

Pt redistribution during NiSi formation

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Abstract

We report on a real-time Rutherford backscattering spectrometry (RBS) 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 Ni₂Si compared to NiSi and the measured limited mobility of Pt in NiSi. Pt further acts as a diffusion barrier and resides in the Ni₂Si grain boundaries, significantly slowing down the Ni₂Si 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 the development of the Ni(Pt)Si texture.

Ni(Pt)Si thin film alloys are currently used as contact layers in CMOS technology. Adding Pt to the compound results in an increased thermal stability of the monosilicide thin film¹. 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 energy². It is believed that the NiSi lattice expansion caused by the incorporation of Pt lies at the origin of the dependence between the texture and the initial Pt concentration. This interpretation however critically depends on the amount of Pt present at the NiSi/Si interface in the initial stage of Ni(Pt)Si formation, as it are those seeds that determine the overall final texture. Cojocar-Mirédin *et al.*³ have shown that Pt does not remain homogeneously distributed throughout the thermal treatment, but gets 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 distinct influence on 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)⁴ measurements as will be elucidated below.

A set of 75 nm thick homogeneous Ni(Pt) alloys with Pt concentrations of 1, 3, 7 and 10 at.%, were sputtered on RCA 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 beam (backscattering-angle=165 °). The ramped anneals were continued until no further redistribution was observed for at least 20 minutes. A prolonged annealing (ramped at 2 °C/min to 600 °C for 30 min) was applied to the sample with 7 at.% Pt to investigate the thermal stability of the Pt distribution in the NiSi phase. Artificial neural networks (ANNs)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.

Figure 1(a) shows two RBS spectra captured during the annealing of a film with 3 at.%Pt. The squares and dots 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. Channels (x-axis) 150-280 cover the Si signal, channels 310-390 the Ni signal and channels 400-465 cover the Pt signal. From the energy loss, a depth scale, as shown in Fig. 1(a), can be associated with each element, with the highest energy (channel) corresponding to elements at the surface. The relative height of the signals, i.e. the backscattering yield (y-axis), is a measure for the elemental concentration in the film. Hence, RBS spectra provide quantitative, depth sensitive information on the composition of the analyzed films. The higher Ni signal for the as deposited specimen in Fig. 1(a) shows that the relative Ni content in the surface layer is higher for the as deposited film compared to the annealed film. For comparison the theoretical heights for a pure Ni film, a pure Ni₂Si film, and a pure NiSi film are indicated in the picture, which shows that a NiSi film has formed after annealing. The larger width of the Ni signal after annealing on the other hand, shows that the Ni(Pt)Si film is thicker than the initial Ni(Pt) film. For more details on RBS and the interpretation of RBS spectra, the reader is directed to the literature⁶. From the RBS spectra in Fig. 1 (a) it can be deduced that despite the homogeneous Pt distribution in the as-deposited metal alloy, an absolutely not homogeneous Pt distribution is established in the final Ni(Pt)Si film. Three Pt concentration regions can be distinguished and are shown in the inset of Fig. 1 (a). In channels 400-420 a region with a very low Pt concentration (ANN-analysis yields Pt/Ni~0.3 at.%, thickness \approx 98nm) is found near the silicide/Si interface, followed by a Ni(Pt)Si layer in the middle of the film that is very rich in Pt (Pt/Ni~6 at.%, $t \approx$ 77nm) (channels 420-435) and finally a silicide with a moderate Pt concentration (Pt/Ni~1 at.%, $t \approx$ 96nm) is found at the surface of the film. However, 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 (a) is largely insufficient. Detailed, depth sensitive information on the film composition throughout the growth process, as provided by *real-time* RBS, is therefore crucial to grasp the full formation process. Moreover, the especially 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 as in Fig. 2, which shows the data for the specimens containing 1, 3 and 10 at.% Pt. Every horizontal line in such a contour plot corresponds to an RBS spectrum as shown in Fig. 1. The backscattering

yield is now represented by a color scale, with red indicating a high yield and blue a low yield. The contour plot is constructed from the consecutively acquired RBS spectra during annealing, the y-axis therefore represents the annealing temperature. For example, the horizontal line at 375 °C in Fig. 2(b) corresponds to the spectrum in Fig. 1 (b). The Si, Ni and Pt regions can be distinguished in the contour plots and depth scales are added in Fig. 2 for interpretation purposes.

A first glance at Fig. 2 shows that the Pt distribution during silicide formation is quite erratic. Performing this study *ex situ* and with discrete temperature steps would thus yield a large risk to miss important steps in the formation process, favoring the real-time approach. Focussing on the sample with 3 at. % Pt (Fig. 2(b)) it is clear that little or no reaction takes place below 250 °C . Above that temperature, the gradual broadening of the Ni signal and the shift of the Si signal towards higher channel numbers mark the formation of the Ni₂Si phase that coincides with the first inhomogeneities in the Pt distribution. At this stage of the reaction, the low solubility of Pt in Ni₂Si³ results in the expulsion of Pt, causing a Pt enrichment of the Pt alloy. This enriched layer is gradually pushed towards the surface, i.e. higher channel numbers, as more Ni₂Si forms underneath in a process that is referred to as the snowplow effect³. As the Ni diffuses through the Pt rich layer to form the Ni₂Si phase, a fraction of the Pt is incorporated into the Ni₂Si layer. For all initial Pt concentrations we observe a homogeneous Pt content in the Ni₂Si , 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 Ni₂Si layer does not correspond to the solubility limit of Pt into Ni₂Si. As such, Pt is more likely to reside at the silicide grain boundaries, supporting the findings of Imbert *et al.*⁷. During Ni₂Si 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 that corresponds to the point where the Si signal reaches channel 280, i.e. Si reaches the sample surface or the metal completely penetrated the substrate. This point is achieved at ± 350 °C for 1 at.% Pt, ± 375 °C for 3 at.% Pt and ± 400 °C for 10 at.% Pt.

At approximately 350 °C for the 3 at.% Pt specimen (Fig.2.(b)), a new Pt contour appears at low channel numbers (channel 425), i.e. the interface with the substrate. Figure 1(b) shows the RBS spectrum measured at this temperature. Detailed analysis of this spectrum shows that the appearance of this Pt contour coincides with the initial stage of NiSi formation,

as can be deduced from the shoulder at lower channel numbers in the Ni signal (indicated by an arrow in Fig. 2(b)). The Pt concentration in this NiSi seed layer is very high in contrast to the Ni₂Si layer, and even exceeds the initial concentration in the metal alloy. This seed layer later develops into the middle, Pt rich, NiSi layer as already identified in the final NiSi film (Fig. 1(a)). The high Pt concentration in the NiSi seed layer can be understood by realizing that Pt is highly soluble in NiSi compared to Ni₂Si. This presents a driving force for the integration of Pt into the freshly formed NiSi seeds. Consequently, the Pt concentration in the Ni₂Si layer decreases as the NiSi seed layer is forming. Pt thus diffuses out of the Ni₂Si layer and is incorporated in the growing NiSi.

At slightly higher temperatures (~ 390 °C, Fig.2(b), 3 at.%Pt), the RBS signal of this Pt rich NiSi layer starts to shift to higher channels, due to the formation of another NiSi layer underneath, with a much lower Pt concentration. At the same time a third NiSi layer 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 mentioned before, with the Pt rich NiSi seed layer exactly in the center of the film (Fig. 1(a)). The origin of this final configuration lies within the growth of NiSi at two interfaces. Above the Pt rich NiSi layer, Ni₂Si 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 layer and drag effects are limited, which results in the low Pt concentration in this layer. The Pt concentration gradient in this layer however, shows that these effects are present. For the NiSi layer that forms from the dissociation of Ni₂Si on top of the Pt rich layer, Pt is available and directly incorporated in the forming monosilicide. The Pt concentration in this layer is therefore equal to that in the Ni₂Si layer. We want to point out that the same triple layered structure is obtained after reacting a 30 nm Ni(Pt) film, indicating that the formation process is independent of the thin film thickness.

To investigate the thermodynamical stability of the Pt configuration after complete NiSi formation, an extended 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 full NiSi film is thermodynamical relatively unstable, only a marginal redistribution of the Pt could be observed. This proves that the Pt mobility in NiSi is very low 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 at the Ni₂Si growth interface. The presence of Pt at the Ni₂Si grain boundaries, where the majority of the mass transport takes place further limits this supply, which is reflected in the delay of the complete silicidation to higher temperatures for higher initial Pt concentrations. The slowed down Ni₂Si growth kinetics significantly influence the subsequent NiSi growth kinetics as well, even to this extent that simultaneous growth of NiSi and Ni₂Si has been observed. The altered growth kinetics can influence the properties of the silicides (e.g. texture, thermal stability, 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, we revealed a major effect of Pt on the Ni(Pt)Si texture development. We showed here that the NiSi film grows from NiSi seeds with a high Pt concentration 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 increased lattice parameter proportional to the initial Pt concentration. Pt addition will therefore indeed play a distinct role in the NiSi texture development and consequently in the stabilization of the alloyed NiSi film, as shown by Detavernier *et al.*⁸. Clearly, the Pt concentration in the NiSi close to the interface varies throughout the monosilicide formation, ranging from very high (6 at.% Pt at 350°C for the 3 at.% Pt specimen) to extremely low (0.3 at.% Pt at the end of the reaction for the 3 at.% Pt specimen). This has a significant influence on 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. 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 up to temperatures of at least 600 °C , indicating that Pt is highly immobile in NiSi at those temperatures.

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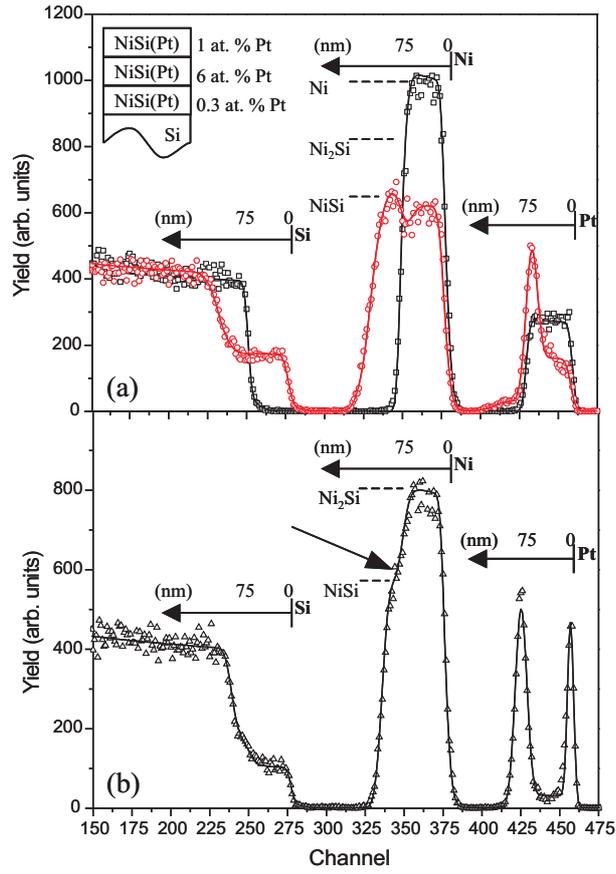


FIG. 1: Experimental RBS spectra (data points) acquired during ramped annealing ($2\text{ }^{\circ}\text{C}/\text{min}$) of a Ni(Pt) (3 at.% Pt) alloy on Si together with the RUMP simulation (solid line) of the data, (a) at the beginning of the annealing ($35\text{ }^{\circ}\text{C}$, black squares), after complete transformation of the film in NiSi ($445\text{ }^{\circ}\text{C}$, red dots) and (b) at $375\text{ }^{\circ}\text{C}$ where the NiSi seed layer (indicated with arrow) is formed.

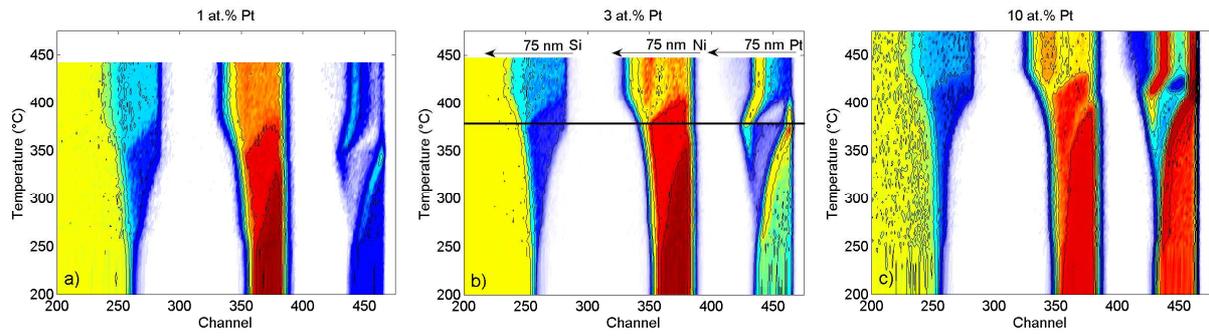


FIG. 2: Real-time RBS measurements on 75 nm Ni(Pt) alloyed thin films on Si(100) ramped at 2 °C /min, containing (a) 1 at.% Pt, (b) 3 at.% Pt, (c) 10 at. % Pt.