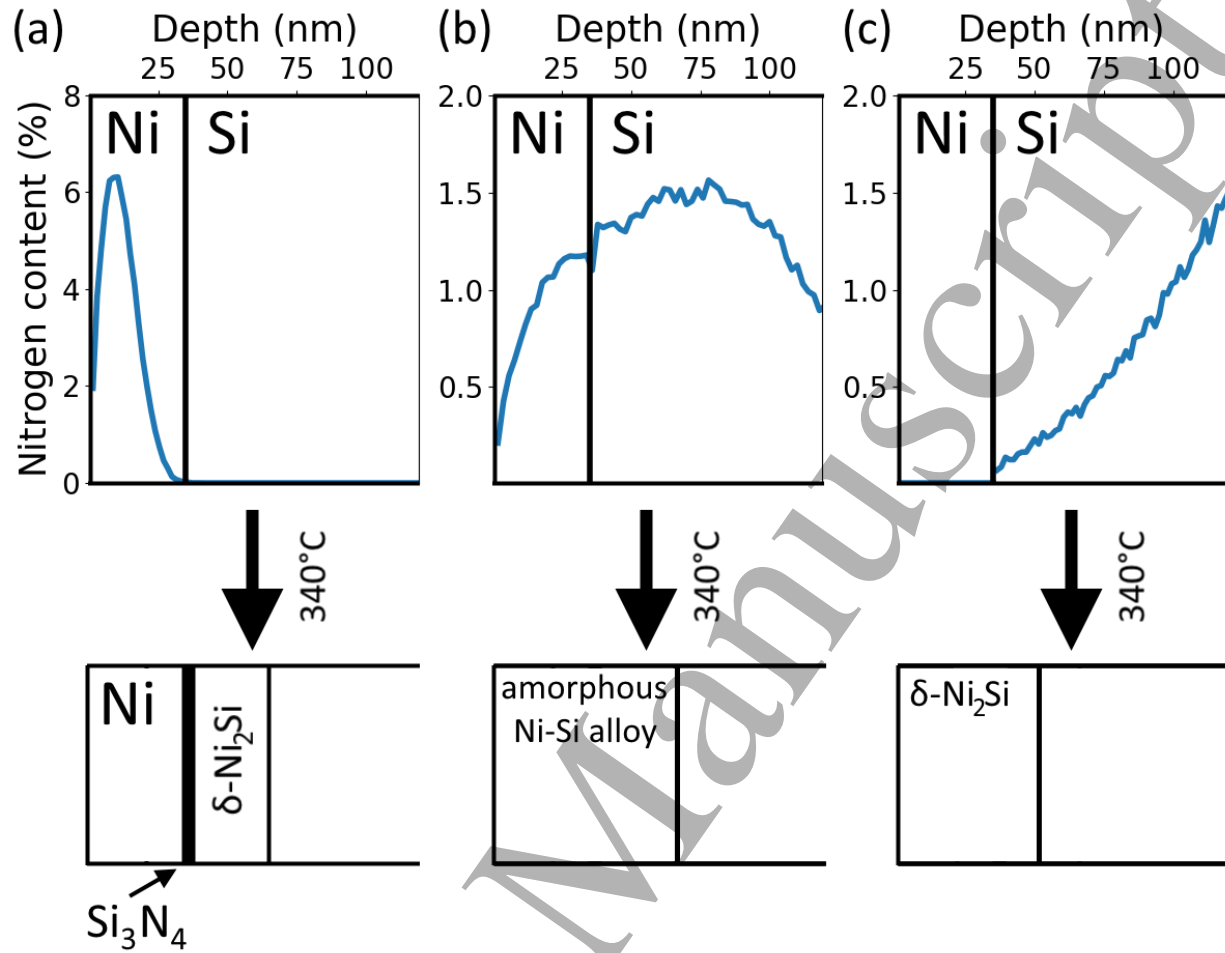


FIG. 7. Schematic overview of how different nitrogen distributions in a 35 nm Ni/Si sample lead to different reaction paths. If  $1 \times 10^{16} \text{N/cm}^2$  is implanted at (a) 7.5 keV/atom, (b) 40 keV/atom or (c) 40 keV/atom prior to Ni deposition, the sample transforms differently upon annealing. The entire film converts to the amorphous phase only if the interface between the film and the Si substrate contains sufficient nitrogen throughout the reaction. This schematic overview illustrates the importance of the initial nitrogen distribution; all examples shown here are based on actual experiments.

nitrogen is implanted into the Ni layer, a  $\text{Si}_3\text{N}_4$  diffusion barrier forms, halting the silicide reaction.<sup>52</sup> Nitrogen is mobile in the metal layer and accumulates at the interface,<sup>52</sup> either by its own mobility or by a snowplough effect of the moving interface. The combination of mobility and large amounts of nitrogen allows for the growth of a  $\text{Si}_3\text{N}_4$  barrier, impenetrable to Ni diffusion at these temperatures. This is demonstrated for a film of 80 nm Ni on



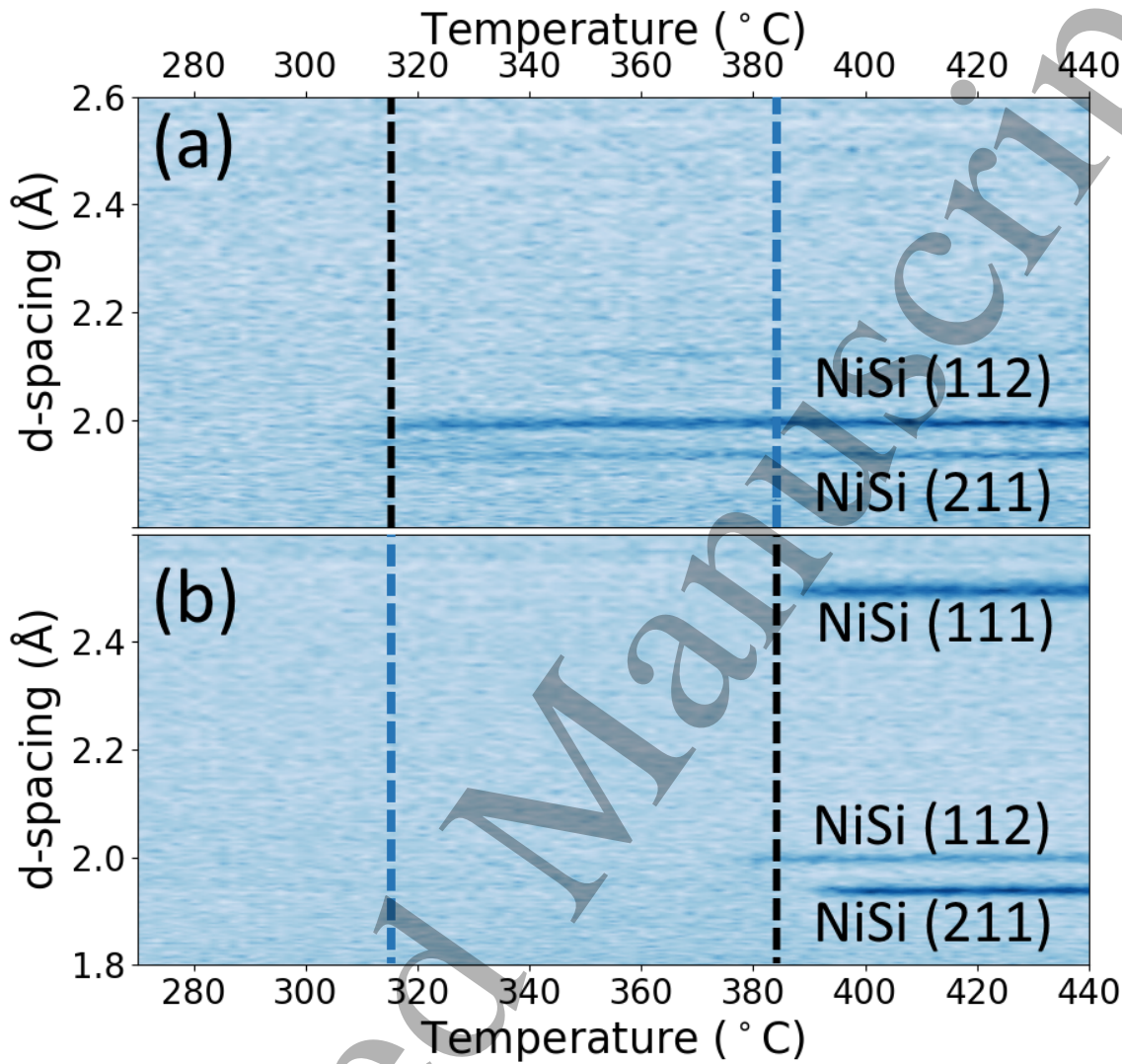


FIG. 8. *In situ* XRD measurement of the crystallization of an amorphous Ni-Si film (35 nm, 46% Si) deposited onto amorphous Si and annealed at 0.25 °C/s, (a) without implantation and (b) with  $1 \times 10^{16}$  N/cm<sup>2</sup> implanted after deposition at 40 keV/atom. Dashed lines indicate the crystallization temperature for both samples.

Si, implanted such that nearly all nitrogen is confined to the Ni layer (Fig. 6(b)). Upon annealing, diffraction from the Ni layer remains present throughout the entire reaction.

In summary, the enhanced SSA reaction occurs only when the interface between the film and the substrate contains sufficient nitrogen throughout the reaction (Fig. 7).



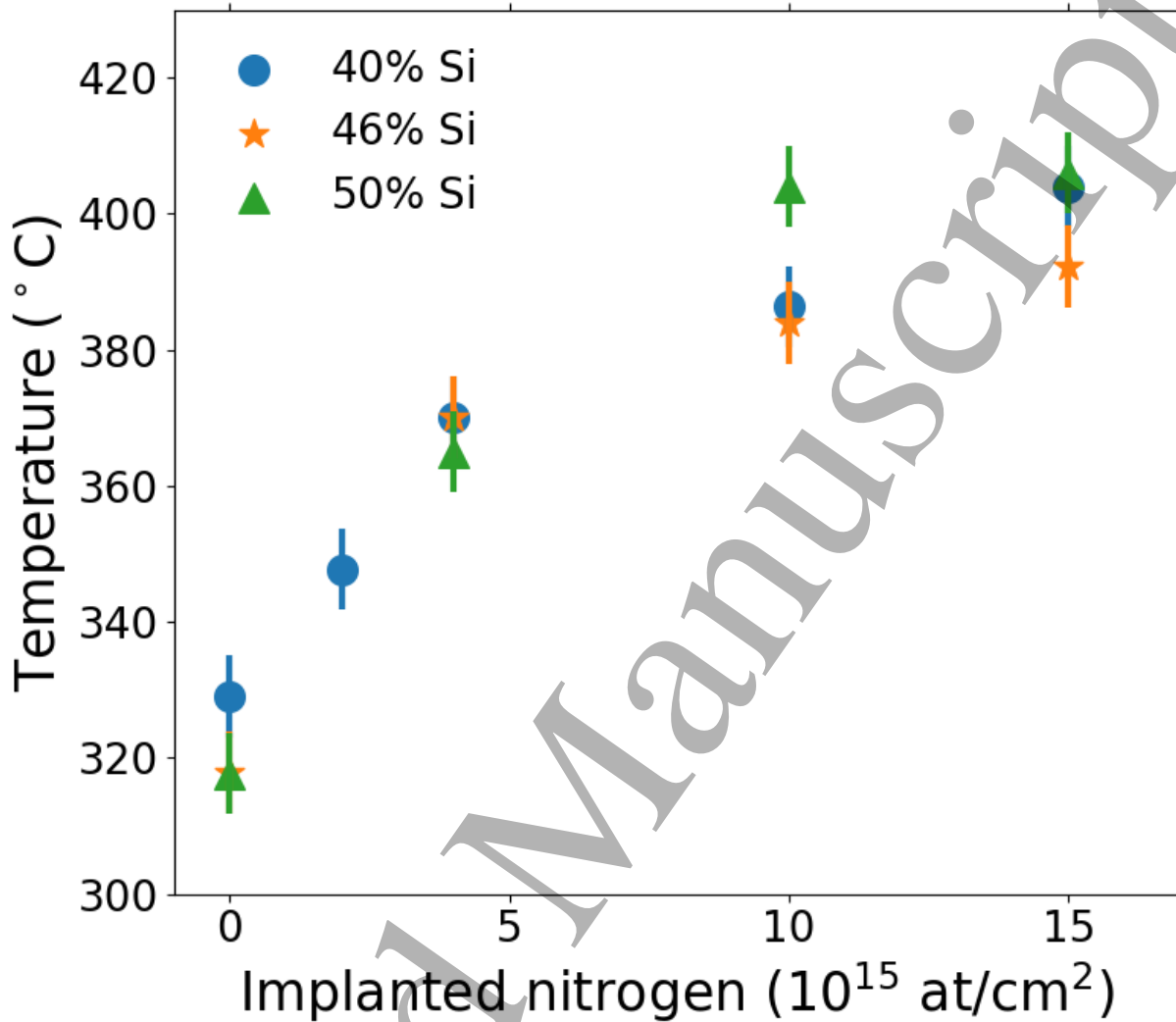


FIG. 9. The NiSi crystallization temperature of amorphous Ni-Si films (with different Si content, all 35 nm) on amorphous Si, implanted with nitrogen to varying fluences at 40 keV/atom. Temperatures were derived from *in situ* XRD measurements, such as those in Fig. 8.

### C. Stability of amorphous phase

The altered reaction seen in Fig. 2(b) is peculiar for two reasons. The first reason is the suppression of the conventional metal-rich  $\delta$ -Ni $_2$ Si and  $\theta$ -Ni $_2$ Si phases. The second reason is that the amorphous layer remains stable to significantly higher temperatures (at least 340°C) compared to those in unimplanted samples (which crystallize around 235°C in contact with unreacted Ni).<sup>23</sup> However, it is not immediately clear whether this stabilization

stems from the altered reaction path and its accompanying stresses, moving interfaces, elemental redistribution... or whether the amorphous alloy becomes intrinsically more stable. In other words, does nitrogen stabilize *any* amorphous Ni-Si alloy, or only those growing during the Ni-Si solid phase reaction with a specific stoichiometry?

To answer this question, amorphous films of varying Ni:Si composition were prepared (40%, 46% and 50% Si, 35 nm) by MBE co-deposition of Ni and Si onto an amorphous Si substrate at room temperature. After deposition, these films were implanted with N<sub>2</sub> to several fluences (ranging from 0 to  $1.5 \times 10^{16}$  N/cm<sup>2</sup>) at 40 keV/atom. This way, the influence of nitrogen implantation on the stability of amorphous Ni-Si alloys can be studied directly. Figure 8 shows a comparison between the crystallization of an amorphous Ni-Si (46% Si) film, without and with nitrogen implantation. Clearly, nitrogen stabilizes the amorphous film: NiSi crystallization is delayed by about 55°C after  $1 \times 10^{16}$  N/cm<sup>2</sup> was implanted. Moreover, the stabilizing effect of nitrogen scales with implantation fluence and holds for various Ni:Si ratios, with the layer composition having hardly any influence on the NiSi crystallization temperature (Fig. 9). This suggests that the stabilizing influence of nitrogen on the amorphous phase is not a particularity of the solid-phase reaction of a thin Ni film on Si(100), but a general feature of the Ni-Si system.

#### IV. DISCUSSION

As mentioned in the introduction, nucleation barriers are responsible for the growth of an amorphous phase in the unimplanted Ni-Si system by suppressing the formation of crystalline phases. This is also the case for the nitrogen-implanted Ni-Si system. Indeed, we have shown that the stabilizing effect of nitrogen on the amorphous phase is a general feature of the Ni-Si system (section III B). The alternative explanation for SSA, the model of growth instability (section I A), relies on moving interfaces and long-range diffusion, which are absent in the crystallization of the as-deposited amorphous layers. Moreover, these nucleation barriers are kinetic in nature, as they are for the unimplanted Ni-Si system, rather than thermodynamic. Nitrogen is unlikely to significantly increase the thermodynamic nucleation barrier  $\Delta G^* = \frac{\Delta \sigma^3}{(\Delta H - T \Delta S)^2}$ , which is very small for the (unimplanted) Ni-Si system. On the one hand, the effect of 1-2 at.% of nitrogen in the amorphous layer on the volume terms

$\Delta H$  and  $\Delta S$  will be linear, and consequently, the effect on the nucleation barrier will be on the order of a few percent. On the other hand, nitrogen is expected to lower the interface and grain boundary energy  $\Delta\sigma$  of the crystalline phases,<sup>53</sup> which facilitates nucleation. In short, the origin of the solid-state amorphization reaction for the nitrogen-implanted Ni-Si system is the same as that for the unimplanted system, i.e. kinetic nucleation barriers prevent the crystalline phases from forming at lower temperatures. Introducing nitrogen raises these barriers, allowing the amorphous phase to grow until the entire Ni supply is consumed.

Two properties of nitrogen play a role in raising the kinetic nucleation barriers: it is insoluble in any stable, crystalline Ni silicide;<sup>54</sup> and it binds strongly with Si, rendering it immobile in the substrate.<sup>52</sup> The insolubility of nitrogen slows down the formation of crystalline Ni silicides: the volume in which the crystalline nuclei form will contain some (average) amount of nitrogen atoms, which must be segregated from that volume if the phase is to grow. Hence, additional atomic rearrangement, proportional to the amount of implanted nitrogen, is required for the nucleation of crystalline phases. Moreover, the strong nitrogen-silicon bonds must be broken before the impurity can become mobile and (local) redistribution can occur. The reason why nitrogen implantation enhances the amorphization reaction becomes clear. Introduction of a third, insoluble element in the binary system increases the need for atomic rearrangement for nucleation of crystalline phases. Moreover, the ability of the third element to bind strongly to Si renders the impurity immobile, thus reinforcing the kinetic asymmetry between mobile (Ni) and immobile (Si, N) elements which lies at the heart of the SSA reaction.

Parallels can be drawn between our results and previous reports which have either confirmed<sup>16</sup> or suggested<sup>44</sup> that the amorphous phase at the Ni/Si interface can grow much thicker after contaminating the Si with C, N or O. Indeed, the arguments as to why nitrogen causes an enhanced SSA reaction (insoluble in crystalline silicides and forming strong bonds with Si) can be applied to carbon<sup>55</sup> or oxygen<sup>56</sup> as well. Another related phenomenon to the impurity-enhanced SSA reaction is the recrystallization of silicon. Small quantities (0.5 at.%) of an impurity such as C, N or O can significantly slow down the recrystallization of an amorphous Si layer.<sup>50</sup> For both transformations, the mobility of Si atoms is the limiting factor, and the (re)arrangement of Si into a crystal lattice is hindered by the addition of

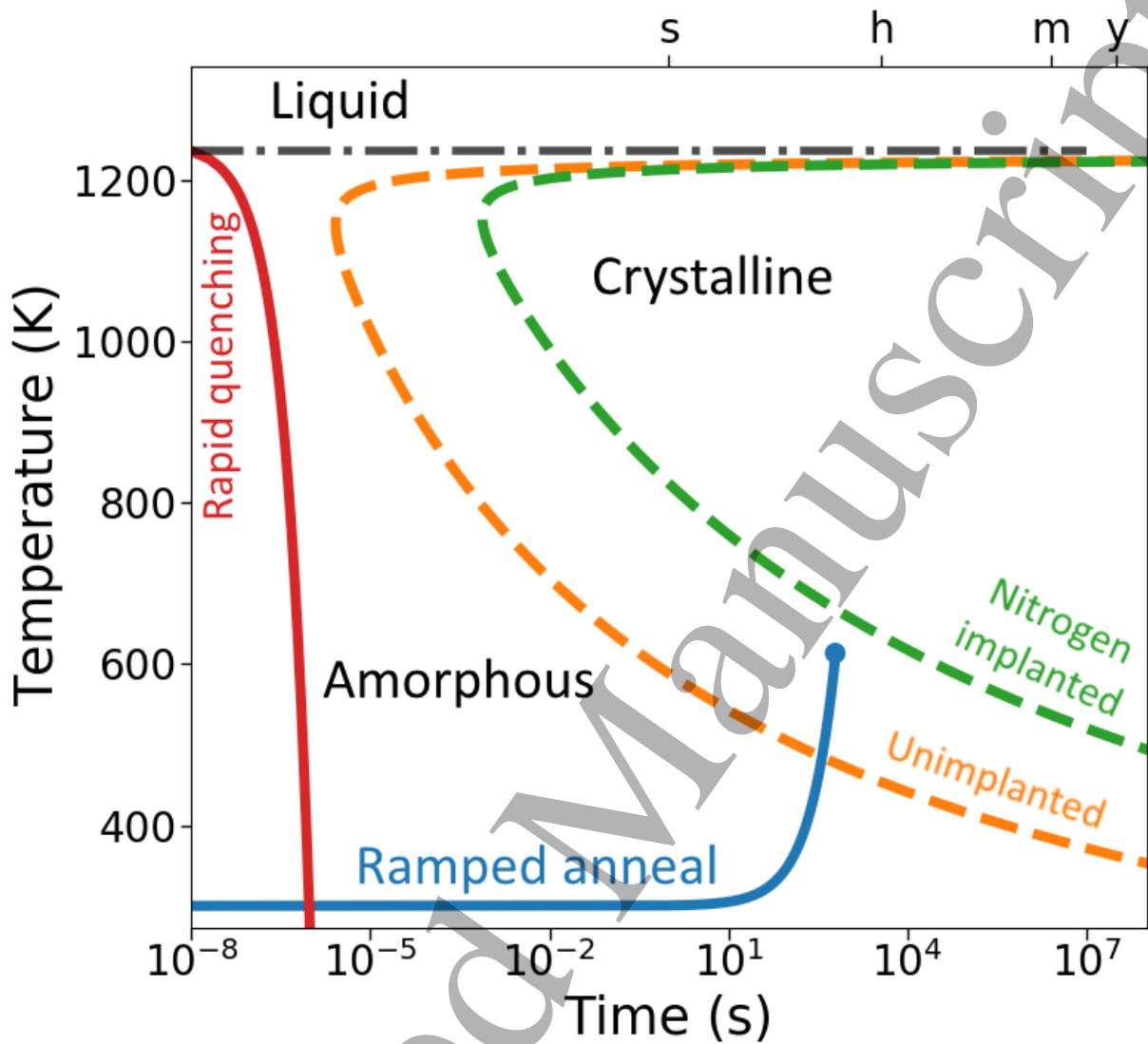


FIG. 10. Schematic time-temperature-transition (T-T-T) diagram, representing the evolution of a Ni film on Si upon annealing (blue solid line). The dashed curves represent the onset of nucleation, with and without nitrogen implantation. At the blue circle, the amorphous phase has consumed the entire Ni supply, if no crystallization takes place. The rapid quenching of a liquid from high temperature (the liquidus minimum of the Ni-Si phase diagram) to an amorphous phase at room temperature is indicated as well (red solid line). The values shown here are only approximate, particularly at temperatures above 650K; a dedicated study would be required for an accurate time axis.

immobile impurities. This comparison should not be taken too literally. Indeed, the microstructure of the Ni-Si alloy and amorphous Si are different, as are the crystalline phases they convert to. Nevertheless, in light of this analogy, it is not surprising that impurities (C, N, O) which are known to retard the recrystallization of Si,<sup>50</sup> are also those known (C, N)<sup>16</sup> or assumed (O)<sup>44</sup> to enhance the growth of an amorphous phase during the formation of Ni silicides. Indeed, the comparison with amorphous Si might be useful in future research. Amorphous Si can store additional energy due to strain, and can subsequently release that energy by relaxing.<sup>57</sup> The amorphous Ni-Si mixture might analogously be in a strained state, either due to the intrinsic stresses associated with a solid-phase reaction, or due to the contained nitrogen, or both. Stresses can have an impact on the precise energy balance of the reaction, albeit a typically limited one. However, studying this is beyond the scope of this study, as the phenomenon of (IE)SSA is rooted in a kinetic barrier, not an energetic one.

We can graphically summarize our results using a time-temperature-transition (T-T-T) diagram (Fig. 10), as is often done for transformations in steel, or for the formation of bulk metallic glasses. In such a diagram, the time needed for a thin layer of a new, crystalline phase to nucleate at different temperatures is plotted (inversely proportional to the nucleation rate, Eq. 1), illustrating the rate of transformation of a system at different temperatures.<sup>58</sup> At low temperature, the low mobility of the atoms limits the transformation rate from the amorphous to a crystalline phase; the kinetic factor  $Q$  is the dominant barrier to overcome. At higher temperature, the driving force for crystallinity  $\Delta G$  decreases as the entropy term  $T\Delta S$  approaches the enthalpy term  $\Delta H$ , reducing the nucleation rate (Eq. 2). As a result, the curves in these T-T-T diagrams typically have a “bell jar” shape (Fig. 10, dashed lines). Forming amorphous films by rapid quenching from the liquid phase, for example, requires cooling rates high enough to avoid intersecting the ‘nose’ of the crystallization curve. Implantation of nitrogen increases the kinetic term  $Q$  in Eq. 1, thus decreasing the nucleation rate at lower temperatures. The blue solid line represents the temperature evolution of the sample during annealing. Its endpoint is the time needed for the amorphous phase to consume the entire Ni supply (if no crystallization occurs). For the unimplanted system, nucleation sets in earlier and the amorphous phase crystallizes. When nitrogen is implanted, however, the point at which the entire film converts to the amorphous phase is reached before any crystalline phase can nucleate.

## V. CONCLUSION

We have demonstrated that the reaction of thin Ni films with Si can be significantly influenced by the addition of small amounts of impurities. By implanting nitrogen under the right conditions, the entire Ni film is converted to an amorphous layer upon annealing. The growth of metal-rich silicide phases is circumvented, as the film converts directly from the amorphous phase to the NiSi phase. Nitrogen stabilizes amorphous Ni-Si films and suppresses nucleation of crystalline phases: more short-range atomic rearrangement is required to form crystalline phases, thus increasing kinetic nucleation barriers.

This effect is likely applicable to other aspects of the Ni-Si system as well. For example, the creation of amorphous Ni-Si films by rapid quenching might be facilitated by the introduction of nitrogen, as suggested by the nucleation curves in the T-T-T diagram (Fig. 10); the cooling rate of the sample with nitrogen does not need to be as high as for the unimplanted system. This would be analogous to the creation of bulk metallic glasses, which often include a metalloid or organic element in the mixture of two or more metals to increase the alloy's "glass-forming ability".<sup>59</sup>

Our results illustrate the importance of nucleation barriers and short-range diffusion in the complex early stages of a thin film reaction. These barriers are often overlooked, yet they can have profound effects on the reaction path. Moreover, the ability to tailor these barriers using small amounts of impurities opens up new possibilities of modifying thin film reactions. This is not only scientifically interesting, it is important for applications as well. Several technologically relevant silicide systems undergo solid-state amorphization to some degree, including the Ni-Si, Ti-Si<sup>60</sup> (contact material for transistors), Cu-Si<sup>61</sup> (barrierless interconnects) and Li-Si<sup>62</sup> (energy storage) systems. By selecting the optimal impurity and its concentration, one might find ways of enhancing these SSA reactions, leading to new reaction paths and/or new thin film applications.

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## SUPPLEMENTARY INFORMATION

### A. The Ni-Si reaction on amorphous or damaged Si

As mentioned in section IIIB, the remarkable enhanced SSA reaction only takes place when introducing nitrogen impurities, whereas creating crystalline damage via ion implantation or using amorphous Si is not sufficient to induce the phenomenon. Indeed, after implanting Ar ions into the Si substrate before deposition of the Ni film, the metal-rich  $\delta$ -Ni<sub>2</sub>Si phase still forms during the Ni/Si solid-phase reaction, both for implantation fluences below and above the amorphization threshold (between 1 and  $2 \times 10^{14}$  Ar/cm<sup>2</sup>) (Fig. S1). Similarly, the crystalline  $\delta$ -Ni<sub>2</sub>Si phase is observed in the reaction of Ni films with a Si substrate onto which a thin amorphous Si layer has been deposited (Fig. S2). Both in the case where the amorphous Si layer is consumed before the entire metal supply is consumed (Fig. S2(a)) or whether some amorphous Si is still present after the entire metal supply is consumed before the film is fully converted to the NiSi phase (Fig. S2(b)), diffraction peaks originating from crystalline Ni silicides can be seen throughout the reaction.

### B. Selected area electron diffraction

As shown by TEM (Fig. 3), the film is converted to a thick, amorphous Ni-Si layer. The non-crystalline nature of the layer in the TEM images was confirmed by selected area electron diffraction (Fig. S3). The area selected for diffraction (Fig. S3(a)) contain only Si (both amorphous and crystalline) and the Ni-Si mixture. The diffraction pattern (Fig. S3(b)) shows only the single-crystalline Si diffraction peaks, with no indication of any other crystalline phase. Using synchrotron XRD (Fig. 4), it was already shown that after nitrogen implantation, the Ni layer converts to an amorphous layer upon annealing. However, SAED probes the crystallinity on a very small, local scale, providing complementary evidence to synchrotron XRD, which probes a large, lateral area.

### C. Growth of amorphous phase at the interface

Our measurements show that the Ni film is fully converted to an amorphous phase upon annealing, when nitrogen is implanted under the right conditions (Fig. 5). Moreover, this

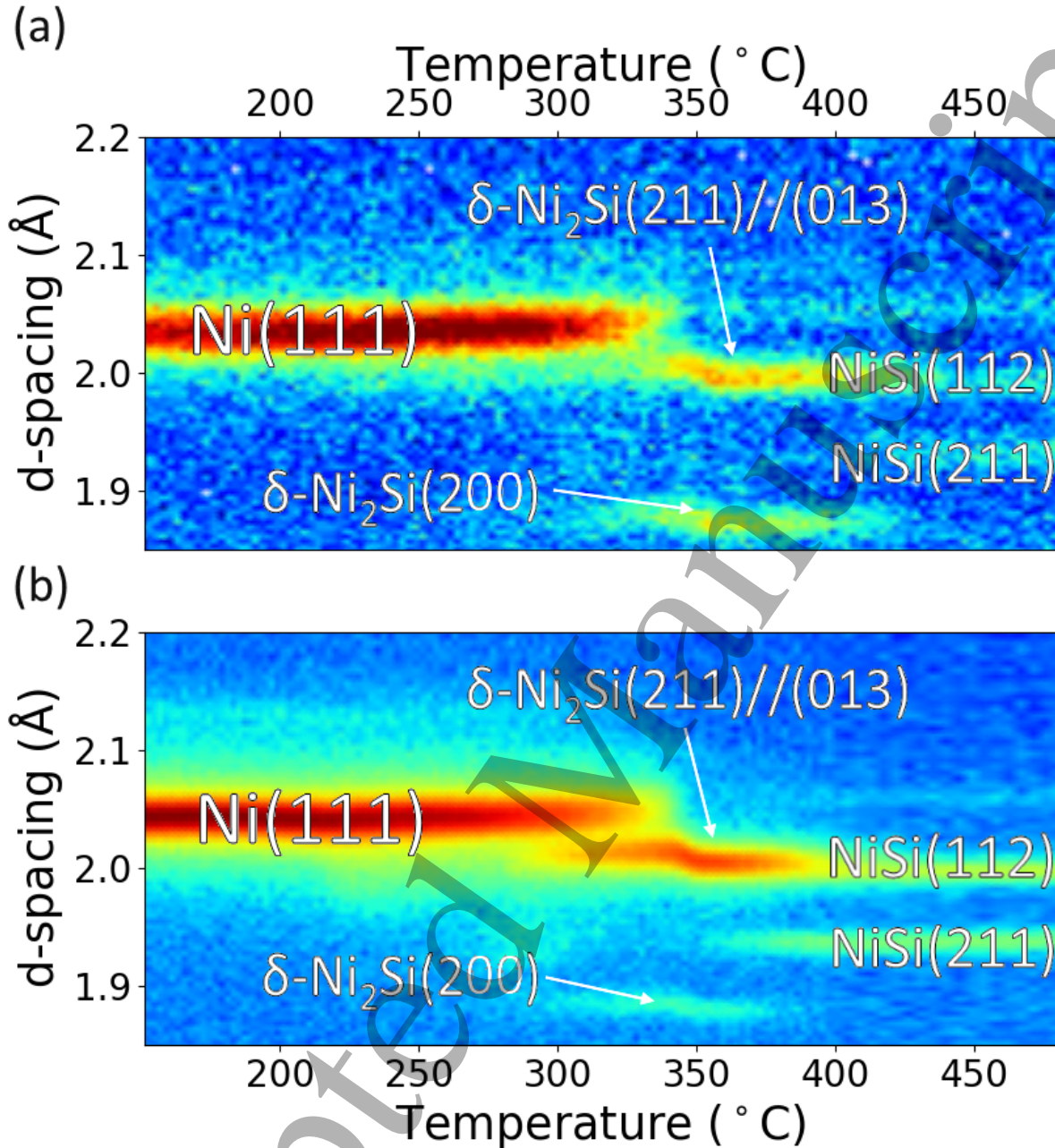


FIG. S1. *In situ* XRD measurements of the reaction of a 35 nm Ni film with a Si substrate that was implanted (prior to film deposition) with (a)  $8 \times 10^{13} \text{ Ar}^+/\text{cm}^2$  at 60 keV/atom and (b)  $1 \times 10^{15} \text{ Ar}^+/\text{cm}^2$  at 60 keV/atom. In (a), the Si near the substrate surface is heavily damaged, but not completely amorphized. In (b), the near-surface Si is completely amorphized. In both cases, the crystalline  $\delta\text{-Ni}_2\text{Si}$  phase forms, i.e. no impurity-enhanced SSA takes place.



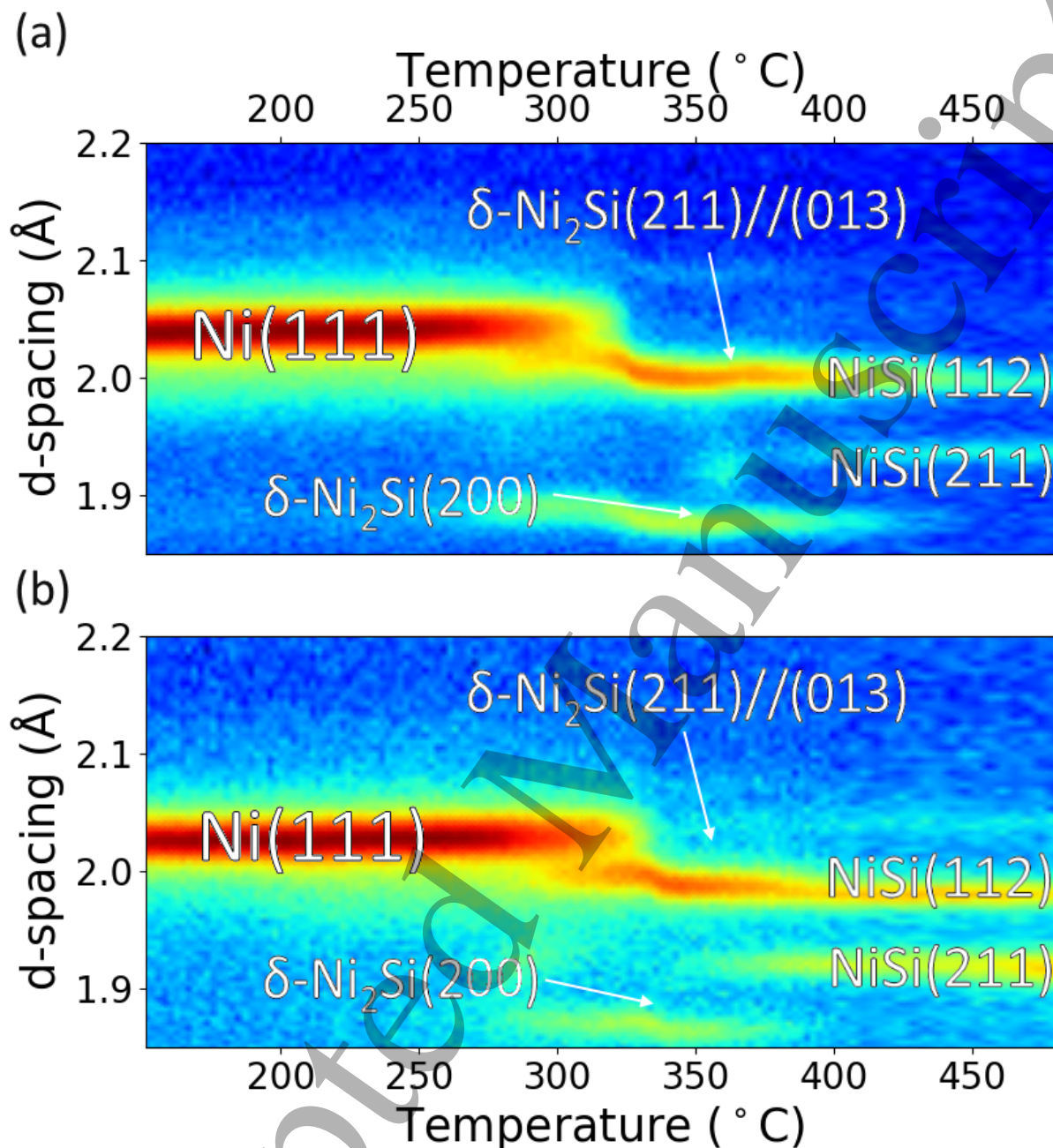


FIG. S2. *In situ* XRD measurements of the reaction of a 35 nm Ni film with a Si substrate onto which an amorphous Si layer (prior to Ni film deposition) was deposited, with a thickness of (a) 20 nm and (b) 100 nm. For (a), the growth of the  $\delta$ -Ni<sub>2</sub>Si (or the Ni-Si phase) phase fully consumes the amorphous Si layer (and some crystalline Si as well). For (b), around 30 nm of amorphous Si remains present at the interface, even when all Ni is consumed and the NiSi growth is complete. In both cases, the crystalline  $\delta$ -Ni<sub>2</sub>Si phase forms, i.e. no impurity-enhanced SSA takes place.

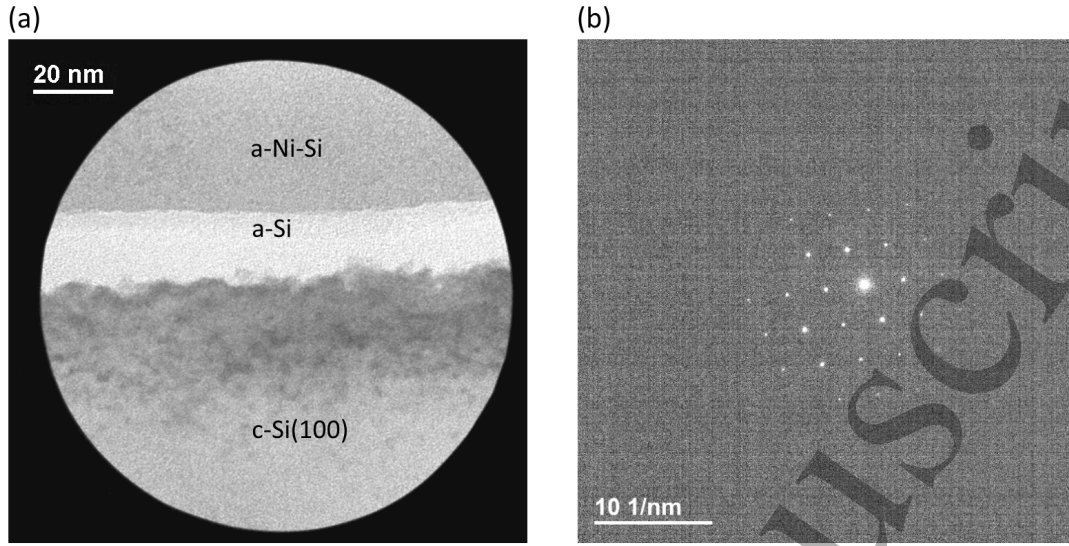


FIG. S3. (a) *Selected area* of a TEM image of a 35 nm Ni film on Si(100) implanted with  $1 \times 10^{16}$  N/cm<sup>2</sup> at 30 keV/atom and annealed to 330°C, used for SAED. It includes the amorphous layer, the amorphous or damaged Si layer (due to ion implantation) and the pristine Si substrate. (b) The SEAD pattern. Only diffraction from the Si substrate is seen, indicating the Ni-Si layer is indeed amorphous.

amorphous interlayer grows as a planar film in a layer-by-layer, as most silicide phases do during solid-phase reactions. To prove this, an RBS experiment (Fig. S4) was performed on a nitrogen-implanted sample which was quenched at 330°C (i.e. just before all Ni was consumed). This measurement shows the amorphous phase grows at the interface between the Ni layer and the substrate. Indeed, the fit indicates the sample consists of a 50 nm mixture of Ni and Si (46% Si, assuming the same density as the crystalline NiSi phase) in between a 10 nm pure Ni layer at the surface and the Si substrate. Furthermore, analysis shows that both interfaces of the amorphous layer are very sharp, each having a roughness of less than 5 nm. This shows the phase grows in a layer-by-layer way, suggesting the layer growth is diffusion-limited, which is characterized by sharp interfaces of the layers and a growth rate proportional to  $\sqrt{t}$  in isothermal anneals. Moreover, it shows the composition range (i.e. between 44 and 48% Si) of the amorphous mixture is the same during growth as it is after full consumption of the metal supply. In other words, its stoichiometry is not determined or limited by the amount of Ni atoms available, but is a fundamental property



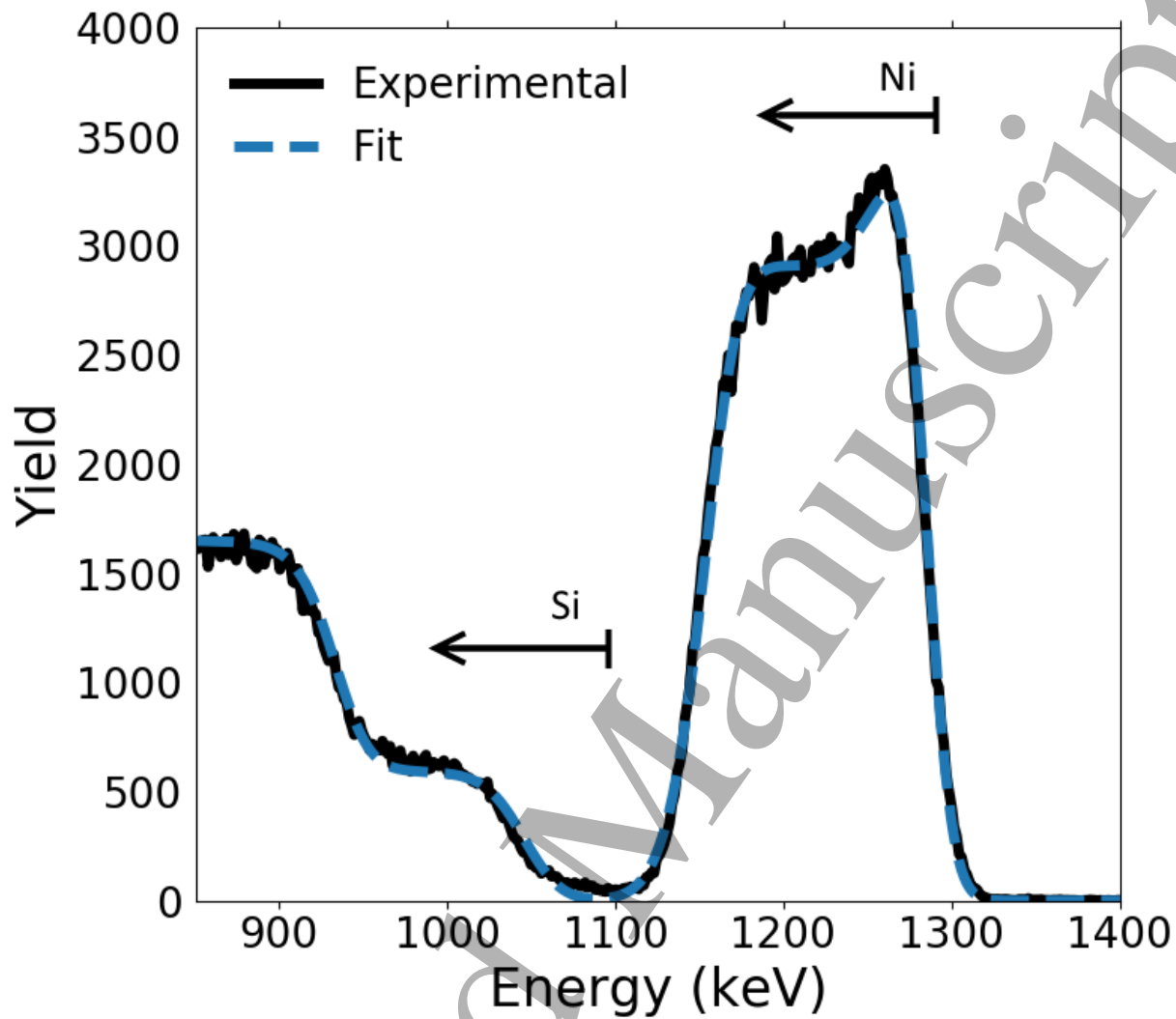


FIG. S4. RBS spectrum of a 35 nm Ni film on Si(100), implanted with  $1 \times 10^{16}$  N/cm<sup>2</sup> at 40 keV/atom and annealed at 330°C, using a scattering angle of 105° and an energy of 1.57 MeV.

of the amorphous Ni-Si phase growing during the solid-phase reaction.