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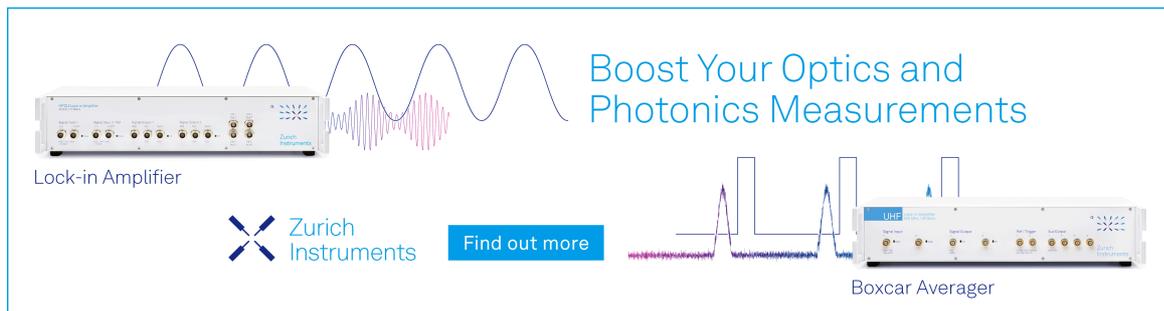
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## Pt redistribution during Ni(Pt) silicide formation

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We report on a real-time Rutherford backscattering spectrometry study of the erratic redistribution of Pt during Ni silicide formation in a solid phase reaction. The inhomogeneous Pt redistribution in Ni(Pt)Si films is a consequence of the low solubility of Pt in Ni<sub>2</sub>Si compared to NiSi and the limited mobility of Pt in NiSi. Pt further acts as a diffusion barrier and resides in the Ni<sub>2</sub>Si grain boundaries, significantly slowing down the Ni<sub>2</sub>Si and NiSi growth kinetics. Moreover, the observed incorporation of a large amount of Pt in the NiSi seeds indicates that Pt plays a major role in selecting the crystallographic orientation of these seeds and thus in the texture of the resulting Ni<sub>1-x</sub>Pt<sub>x</sub>Si film. © 2008 American Institute of Physics. [DOI: 10.1063/1.3058719]

Ni(Pt)Si thin film alloys are currently used as contact layers in complementary metal-oxide-semiconductor technology. Adding Pt to the compound results in an increased thermal stability of the monosilicide thin film.<sup>1</sup> The exact role of Pt in this stabilization effect is not completely understood. Pt has a distinct influence on the NiSi texture, causing stabilization in terms of interface energy.<sup>2</sup> It is believed that the NiSi lattice expansion caused by the incorporation of Pt lies at the origin of the correlation between the texture and the initial Pt concentration. This interpretation however critically depends on the amount of Pt present at the NiSi/Si interface during the initial stage of Ni(Pt)Si formation. Cojocar-Mirédin *et al.*<sup>3</sup> showed that Pt does not remain homogeneously distributed throughout the thermal treatment but is extruded in a snowplow process. As such, Pt influences the growth kinetics by acting as a diffusion barrier. Furthermore, Pt incorporation into the NiSi matrix is expected to have a considerable influence on the stress during formation, which plays a major role in determining the mechanical, morphological, and electrical properties of the Ni(Pt)Si thin film. Hence, to understand the influence of the Pt addition on texture development, the growth kinetics, as well as the stress behavior, detailed information on the Pt distribution during annealing is crucial. Such information is readily accessible with *real-time* Rutherford backscattering spectrometry (RBS) measurements, as will be elucidated below.<sup>4</sup>

A set of 75 nm thick homogeneous Ni(Pt) alloys with Pt concentrations of 1, 3, 7, and 10 at. % was sputtered on chemically cleaned Si(100) substrates. All samples were annealed in high vacuum ( $\sim 10^{-7}$  Torr) at a heating rate of 2 °C/min while simultaneously conducting RBS with a 2 MeV He<sup>+</sup> beam (backscattering angle=165°). Every 2 min an RBS spectrum was collected, resulting in a temperature resolution of 4 °C. The ramped anneals were continued until no further redistribution was observed for at least 20 min. A prolonged annealing (ramped at 2 °C/min to 600 °C and kept there for a further 30 min) was applied to the sample

with 7 at. % Pt to investigate the Pt diffusion in the NiSi phase. Artificial neural networks (ANNs) (Ref. 5) were used for the quantitative analysis of all acquired RBS spectra. This analysis yields the thickness of the individual phases growing during the annealing, as well as detailed information on the relative atomic concentrations throughout the film and throughout the annealing process. The results for selected representative spectra were confirmed by simulations made with the standard codes NDF (Ref. 6) and RUMP.<sup>7</sup>

Figure 1 shows two RBS spectra obtained during the annealing of a film with 3 at. % Pt. The squares and circles represent the RBS spectra acquired at room temperature and 450 °C, respectively. Three regions, corresponding to the three elements in the specimen, can be distinguished in these spectra. As shown in Fig. 1, a depth scale can be associated with each element, with the highest backscattering energy corresponding to elements at the surface. The relative height of the signals, i.e., the backscattering yield, is a measure of

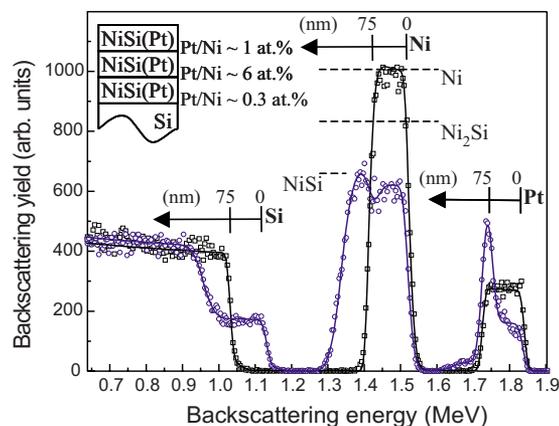


FIG. 1. (Color online) RBS spectra (data points) acquired during ramped annealing (2 °C/min) of a Ni(Pt) (3 at. % Pt) alloy on Si together with the simulation (solid line) at the beginning of the annealing (RT, black squares) and after complete transformation of the film in NiSi (450 °C, blue circles). The inset represents the sample structure at 450 °C as obtained from simulations.

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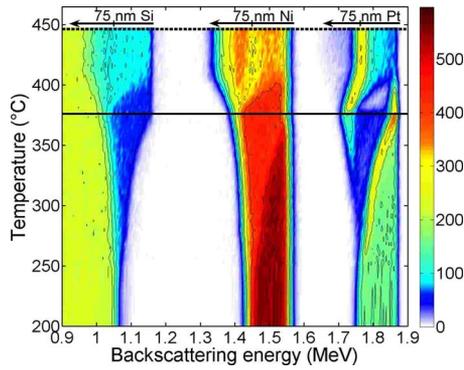


FIG. 2. (Color online) Real-time RBS measurement on a 75 nm Ni(Pt) thin film containing 3 at. % Pt on Si(100) annealed at 2 °C/min.

the elemental concentration in the film. For comparison the theoretical heights for a pure Ni film, a pure Ni<sub>2</sub>Si film, and a pure NiSi film are indicated in the figure. Hence, RBS spectra provide quantitative, depth sensitive information on the composition of the analyzed films.<sup>8</sup> Figure 1 shows that despite the homogeneous Pt distribution in the as-deposited metal alloy, an utterly inhomogeneous Pt distribution is established in the final Ni(Pt)Si film. Three Pt concentration regions can be distinguished and are represented in the inset of Fig. 1. A region with a very low Pt concentration is found near the silicide/Si interface (ANN analysis yields Pt/Ni of ~0.3 at. % and thickness of ≈98 nm) (1.6–1.7 MeV), followed by a Ni(Pt)Si layer in the middle of the film that is rich in Pt (Pt/Ni of ~6 at. %,  $t \approx 77$  nm) (1.7–1.77 MeV), and finally a silicide with a moderate Pt concentration is found at the surface of the film (Pt/Ni of ~1 at. %,  $t \approx 96$  nm). For a thorough understanding of the role of Pt and its redistribution in texture and stress development, thermal stability, growth kinetics, etc., an investigation of the sample at the end of the annealing sequence only, as shown in Fig. 1, is however largely insufficient. Detailed, depth sensitive information on the film composition throughout the growth process, as provided by real-time RBS, is crucial to grasp the full formation process. Moreover, the high sensitivity of RBS to heavy elements enables accurate investigation of specimens with a low Pt concentration, making real-time RBS the ideal technique to study the redistribution of Pt during Ni(Pt)-silicide formation. Real-time RBS data are conveniently plotted in a contour plot such as Fig. 2, which shows the data for the specimen containing 3 at. % Pt. Every horizontal line in such a contour plot corresponds to an RBS spectrum, with a color scale representing the backscattering yield. The contour plot is constructed from the consecutively acquired RBS spectra during annealing. For example, the horizontal dashed line in Fig. 2 at the end of the annealing (450 °C) corresponds to the high temperature spectrum displayed in Fig. 1. The Si, Ni, and Pt depth scales are added to Fig. 2 for interpretation purposes.

A first glance at Fig. 2 reveals that the Pt redistribution during silicide formation is quite erratic. Mapping such a redistribution using quenches and *ex situ* measurements is not only time consuming, the discrete character of that approach involves a large risk of overlooking important steps in the formation process as well. Performing this study with varying initial Pt concentrations further favors the real-time approach. From Fig. 2 it is clear that little or no reaction takes place below 250 °C. Above that temperature, the

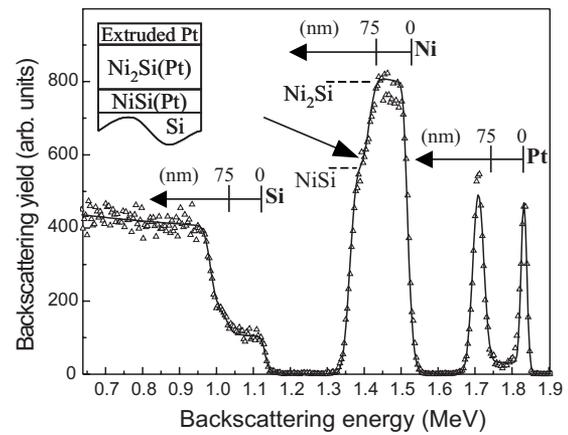


FIG. 3. RBS spectrum (data points) acquired at 375 °C during ramped annealing (2 °C/min) of a Ni(Pt) (3 at. % Pt) alloy on Si together with the simulation (solid line). At this temperature the NiSi seed layer (indicated with an arrow) is formed. The inset represents the sample structure as obtained from simulations.

gradual broadening of the Ni signal and the shift in the Si signal toward higher energies mark the formation of the Ni<sub>2</sub>Si phase that coincides with the first inhomogeneities in the Pt distribution. At this stage of the reaction, the low solubility of Pt in Ni<sub>2</sub>Si results in the expulsion of Pt, causing a Pt enrichment of the Ni(Pt) alloy. This enriched layer is gradually pushed toward the surface, as more Ni<sub>2</sub>Si forms underneath in a process that is referred to as the snowplow effect.<sup>3</sup> As the Ni diffuses through the Pt rich layer to form the Ni<sub>2</sub>Si phase, a fraction of the Pt is incorporated into the Ni<sub>2</sub>Si layer. For all Pt concentrations studied we observe a homogeneous Pt content in the Ni<sub>2</sub>Si that scales with the Pt concentration in the as-deposited alloy but is markedly lower than that. These observations suggest that the Pt amount in the Ni<sub>2</sub>Si layer does not correspond to the solubility limit of Pt into Ni<sub>2</sub>Si. As such, Pt is more likely to reside at the silicide grain boundaries, supporting the findings of Imbert *et al.*<sup>9</sup> During Ni<sub>2</sub>Si formation increasingly more Pt is incorporated in the Pt enriched layer that acts as a diffusion barrier. This is reflected in the increased temperature for the complete silicidation. Ramped anneals on all samples revealed that for increasing initial Pt concentrations, the point where the metal alloy is completely transformed into a silicide film is shifted to higher temperatures.

At approximately 350 °C (Fig. 2), a new Pt contour appears at lower energy ( $\pm 1.7$  MeV), i.e., the interface with the substrate. Figure 3 shows an RBS spectrum acquired at this stage of the reaction (375 °C, solid horizontal line in Fig. 2). Detailed analysis of the data shows that the appearance of this Pt contour coincides with the initial stage of NiSi formation, as illustrated in Fig. 3 where the shoulder at lower energy in the Ni signal marks the formation of the NiSi phase and a high Pt concentration is observed (peak at 1.71 MeV). The Pt/Ni ratio in this NiSi seed layer (6 at. %) is very high compared to the Ni<sub>2</sub>Si layer and even exceeds the initial Pt/Ni ratio in the metal alloy. This seed layer later develops into the middle, Pt rich NiSi region as already identified in the final NiSi film (Fig. 1). The high Pt concentration in the NiSi seed layer can be explained by realizing that Pt has a higher solubility in NiSi compared to Ni<sub>2</sub>Si. This presents a driving force for the integration of Pt into the freshly formed NiSi seeds. Consequently, the Pt concentration in the Ni<sub>2</sub>Si

layer is observed to decrease as the NiSi seed layer is forming. Pt thus diffuses out of the Ni<sub>2</sub>Si layer and is incorporated in the growing NiSi.

At slightly higher temperatures ( $\sim 390$  °C, Fig. 2), the RBS signal of this Pt rich NiSi layer starts to shift to higher energies due to the formation of NiSi underneath, with a much lower Pt concentration. At the same time a third NiSi region forms on top of the Pt rich NiSi. Once the reaction is completed, the thin film is transformed into a NiSi film with three distinct regions in Pt concentration as shown in the inset of Fig. 1, with the Pt rich NiSi seed region exactly at the center of the film. The origin of this final configuration lies within the growth of NiSi at two interfaces. Above the Pt rich NiSi region, Ni<sub>2</sub>Si dissociates into NiSi and Ni. The atomic Ni diffuses through the NiSi seed layer and forms NiSi at the interface with the substrate. Pt outdiffusion from the Pt rich NiSi region and drag effects are limited, which result in the low Pt concentration in this region. The Pt concentration gradient in this region, however, shows that these effects are present. For the NiSi that forms from the dissociation of Ni<sub>2</sub>Si on top of the Pt rich region, Pt is available and directly incorporated in the forming monosilicide. The Pt concentration in this layer is comparable to that in the Ni<sub>2</sub>Si layer. We want to point out that the same formation process is observed for each studied initial Pt concentration. Moreover, the same triple layered structure is obtained after reacting a 30 nm Ni(Pt) film, indicating that the formation process does not strongly depend on the film thickness.

To investigate the thermodynamical stability of the Pt configuration after complete NiSi formation, an extended *in situ* annealing of the 7 at. % Pt specimen at 600 °C for 30 min was performed while continuing the real-time RBS measurement. Although this inhomogeneous Pt distribution throughout the NiSi film is thermodynamically relatively unstable, only a marginal redistribution of the Pt was observed. This proves that the Pt mobility in NiSi is very low even at temperatures as high as 600 °C.

As illustrated, the addition of Pt has a major influence on the Ni silicide growth kinetics since the formation of a Pt rich diffusion barrier limits the supply of Ni to the Ni<sub>2</sub>Si growth interface. The presence of Pt in the Ni<sub>2</sub>Si grain boundaries, where the majority of the mass transport takes place, further limits this supply. The consequences of these effects are reflected in the delay of the complete silicidation to higher temperatures for higher initial Pt concentrations. The slower Ni<sub>2</sub>Si growth kinetics significantly influences the subsequent NiSi growth kinetics as well, even to this extent that simultaneous growth of NiSi and Ni<sub>2</sub>Si has been observed. The altered growth kinetics can influence the properties of the silicides (e.g., texture, thermal stability, and morphology), while the limited Pt diffusion in NiSi is expected to contribute to the enhanced thermal stability of the alloyed films. Besides the influence on the growth kinetics, the Pt redistribution during silicide formation has a major effect on the Ni(Pt)Si texture development. We showed here that the

NiSi film grows from NiSi seeds with a high Pt/Ni ratio that scales with—and even exceeds—the initial Pt concentration in the metal alloy. As a consequence, those seeds that establish the NiSi texture are characterized by an increase in lattice parameter proportional to the initial Pt concentration. This explains how relatively small amounts of Pt can significantly influence the NiSi texture development and consequently the stabilization of the alloyed NiSi film.<sup>2</sup> Clearly, the Pt concentration in the NiSi close to the interface varies throughout the monosilicide formation, ranging from very high (Pt/Ni of  $\sim 6$  at. % at 375 °C for the 3 at. % Pt specimen) to extremely low (Pt/Ni of  $\sim 0.3$  at. % at the end of the reaction for the 3 at. % Pt specimen), which may significantly influence the stress behavior of the film. This result is useful input for the interpretation of stress measurements and has major implications for device applications since stress effects are of increasing importance in the determination of the morphological, mechanical, and electrical properties of contact layers as device dimensions are shrinking.

In conclusion, we emphasize that Pt redistributes in an erratic, inhomogeneous way during Ni(Pt) silicide formation and has a major effect on the silicide growth kinetics. Moreover, at the initial point of NiSi formation a large amount of Pt, exceeding the as-deposited Pt/Ni ratio, is incorporated in the monosilicide seeds. This indicates that Pt, even for low initial Pt concentrations, is highly involved in the texture and stress development since Pt incorporation results in NiSi lattice expansion. As a result of the NiSi formation at two interfaces, the monosilicide ends up with three separate Pt concentration regions. This configuration remains stable for at least 30 min at temperatures as high as 600 °C, indicating that Pt is highly immobile in NiSi at elevated temperatures.

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