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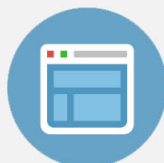
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## On the nucleation of PdSi and NiSi<sub>2</sub> during the ternary Ni(Pd)/Si(100) reaction

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During the solid phase reaction of a Ni(Pd) alloy with Si(100), phase separation of binary Ni- and Pd-silicides occurs. The PdSi monosilicide nucleates at temperatures significantly below the widely accepted nucleation temperature of the binary system. The decrease in nucleation temperature originates from the presence of the isomorphous NiSi, lowering the interface energy for PdSi nucleation. Despite the mutual solubility of NiSi and PdSi, the two binaries coexist in a temperature window of 100 °C. Only above 700 °C a Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution is formed, which in turn postpones the NiSi<sub>2</sub> formation to a higher temperature due to entropy of mixing. Our findings highlight the overall importance of the interface energy for nucleation in ternary systems. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818333>]

### I. INTRODUCTION

Metal silicides, i.e., compounds between metal and silicon, have been subjected to scrutiny over the last four decades due to their beneficial properties as electrodes in semiconductor devices.<sup>1</sup> Silicides are typically formed by a thermal reaction of a metallic thin film with Si, in which crystalline silicide phases form sequentially. Nucleation often plays an important role in the formation of a next phase, especially when the free energy gain  $\Delta G$  for the phase transition is small. In this case, the nucleation barrier, which is a measure for the energy needed to nucleate and grow a phase, increases and it is likely that phase formation does not proceed for insufficient temperatures.<sup>2</sup> A well-known example of a nucleation controlled reaction is the formation of NiSi<sub>2</sub> from NiSi and Si. The NiSi monosilicide phase is currently implemented as electrical contact material in transistor devices, and nucleation of the highly resistive NiSi<sub>2</sub> is detrimental for the purpose of contact formation due to its high resistivity and its non-uniform interface.<sup>3</sup> To increase the NiSi processing window, research has been dedicated to postpone the NiSi<sub>2</sub> nucleation, which in fact comes down to controlling the nucleation barrier of NiSi<sub>2</sub>. This can, for instance, be achieved by alloying the Ni thin film. The effect of alloying elements can be qualitatively understood in terms of the classical nucleation theory in which a nucleation barrier  $\Delta G^*$  is introduced

$$\Delta G^* \approx \frac{\Delta\sigma^3}{(\Delta H - T\Delta S)^2}, \quad (1)$$

with  $T$  the temperature,  $\Delta\sigma$  the difference in interfacial energy,  $\Delta H$  the enthalpy change of the transition, and  $\Delta S$  the entropy change. The energy needed for the creation of a new

interface between the nucleating phase and the original matrix depends on the lattice match and interface structure. For example, the transition temperature of GdSi<sub>1.7</sub> → GdSi<sub>2</sub> is related to the crystalline quality of the hexagonal GdSi<sub>1.7</sub>, which can be strongly improved by forming the silicide epitaxially, through channeled ion beam synthesis.<sup>4</sup> Alloying elements will alter  $\Delta\sigma$  by altering the texture or offering low energy interfaces. Conversely, because  $\Delta H$  is typically small for nucleation controlled reactions, alloying elements significantly increase the importance of  $\Delta S$ , especially when isomorphous phases exist which exhibit mutual solid solubility. Based on the entropy of mixing two cases can be distinguished that will either decrease or increase the nucleation barrier, namely for a phase transition from a mixed phase to a non-mixed phase or vice versa. An example of both cases, focussing on the nucleation controlled transition NiSi → NiSi<sub>2</sub>, is the enhanced formation of the disilicide Co<sub>1-x</sub>Ni<sub>x</sub>Si<sub>2</sub> from a CoSi/NiSi mixture and the delayed nucleation of NiSi<sub>2</sub> from a Ni<sub>1-x</sub>Pt<sub>x</sub>Si solid solution.<sup>5-7</sup> The presence of the *isomorphous* phases NiSi<sub>2</sub> and CoSi<sub>2</sub> on the one hand and NiSi and PtSi on the other hand is crucial to allow solid solubility and, consequently, to affect the sign of  $\Delta S$ . As NiSi and PtSi, PdSi also shares the same crystal structure and alloying Ni with Pd has been shown to delay NiSi<sub>2</sub> nucleation.<sup>8,9</sup> The effect is generally explained similar to Pt by stating that a Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution forms.<sup>8,10-14</sup> On the other hand, significant differences between the Pt-Si and Pd-Si solid phase reaction imply that the formation of a Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution cannot be simply assumed. Although the binary reaction sequences for both elements are similar, i.e.,  $M \rightarrow M_2Si \rightarrow MSi$  (with  $M = Pt$  or  $Pd$ ), the very small  $\Delta H$  for the reaction Pd<sub>2</sub>Si → PdSi, makes PdSi a high temperature nucleation controlled phase, in contrast to the diffusion controlled formation of PtSi at much lower temperatures: on Si(100) substrates PdSi only nucleates above 735 °C and on Si(111) only above 850 °C, while PtSi can form at temperatures as low as 350 °C.<sup>2</sup> Furthermore, annealing below the

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eutectic temperature, drives PdSi back to Pd<sub>2</sub>Si.<sup>15,16</sup> In order for a NiSi-PdSi mixture or Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution to form, assumed to delay NiSi<sub>2</sub> formation, PdSi should thus nucleate at a temperature *below* the NiSi degradation temperature to NiSi<sub>2</sub>. As the latter already occurs around a temperature of 800 °C in the pure Ni-Si system, together with the high nucleation temperature of PdSi, the entropy of mixing cannot be automatically assumed as an explanation and the mechanism for NiSi<sub>2</sub> postponement by adding Pd is thus unclear at present.

In most cases, the reaction of a ternary system is by far more complex than that of the binary constituents. In this paper, we will focus on how the isomorphous phases NiSi and PdSi influence the nucleation controlled growth of PdSi and NiSi<sub>2</sub>, respectively. The understanding of these results will lead to new insights in the reaction mechanisms and important parameters for ternary reactions in general. To this end the crystalline phase formation and Pd redistribution during the reaction is studied *in situ* using real-time X-ray diffraction (XRD) and real-time Rutherford backscattering spectrometry (RBS) and *ex situ* with atom probe tomography (APT).

## II. EXPERIMENTAL DETAILS

A set of 45 nm Ni(Pd) alloy thin films containing increasing amounts of Pd (0%, 5%, 10%, and 15% Pd) were prepared. All metallic films were sputter deposited on Si(100) substrates, which had previously been cleaned by the standard RCA procedure and subsequent HF-dip. The crystalline phase formation sequence was studied using *in situ* XRD. Every 2 s, a linear detector covering 20° in 2θ records the diffracted x-rays originating from a Cu K<sub>α</sub> source, while ramp annealing the sample at 1 °C/s to 910 °C. Such *in situ* XRD measurements are conventionally displayed as contour plots of the diffracted intensity as a function of diffraction angle (y-axis) and temperature (x-axis), see Fig. 1. The appearance and subsequent disappearance of sets of diffraction peaks represents the transformation of crystalline phases as a function of temperature, in a single run. For clarity, the crystalline phases that could be identified are indicated in the figure at their corresponding diffraction peaks.

To complement the information on crystalline phase formation extracted from *in situ* XRD with elemental depth information, two techniques have been used: (i) RBS and (ii) APT. RBS is a well-established ion beam technique in thin film research, which is fully quantitative in elemental composition and depth. In this study, RBS is applied *in situ*, i.e., during the thermal treatment.<sup>17</sup> This approach provides the concentration depth profile of all elements as a function of temperature. In addition, to obtain *lateral* information on the Pd distribution, including Pd grain boundary decoration and Pd clustering, quenches were made at important stages during the growth and were investigated with APT. In an APT experiment, a tip is fabricated from the silicide film, using focussed ion beam milling. Atom per atom is then released from the apex of the tip by the application of regular laser pulses providing the energy needed for evaporation and ionization. The applied electric field between the tip and the 2D

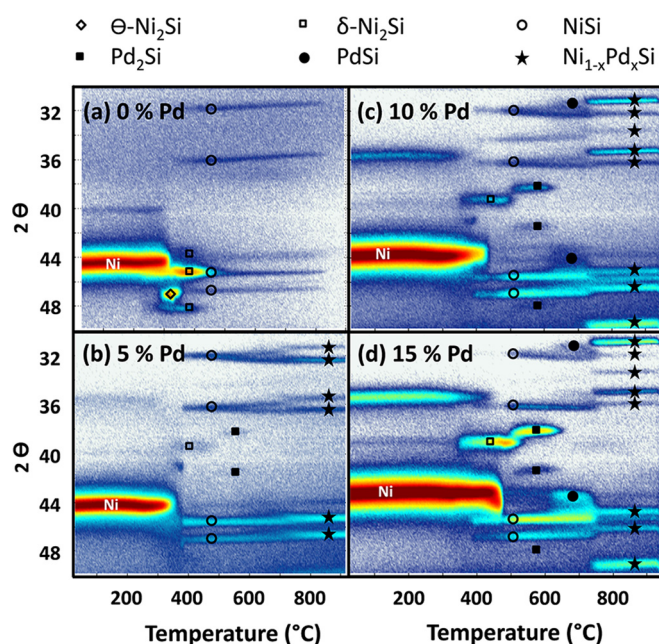
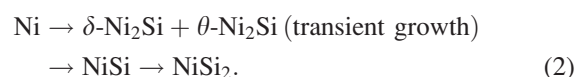


FIG. 1. *In situ* XRD measurements collected from 45 nm Ni(Pd) alloys containing increasing amounts of Pd, ranging from (a) 0% (reference) to (b) 5% and (c) 10% to (d) 15% of Pd. The allocated crystalline phases are indicated on the figures.

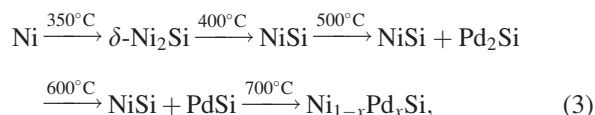
position sensitive detector (PSD) guides the ions to the PSD. Together with the laser pulse frequency, a 3D quantitative elemental map of the tip can be reconstructed with atomic resolution.<sup>18</sup>

## III. RESULTS AND DISCUSSION

Figure 1(a) displays the *in situ* XRD measurement for the reaction of a 45 nm pure Ni film with Si(100), which serves as a reference to disentangle the effect of Pd addition. The reaction sequence proceeds as follows:



During the reaction between 200 °C and 450 °C, generally referred to as the metal rich phase formation, first the  $\delta\text{-Ni}_2\text{Si}$  forms after which the metastable non-stoichiometric  $\theta$  phase transiently grows through texture inheritance from the preceding  $\delta\text{-Ni}_2\text{Si}$  fiber.<sup>19</sup> NiSi subsequently grows at the expense of  $\delta\text{-Ni}_2\text{Si}$  around 320 °C and degrades at about 820 °C. This corresponds to NiSi<sub>2</sub> formation, but NiSi<sub>2</sub> escapes detection due to its expected epitaxial growth on Si(100). These observed results correspond to what is known from literature.<sup>20</sup> Adding Pd changes the reaction sequence significantly, as can be inferred from Figs. 1(b)–1(d) showing the *in situ* XRD measurements on 45 nm Ni(Pd) films containing 5%, 10%, and 15% of Pd, respectively. The reaction sequence in all three cases generally proceeds as



as indicated in Fig. 1. In all three cases, adding Pd prevents the formation of the transient  $\theta$  phase. This is not surprising as its metastable character and growth through texture inheritance of the preceding  $\delta$ -Ni<sub>2</sub>Si, make nucleation of the  $\theta$  phase very sensitive to the addition of an alloying element. Moreover, the texture of  $\delta$ -Ni<sub>2</sub>Si forming around 350 °C is altered; now only the [132] ( $2\theta = 39.49^\circ$ ) diffraction peak appears, instead of the [133] ( $2\theta = 49.21^\circ$ ) and the [203] ( $2\theta = 45.79^\circ$ ) diffraction peaks that were present in the reference sample (Fig. 1). A second important occurrence is the sequential formation of binary Pd-silicides, after the full consumption of Ni<sub>2</sub>Si by NiSi, and thus, after the completion of NiSi growth. The growth of Pd<sub>2</sub>Si starts around 500 °C and is observed in each of the Pd containing samples, with a peak intensity scaling with the initial Pd content. Sequentially after Pd<sub>2</sub>Si formation, and at a temperature of about 600 °C, Pd<sub>2</sub>Si converts to PdSi, which is more than 130 °C below its nucleation temperature in the binary Pd-Si system. Neither intensity change nor any peak shift can be observed in the NiSi signal, when Pd-silicide diffraction peaks appear. Therefore, we can conclude that up to this stage in the reaction a mixture of the binary NiSi and PdSi phases exists, instead of a ternary compound. Around 700 °C a sudden shift of the NiSi monosilicide diffraction peaks to lower  $2\theta$  values (i.e., larger d-spacings) occurs for all three concentrations, indicating an expansion of the NiSi lattice. This lattice expansion occurs simultaneously with the disappearance of the PdSi diffraction peaks. As the monosilicide peak shift increases with increasing Pd content, we conclude that a solid solution NiSi + PdSi  $\rightarrow$  Ni<sub>1-x</sub>Pd<sub>x</sub>Si has formed. This conjecture is further supported by PdSi having slightly larger lattice parameters than NiSi, suggesting intermediate d-spacings for the solid solution. The Ni<sub>1-x</sub>Pd<sub>x</sub>Si phase remains present up to temperatures as high as 910 °C. Hence, Pd addition postpones NiSi<sub>2</sub> nucleation by at least 100 °C.

Figs. 2(a) and 2(b) depict the Ni and Pd depth profiles as a function of temperature during the reaction of a 45 nm Ni(Pd) alloy containing 5% of Pd. Both depth profiles are extracted from a single *in situ* RBS measurement and are projected such that the sample surface (i.e., surface energy) is at the top of the figure, with an indicative depth scale (backscattering energy) ranging from the sample surface to the sample interior. The x-axis represents the temperature ranging from 100 °C to 600 °C, while the color scale is a measure for the elemental concentration (i.e., backscattering yield). To acquire RBS spectra with sufficient statistics, the temperature was ramped at 2 °C/min which is much slower than the ramp rate applied for the *in situ* XRD measurements. As such, formation temperatures obtained with *in situ* RBS are not directly comparable to those obtained from *in situ* XRD due to the different thermal budget applied at a specific temperature.

According to the *in situ* RBS data, the Ni-Si silicide formation sequence proceeds as follows: Ni  $\rightarrow$  metal rich phases  $\rightarrow$  NiSi, as indicated in Fig. 2(a). The reaction starts around 200 °C with the growth of the metal rich phases at the Si-interface, indicated by the concentration drop and bending of the contour line from the interface towards the surface. We refer to metal rich phases in general, because

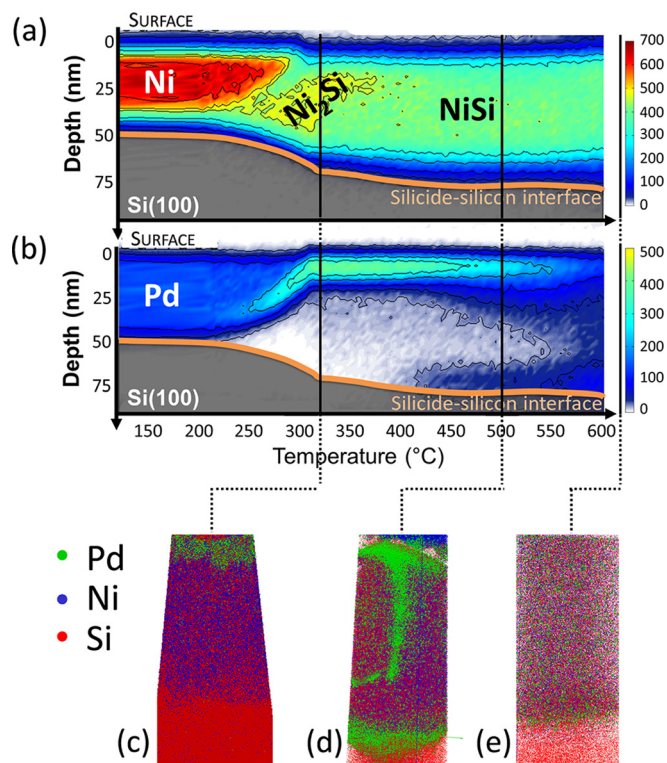


FIG. 2. Depth profiles of (a) Ni and (b) Pd as a function of temperature (x-axis), extracted from *in situ* RBS on a 45 nm Ni(Pd) alloy containing 5 at. % Pd. An indicative depth scale ranging from the sample surface to the sample interior is added. The color scale represents the elemental concentration. Atom probe results, taken on quenches made at three different stages during the reaction, are shown in (c)–(e).

the distinction between  $\delta$ -Ni<sub>2</sub>Si and  $\theta$  phase cannot be made from *in situ* RBS, as RBS only yields stoichiometric information. From *in situ* XRD, however, we know that the addition of Pd rules out the formation of the metastable  $\theta$  phase, hence that in this case as well only  $\delta$ -Ni<sub>2</sub>Si grows. Subsequently, around 300 °C NiSi starts to grow and consumes Ni<sub>2</sub>Si, indicated by the second concentration drop. Around 400 °C all remaining Ni<sub>2</sub>Si has been converted to NiSi.

The Pd (re)distribution and its relation to Ni-silicide formation are shown in Fig. 2(b) and are schematically represented in Figs. 3(1)–3(6). The homogeneous blue color in Fig. 2(b) below 200 °C confirms a uniform Pd distribution in the Ni(Pd) alloy (Fig. 3(1)). Next, together with the Ni<sub>2</sub>Si formation between 200 °C and 300 °C (Fig. 2(a)), Pd is extruded from the growing Ni-rich silicide, indicated by the Pd contour lines bending towards the surface, away from the inward moving silicide-silicon interface. The Pd expulsion is a consequence related to the low solubility of Pd in Ni<sub>2</sub>Si, which is estimated to be less than 4% at 800 °C.<sup>21</sup> Pd is therefore pushed to the surface by the moving interface of the growing Ni<sub>2</sub>Si (Fig. 3(2)). The upward shift in the Pd contours at the surface is related to the finite detector resolution of 15 keV. This yields additional counts at the high energy side of the RBS spectrum, when Pd accumulates at the surface. A quench was made at the onset of NiSi growth and studied with APT, shown in Fig. 2(c) and corresponding to stage 3 (Fig. 3(3)). The measurement confirms that, at this

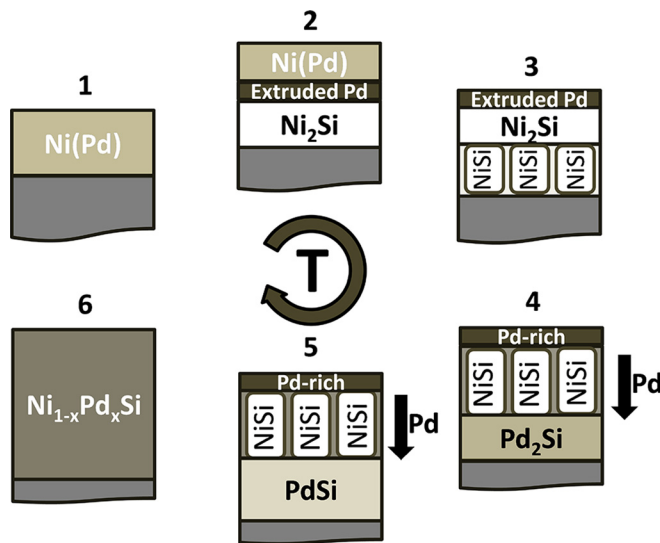


FIG. 3. Schematic representation of the important stages during the solid phase reaction of the Ni(Pd) alloy with Si(100).

stage, the vast majority of the Pd atoms is located at the surface, leaving a Pd content below 1% in the Ni-silicide. During the whole NiSi formation process from 300 °C to 400 °C, Pd remains highly concentrated at the sample surface, as can be deduced from Figs. 2(a) and 2(b) and illustrated in Fig. 3(3).

At 400 °C, coincident with the full consumption of the Ni<sub>2</sub>Si by NiSi, Pd transport is initiated towards the silicide-silicon interface (Figs. 2(b) and 3(4)). A 2D projection of an APT measurement taken at this stage is shown in Fig. 2(d). The 3D elemental map reveals that Pd is highly concentrated in a planar arrangement separating two Pd-deficient regions. This points to the presence of a grain boundary and indicates that Pd diffuses mainly along the NiSi grain boundaries, from the surface towards the silicide-silicon interface. The Pd concentration in the interface region progressively increases for increasing temperatures, indicating interface segregation or the growth of a Pd-phase. Determining the exact stoichiometry of this phase from the *in situ* RBS data is ambiguous due to the low Pd concentration and the rough interface (Fig. 2(b)). From *in situ* XRD, however, we know that Pd<sub>2</sub>Si nucleates, sequentially after the  $\delta$ -Ni<sub>2</sub>Si consumption by NiSi, hence coincident with the onset of Pd transport to the silicide-silicon interface. The Pd transport is thus driven by the formation of Pd<sub>2</sub>Si at the NiSi/Si(100) interface. However, compared to the Pd<sub>2</sub>Si formation in the binary Pd-Si system, the Pd<sub>2</sub>Si formation from the Ni(Pd) alloy is delayed with about 200 °C ( $T_{\text{form}}$  from *in situ* XRD)—300 °C ( $T_{\text{form}}$  from *in situ* RBS). The delayed formation temperature is believed to be caused by the strong diffusion barrier for Pd transport which Ni<sub>2</sub>Si imposes, as Pd transport only initiates after the full Ni<sub>2</sub>Si consumption by NiSi. The reason is unclear at present, but could be related to the Ni<sub>2</sub>Si microstructure having a low grain boundary density. The absence of any Pd grain boundary decoration in the APT quench taken after Ni<sub>2</sub>Si growth (Fig. 2(c)), supports the idea of having large Ni<sub>2</sub>Si grains.

From *in situ* XRD, we know that PdSi nucleates from Pd<sub>2</sub>Si, prior to the formation of a Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution

(Fig. 3(5)). At stages 4 and 5 in the reaction, a phase separated configuration exists with the Pd-silicide layer located in between the Si-substrate and the NiSi layer, and Pd decorating the NiSi grain boundaries (Figs. 3(4) and 3(5)). As a result, NiSi is no longer in direct contact with Si. As both the Pd<sub>2</sub>Si resistivity and Schottky barrier height to Si are higher compared to NiSi/Si, the electrical contact properties of the resulting ternary silicide film are most probably deteriorated compared to the pure NiSi.<sup>22</sup>

Figure 2(e) shows an APT measurement on a quench that was made at the final stage of the reaction, showing a homogeneous Pd distribution in the silicide film and confirming the formation of the solid solution Ni<sub>1-x</sub>Pd<sub>x</sub>Si, which was observed with *in situ* XRD (Fig. 3(6)). Hence, we conclude that the formation temperature of the nucleation controlled reaction NiSi → NiSi<sub>2</sub> has increased with at least 100 °C by the formation of a Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution. The increase of  $\Delta G^*$  arises from the negative  $\Delta S$  for the reaction Ni<sub>1-x</sub>Pd<sub>x</sub>Si → NiSi<sub>2</sub> + PdSi due to the need to extrude Pd from the homogeneous solution, before NiSi<sub>2</sub> can grow (Eq. (1)). The reduction of the PdSi nucleation temperature is however crucial to enable the Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution to form in the first place. From *in situ* XRD, we know that PdSi nucleates from Pd<sub>2</sub>Si before the Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution is formed and, thus, the mixing entropy will not have a strong impact on the nucleation barrier for PdSi nucleation. Entropy of mixing can therefore not be used as an explanation for the lowering of the PdSi nucleation barrier. Also,  $\Delta H$  will not change significantly compared to the binary Pd-Si case for the reaction Pd<sub>2</sub>Si → PdSi and is thus very low.

Looking at the binary Pd-Si system, the difference of 115 °C in the PdSi nucleation temperature between Si(100) and Si(111) is attributed to the epitaxial growth of Pd<sub>2</sub>Si on Si(111).<sup>2</sup> Hence, it is clear that the difference in interface energy  $\Delta\sigma$  can have an important impact on the nucleation temperature of a phase. It also allows for an explanation of the decreased nucleation barrier  $\Delta G^*$  for PdSi growth from a Ni(Pd) alloy, in which the presence of NiSi plays a crucial role. NiSi and PdSi share the same orthorhombic MnP lattice structure with a close lattice match. The presence of NiSi nuclei may therefore serve as a template for PdSi nucleation by providing a lower interface energy and thus a reduced nucleation barrier for PdSi growth. From the work of Mao *et al.*, it is expected that Pd substitutes for Ni sublattice sites in NiSi, forming a Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution.<sup>23</sup> However, the formation of the solid solution NiSi + PdSi → Ni<sub>1-x</sub>Pd<sub>x</sub>Si only happens after binary PdSi has formed, as an additional amount of energy is needed for atomic rearrangement and an expansion of the monosilicide lattice.

Although strong similarities exist between Pd and Pt, the Pt redistribution studied by Demeulemeester *et al.* differs fundamentally from the Pd redistribution described above, especially during monosilicide formation.<sup>24,25</sup> There they found that during Ni<sub>2</sub>Si formation Pt also piles up at the sample surface due to the low solubility of Pt in Ni<sub>2</sub>Si. However, compared to the complete extrusion of Pd from the growing Ni<sub>2</sub>Si phase in the present work, a small amount of Pt still decorates the Ni<sub>2</sub>Si grain boundaries.<sup>26</sup> At the initiation of monosilicide formation, Pt rapidly redistributes due to the

incorporation of Pt in the growing NiSi seeds or the formation of a Pt-silicide. This strongly dissimilar behavior is a result of the distinct formation temperatures of PdSi (above 730 °C) compared to PtSi and NiSi (both around 300 °C), allowing direct formation and solid solubility of PtSi and NiSi, in contrast to PdSi and NiSi.

#### IV. CONCLUSION

During the Ni(Pd) silicide reaction, phase separation of the binary NiSi and Pd-silicides occurs. As a result Pd<sub>2</sub>Si is in direct contact with Si instead of NiSi, thus deteriorating the electrical contact properties. This is of major importance when considering the use of Pd as an additive element in NiSi contacts. Furthermore, a strong reduction of the binary PdSi nucleation temperature can be achieved in the presence of Ni. The effect is qualitatively understood by making use of the classical nucleation theory. The PdSi formation at temperatures significantly below the widely accepted nucleation temperature in the pure Pd-Si system does not result from the effect of entropy of mixing due to the direct formation of a Ni<sub>1-x</sub>Pd<sub>x</sub>Si solid solution, as previously suggested.<sup>8,10-14</sup> Rather, it is triggered by a reduction in surface energy, induced by the presence of the isomorphous NiSi phase. The coexistence of NiSi and PdSi transforms into a Ni<sub>1-x</sub>Pd<sub>x</sub>Si solution at higher temperatures, which in turn results in an improved monosilicide stability by postponing NiSi<sub>2</sub> nucleation due to entropy of mixing. The isomorphism, and hence the mutual solubility of NiSi and PdSi, plays a crucial, yet distinct role in the nucleation of PdSi and NiSi<sub>2</sub>.

Our work shows that either the interface energy or the entropy of mixing is decisive for altering the nucleation barrier of PdSi and NiSi<sub>2</sub>, respectively. These results are more generally valid, showing that the mutual influence of the two binary systems significantly alters the reaction parameters in the ternary system, such as formation temperatures and phase formation sequence. In other words, knowing the two binary constituents are insufficient to understand the ternary system. This paper fills one of the many gaps in assigning the parameters that are relevant for the understanding of ternary reactions, i.e., the role of interface energy and entropy of mixing.

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