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# Snowplow effect and reactive diffusion in the Pt doped Ni–Si system

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The redistribution of Pt after heat treatment at 290 °C for 1 h has been analyzed by large-angle atom probe tomography assisted by femtosecond laser pulses. Two silicides $Ni_2Si$ and NiSi were found together with the solid solution of Ni and Pt. The redistribution of Pt at the $Ni_{1-x}Pt_x/Ni_2Si$ interface is a clear illustration of the snowplow effect. A segregation of Pt at the $Ni_2Si$/NiSi interface has been observed and is attributed to interfacial segregation.
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The formation of nanometric phases by reacting a thin film with a substrate is an important field both for applied and fundamental tasks. The study of thin film reactions has been developed mainly around silicides due to their application as contacts in microelectronic devices. The reactions in thin films [1] are characterized by sequential growth, the lack of some equilibrium phases, and sometimes the growth of metastable phases while the simultaneous parabolic growth of all the equilibrium phases is usually observed in bulk interdiffusion couples. Nucleation [2] has been shown to play a crucial role in the formation of some phases and, in particular, the silicon-rich silicides ($NiSi_2$, $TiSi_2$,...).

The addition of alloying elements may influence the formation and nucleation of silicides. For example, the addition of Mo, Nb or Ta can promote the formation of the C54 phase of $TiSi_2$. The use of a Ti interlayer may also promote the epitaxy of $CoSi_2$. The addition of 5% Pt to an Ni film has been shown to stabilize the low resistivity NiSi phase through an increase of approximately 150 °C of the temperature of formation of the $NiSi_2$ phase, which is known to have a higher resistivity [3]. This allows the better integration of NiSi as contacts for nanometric transistors [4]. Over the last few years, there has been extensive work on determining the effects of alloying element on the formation and stability of Ni silicides [5]. However, the fundamental mechanisms behind these effects are not fully understood. The redistribution of the alloy element during the formation of the silicide is also not well understood. One of the reasons for this is the difficulty in determine precisely the location of the alloy element at the nanometric scale. Rutherford backscattering has been used to study the redistribution, but the depth resolution of this technique is not sufficient. Composition techniques associated with the transmission electron microscope also have limitations.

Advanced characterization methods with very high spatial resolution are thus required to analyze the redistribution at the nanoscale. Atom probe tomography (APT) has been applied in the analysis of precipitation [6] or thin film formation [7] of nanometric phases. Indeed, APT [8] has unique capabilities to characterize internal interfaces and layer chemistry with sub-nanometer scale resolution in three dimensions. APT has long been limited to materials with good electrical conductivity because fast high electric pulses are required to field evaporate the material. However, it has recently been shown that the use of ultrafast laser pulses (<1 ps) enables the analysis of materials with poor electrical conductivity [9,10]. These innovations in instrumental technology and sample preparation have allowed the

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characterization of the dopant redistribution in Si [11] and metallic multilayers on Si substrate [12]. Recently, Thompson et al. [13] reported the observation of the NiSi and $Ni_2Si$ phases after heat treatment at 350 °C for 10 min. More recently, we observed the early stages of nucleation and lateral growth of Ni silicide alloyed with 5% Pt [14].

In this paper, we report atom probe observations of the redistribution of Pt during the silicide formation using the latest generation of instrument (a laser-assisted wide-angle tomographic atom probe (LaWaTAP), developed by the Laboratory and CAMECA).

Films of polycrystalline Ni, 80 nm thick, containing 5 at.% Pt were deposited at room temperature by co-sputtering of Ni and Pt targets on (1 0 0)Si p-doped (resistivity 0.01 Ω cm) substrates. The $Ni_{1-x}Pt_x$ films were deposited simultaneously on (i) blanket substrates for characterization by X-ray diffraction (XRD) and X-ray reflectivity (XRR); and (ii) high aspect ratio flat-topped ⟨1 0 0⟩ silicon posts for APT analysis. A heat treatment was performed under vacuum at a temperature of 290 °C for 1 h. In the APT technique, a tip is evaporated atomic layer by atomic layer and analyzed by time-of-flight mass spectrometry, allowing a small volume of material (typically $60 \times 60 \times 100\ nm^3$ for large acceptance angle TAP) to be reconstructed in the three dimensions of space, atom by atom, on a nearly atomic scale [10]. For this study, the region of interest was transformed [15] into a tip with a 30 keV $Ga^+$ focused ions beam system, using a beam diameter of 0.05 μm and a beam current of 10–500 pA. A relatively thick (80 nm) film was chosen to prevent the interface region from implantation and damage by Ga. A protective layer of Cr (300 nm) was also deposited to prevent damage due to Ga irradiation.

XRD and XRR were performed using the Bragg–Brentano geometry and a Cu Kα source. The APT characterization was performed using the LaWaTAP. In this instrument, the material is removed by means of femtosecond laser pulses (wavelength 1030 nm, duration 350 fs). When the linear polarization of the wave is set parallel to the tip axis, the rectification of the optical field at the surface generates an ultrafast pulsed field that causes the evaporation of surface atoms in the form of ions [16]. This effect has also been proved to take place in the case of Si based materials.

Figure 1 shows the APT reconstructions of the annealed sample. The distribution of Ni and Si atoms exhibits the presence of four regions: (1) the first is an almost pure nickel region with almost no silicon and a small amount of Pt (3 at.%); (2) and (3) are intermixed regions between the nickel deposit and the silicon substrate; and (4) the silicon substrate. It is quite evident from Figure 1 that regions 2 and 3 do not have the same composition. Depth profiles derived from these images (Fig. 2) reveals that $Ni_2Si$ and NiSi phases (Fig. 2) formed as a consequence of the reactive diffusion between Ni(3 at.%Pt) and the Si substrate. The average of concentration values for Ni, Si and Pt elements in the $Ni_{1-x}Pt_x$, $Ni_2Si$, NiSi and Si phases were found to be, respectively: (1) $94 \pm 0.4/1.2 \pm 0.2/2.9 \pm 0.2$; (2) $64.2 \pm 0.9/35 \pm 0.9/0.6 \pm 0.1$; (3) $49.1 \pm 1.3/49.4 \pm 1.3/0.3 \pm 0.1$; and (4) $0.1 \pm 0.1/98.7 \pm 0.5/0.1 \pm 0.1$.

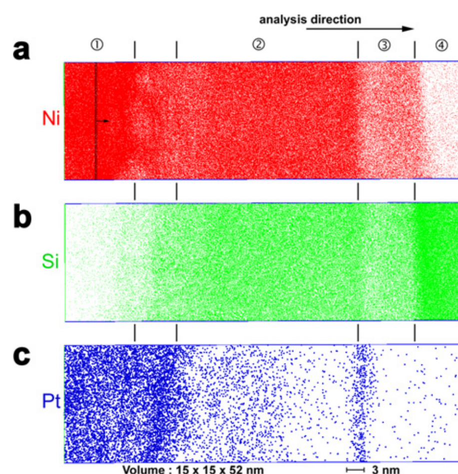


**Figure 1.** Elemental maps of (a) Ni (red), (b) Si (green), (c) Pt (blue) in a small selected volume ($15 \times 15 \times 52\ nm^3$) that was analyzed by LaWaTAP (only a part of the entire analyzed volume is here represented). The tip surface was evaporated layer by layer in a direction nearly perpendicular to the interfaces. Note that regions 2 and 3 do not have the same composition. Pt enrichments at $Ni/Ni_2Si$ and $Ni_2Si/NiSi$ interfaces are clearly exhibited (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.).

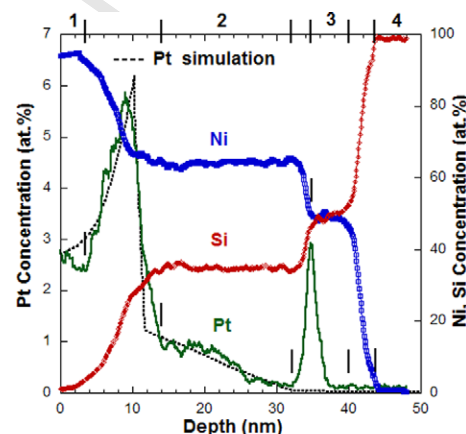


**Figure 2.** Concentration profiles of Ni, Si and Pt showing the presence of both $Ni_2Si$ and NiSi phases (from left to right) as a consequence of the reactive diffusion between Ni (left side) and the Si substrate (right). The depth profiles were drawn by moving a small box (0.1 nm thick and 15 nm wide) along a direction nearly perpendicular to the interfaces (Fig. 1). A simulation of the snowplow effect by finite elements has been included.

Pt enrichments at both the $Ni_{1-x}Pt_x/Ni_2Si$ and $Ni_2Si$/NiSi interfaces are also clearly exhibited. Indeed, two Pt peaks, the first one being broader, are observed at these interfaces. Several reconstructions similar to the one shown in Figure 1 were examined and showed similar features. Profiles in the Ni(Pt) region examined in the left hand region (not presented here) have shown that the concentration of Pt is close to 3 at.%, with small modulations, 0.5 at.% in amplitude.

The Pt level in Si appears to be very low, close to zero because the background noise for Pt in mass spectra was estimated to be 0.1 at.%. Almost no Pt is therefore present in silicon. The very low concentration of Pt and Ni

in Si is in accordance with the low solubility of Pt [17] and Ni [18] in Si.

The low concentration of Pt (<0.3 at.%) in NiSi is more difficult to understand. Indeed, NiSi and PtSi have the same orthorhombic structure (space group Pmna and structure type MnP), and their lattice dimensions are close (misfits less than 10%). NiSi and PtSi are thus expected to be totally miscible. It is thus quite astonishing not to find Pt in NiSi. Most of the Pt atoms seem to have segregated at the $Ni_2Si$/NiSi interface and do not enter in the NiSi layer, suggesting therefore a limited diffusion of Pt in NiSi.

The accumulation of Pt at the $Ni_2Si$/NiSi interface may be attributed to the formation of a silicide or to an interfacial segregation. Figure 1 indicates that the enriched region is 1–2 nm thick. Because of spatial convolutions between interfaces and the sampling box used to construct profiles, this feature is less clearly visible in depth profiles (Fig. 2). Indeed, the rugosity of interfaces, as well as the finite thickness of the sampling box (0.1 nm) and the possible angle between the box and interface (ideally 0°), can lead to an enlargement of the concentration peaks in the profiles. Whatever the case, the limited spatial distribution of the Pt at the $Ni_2Si$/NiSi interface seems to be more in accordance with an interfacial segregation. The origin of this segregation, namely a kinetic segregation (Pt is captured by the moving $Ni_2Si$/NiSi interface) or an equilibrium segregation (Pt decreases the interfacial energy), is another question.

The enrichment of Pt at the $Ni_{1-x}Pt_x/Ni_2Si$ interface deserves to be examined in more detail. Indeed, the redistribution of Pt at the $Ni_{1-x}Pt_x$ (zone 1)/$Ni_2Si$ (zone 2) interface (Fig. 2) is a clear illustration of the snowplow effect. This effect consists in the rejection of an alloy element during the growth of a phase, i.e. an addition or impurities element is pushed away by a moving interface and accumulates at one side of the interface. The more the phase grows, the more the alloy element is being accumulated in one of the parent phases. The use of APT allows some details of this phenomenon to be seen that may not been seen by other techniques with less depth resolution, like Rutherford backscattering. Indeed, Figures 1 and 2 indicate that the enriched region is thicker than the one at the $Ni_2Si$/NiSi and thus does not correspond solely to interfacial segregation. An accumulation of Pt is observed close to the interface half, in particular on the $Ni_{1-x}Pt_x$ side. The Pt concentration decreases on both sides of the interface (i.e. in $Ni_{1-x}Pt_x$ and in $Ni_2Si$), suggesting that Pt diffuses in these two phases while being rejected during the growth of $Ni_2Si$ (the interface half moves from right to left in Fig. 2). A simulation by finite elements of the snowplow effect (rejection of Pt during the growth of $Ni_2Si$ and diffusion in $Ni_{1-x}Pt_x$ and $Ni_2Si$) has been included in Figure 2 and is in agreement with the experimental profile. The snowplow effect has been already observed in several cases [19], including solid solution of Ni with Pt [20–22]. The rejection of Pt in $Ni_{1-x}Pt_x$ means that the flux of Pt is limited in $Ni_2Si$. This could be due to a thermodynamic or a kinetic reason. The solubility of Pt in $Ni_2Si$ is not known but should be limited, since the $Ni_2Si$ and $Pt_2Si$ phases do not share the same structure. Figure 2 shows that the maximum concentration of Pt in $Ni_2Si$ is around 1 at.% and decreases in proportion as one approaches the $Ni_2Si$/NiSi interface. If the grain boundary segregation is not too important this should correspond approximately to the solubility of Pt in $Ni_2Si$ in contact with the $Ni_{1-x}Pt_x$ solid solution. A rather strong partitioning of Pt thus occurs at the $Ni_{1-x}Pt_x/Ni_2Si$ interface since the solubility of Pt in $Ni_2Si$ is limited and the miscibility of Pt in Ni is total. Concurrent with the partitioning, Pt diffuses in both the $Ni_{1-x}Pt_x$ and $Ni_2Si$ layers.

Another interesting feature of Figure 1 is the simultaneous presence of $Ni_2Si$ and NiSi together with the $Ni_{1-x}Pt_x$ solid solution. The simultaneous presence of three phases during silicide growth is rarely observed in thin films. Usually phases appear sequentially. This sequential formation has been explained by a kinetic instability [23,24] due to a competition between reaction rates at interfaces and diffusion in the growing phases. The simultaneous presence of the three phases may be due to the formation of NiSi during the deposition that was observed previously [14]. The addition of Pt can also affect both interface reaction rates and diffusion coefficients properties, and induces a simultaneous growth of $Ni_2Si$ and NiSi. The creation of an Pt-enriched layer at the $Ni_{1-x}Pt_x/Ni_2Si$ interface should also be considered. Since this layer separates the silicide from the Ni source, it may act as a diffusion barrier for Ni and decreases the Ni supply. This may also lead to a change from sequential to simultaneous formation. This role of impurity on Ni silicide formation was also mentioned by Ma et al. [25], who found that $Ni_2Si$ and NiSi form simultaneously when Ni reacts with an amorphous film of Si contaminated with C. Gold can also lead to the simultaneous formation of $Ni_2Si$ and NiSi [26]. A high concentration of oxygen in the metal film may also induce such a change, as shown for other silicides (Mn [27], Mo [28], Pt [29], Co [30]).

In conclusion, the redistribution of Pt associated with the formation of Ni silicide was investigated by the laser-assisted APT of an Ni (5% Pt) film on (1 0 0)Si after heat treatment at 290 °C for 1 h. It has been shown that:

- The formation of $Ni_2Si$ and NiSi occurs simultaneously.
- The Pt redistribution can be measured on the nanometric scale and is relatively complex.
- The snowplow effect of Pt at the $Ni_2Si/Ni_{1-x}Pt_x$ has been clearly demonstrated. It has been explained by a limited solubility of Pt in $Ni_2Si$.
- A rather sharp distribution of Pt at the $Ni_2Si$/NiSi interface has been observed, indicating that an interfacial segregation occurs at this interface.

These results lead to a better understanding of the redistribution of the alloy element on the nanoscale and its effect on the silicide formation.

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