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Atomic-scale redistribution of Pt during reactive diffusion in Ni (5% Pt)–Si contacts

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ABSTRACT

The NiSi silicide that forms by reactive diffusion between Ni and Si active regions of nanotransistors is used nowadays as contacts in nanoelectronics because of its low resistivity. Pt is added to the Ni film in order to stabilise the NiSi phase against the formation of the high-resistivity $NiSi_2$ phase and agglomeration.

In situ X-ray diffraction (XRD) experiments performed on material aged at 350 °C (under vacuum) showed the complete consumption of the Ni (5 at% Pt) phase, the regression of Ni_2Si phase as well as the growth of the NiSi phase after 48 min. Pt distribution for this heat treatment has been analysed by laser-assisted tomographic atom probe (LATAP). An enrichment of platinum in the middle of the NiSi phase suggests that Pt is almost immobile during the growth of NiSi at the two interfaces: Ni_2Si/NiSi and NiSi/Si. In the peak, platinum was found to substitute for Ni in the NiSi phase. Very small amounts of Pt were also found in the Ni_2Si phase close to the surface and at the NiSi/Si interface.

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1. Introduction

The formation of nanometric phases by reactive diffusion between a thin film and a substrate is a fundamental problem that has considerable interest for applications. This is particularly true for silicides due to their use as contacts in microelectronic devices. These silicides are formed through the self-aligned salicidation process.

Thin film reactions [1] are mainly characterized by sequential growth, the lack of certain 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 5% Pt to a Ni film was shown to stabilise the low-resistivity NiSi phase through an increase of approximately 150 °C of the temperature of formation of $NiSi_2$ [3]. As $NiSi_2$ has a higher resistivity, this Pt addition allows for a better integration of NiSi as contacts for nanometric transistors [4]. Over the last few years, there has been an extensive work on determining the effects of alloying element on the formation and stability of Ni silicides [5]. However, the redistribution of alloy elements during the formation of silicide is not well understood. One of the reasons is the difficulty of mapping out the distribution of alloying elements at the nanometric scale. Advanced characterization methods with very high spatial resolution are thus required to analyse the redistribution at the nanoscale. Laser-assisted atom probe tomography (APT) has been developed in this goal [6–9]. Thompson et al. [10] reported the observation of the NiSi and Ni_2Si phases after heat treatment at 350 °C for 10 min. Phase formation and platinum redistribution were previously studied in Ni (5% Pt) films after deposition [11] and after heat treatment at 290 °C [12]. The first study corresponds to silicide formation during deposition and the second to the simultaneous formation of Ni_2Si and NiSi. To complete the study of platinum redistribution, it is important to look at another step in silicide formation, namely the growth of NiSi at the expense of Ni_2Si.

In this paper, we thus studied the redistribution of Pt after a heat treatment at 350 °C for 48 min using the laser-assisted tomographic atom probe (LATAP), X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques.

2. Experimental

Films of polycrystalline Ni, 80 nm thick, containing 5 at% Pt were deposited at room temperature (RT) by co-sputtering of Ni

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and Pt targets on {1 0 0} *p*-doped Si substrates (resistivity 0.01 Ω cm). The $Ni_{1_x}Pt_x$ films were deposited simultaneously on (i) blanket substrate for characterization by XRD and conventional TEM and (ii) high aspect ratio flat-topped {1 0 0} silicon posts for APT analysis. XRD were performed using the Bragg–Brentano geometry [13] and a CuKα source. An isothermal heat treatment was performed in a vacuum chamber attached to the XRD diffractometer. The temperature of 350 °C was reached with a ramp of 30 K/min and the vacuum in the chamber was in the range of 10^{-4} Pa. During annealing at 350 °C, XRD scans of duration 16 min were continuously recorded with a scan rate of 0.6°/min. This made it possible to follow the temporal evolution of peaks diffraction and thus to study in situ silicide formation. Heat treatment was stopped when the Ni_2Si peak intensity started to decrease. In the APT technique, a tip is evaporated atomic layer by atomic layer and analysed by time-of-flight mass spectrometry, allowing a small volume of material (typically $15 \times 15 \times 200\,nm^3$) to be reconstructed in the three dimensions of space, atom by atom, on a nearly atomic scale. A protective layer of Cr (200 nm) was first deposited on the surface of posts to prevent damage due to Ga irradiation. Then the region of interest of silicon posts was transformed into a tip with 30 keV Ga^+ focused ion beam milling. Tips were finally cleaned with a 2 keV gallium beam. The APT experiments were carried out using femtosecond laser pulses (wavelength 515 nm, duration 350 fs) and with the energy of about 0.3 μJ.

3. Results and discussion

Fig. 1 shows the XRD results after deposition and after isothermal annealing at 350 °C for various times. The XRD spectrum for the as-deposited samples shows a peak for $Ni_{1_x}Pt_x$ and a small bump at 47.3° that may correspond to the (2 1 1) NiSi reflexion. This suggests that the NiSi phase is formed during deposition of the nickel alloy on silicon wafers in accordance with our previous results by APT [11]. The phase that forms during deposition at ambient temperature has been reported to be amorphous [16,17]. The low XRD intensity can be in agreement with an amorphous phase but it is very difficult to draw conclusion from such a bump. The formation of this phase can be explained by the large driving force for nucleation during deposition added to the presence of the condensation heat of Ni on Si substrate (approximately 420 kJ/mol [14,15]).

After 16 and 32 min of annealing, the XRD spectra show peaks for Ni_2Si, NiSi, and $Ni_{1_x}Pt_x$. The simultaneous presence of Ni_2Si and NiSi together with the $Ni_{1_x}Pt_x$ solid solution implies a simultaneous growth of these two phases. This confirms the results obtained by APT for a 290 °C heat treatment [12].

Finally, after 48 min of annealing, the intensities of Ni_2Si (2 1 1) and Ni_2Si (0 2 0) decrease. Ni_2Si silicide is consumed to form NiSi silicide and the complete consumption of $Ni_{1_x}Pt_x$ is observed. In order to study the redistribution of Pt during the growth of NiSi at the expense of Ni_2Si, the heat treatment was stopped at this stage.

The TEM image (Fig. 2) obtained for the blanket substrate show that the silicide layers are not uniform and that they exhibit rather large roughnesses. In particular, the Ni_2Si layer varies from a few tens of nm to a few nm in thickness. It is therefore difficult to determine precisely the thickness of Ni_2Si and NiSi phases. The diffraction pattern shows spots belonging to Ni_2Si and NiSi. At this stage, NiSi is thus not anymore amorphous but polycrystalline.

Several tips were extracted from different posts in this sample and analysed by APT. Figs. 3 and 4 show typical LATAP reconstructions obtained for this sample. The distribution of Ni and Si atoms (Fig. 3) exhibits the presence of two intermixed regions: the first region is richer in Ni than the second region. Depth profiles derived from these images (Fig. 3b) reveal that Ni_2Si and NiSi phases formed as a consequence of the reactive diffusion between Ni (5 at% Pt) and the Si substrate at 350 °C. The average concentration of Ni, Si, and Pt elements in the Ni_2Si and NiSi phases is given in Table 1.

The first and second interface, Ni_2Si/NiSi and NiSi/Si (not shown here), appear curved, suggesting a rather large roughness of interfaces in agreement with the TEM images (Fig. 2).

Fig. 3a indicates that Pt is accumulated near the surface of the Ni_2Si phase. The concentration of Pt in Ni_2Si is around 1 at% close

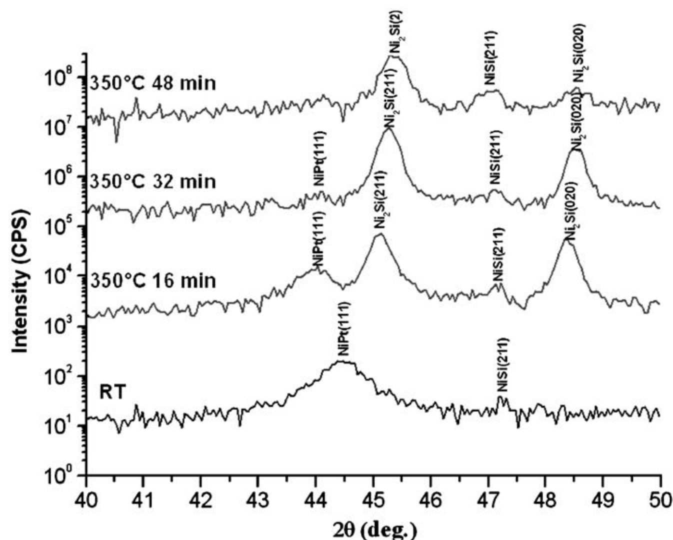

Fig. 1. XRD spectra (CuKα source; Bragg–Brentano geometry) of $Ni_{0.95}Pt_{0.05}$/Si(1 0 0) as deposited and annealed at 350 °C for different times: 16, 32, and 48 min.

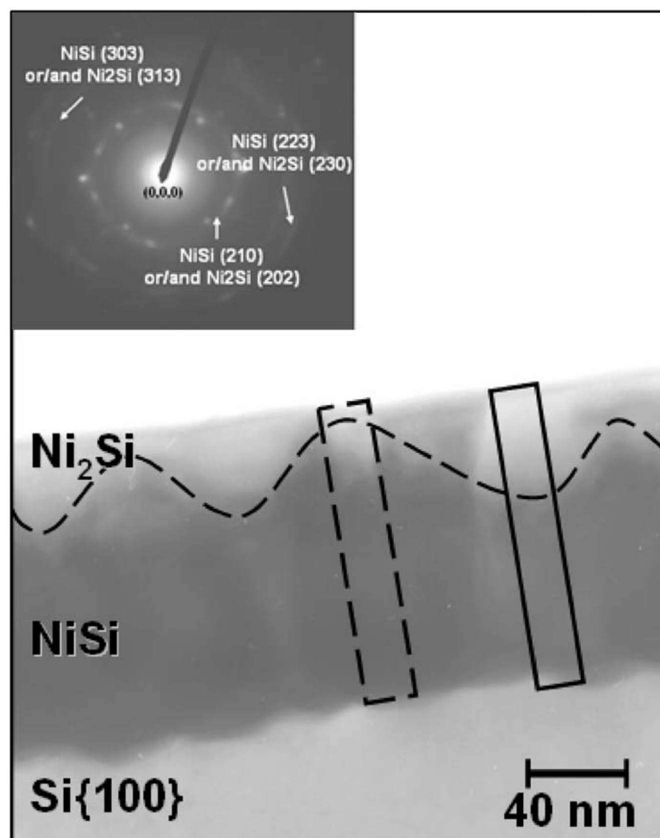

Fig. 2. Conventional TEM image of $Ni_{0.95}Pt_{0.05}$/Si (1 0 0) silicided at 350 °C for 48 min and corresponding diffraction pattern.

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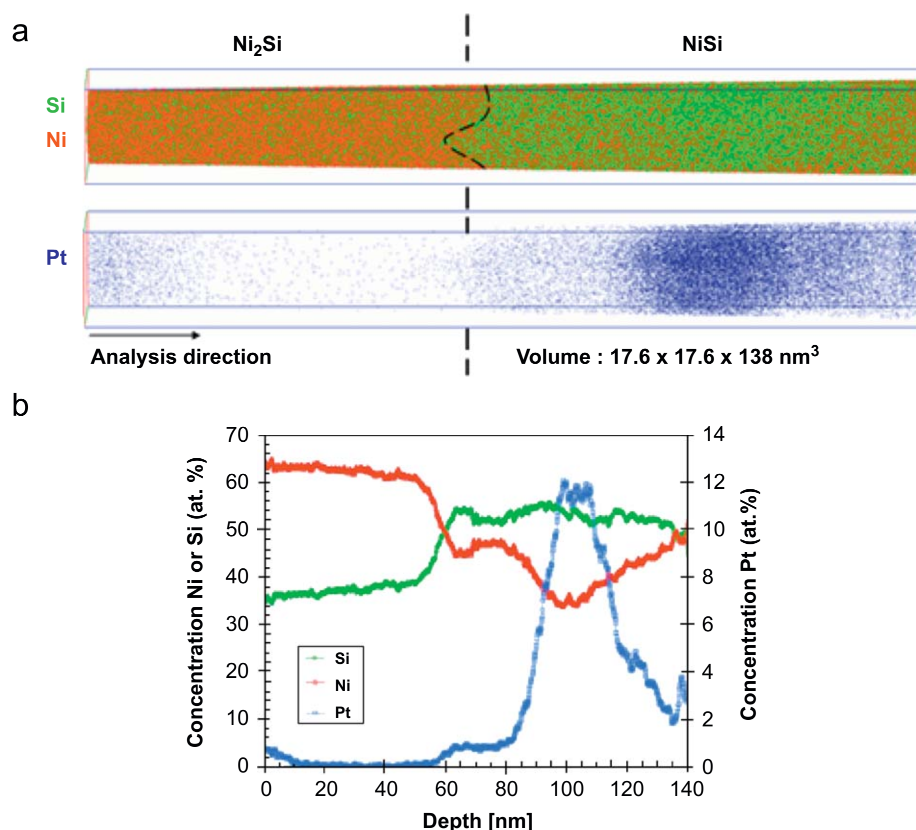

Fig. 3. (a) LATAP elemental maps of silicon (green), nickel (red), and platinum (blue) in the entire volume analysed ($17.6 \times 17.6 \times 138$ nm^3). Pt enrichments in NiSi phase are clearly exhibited. The interface between Ni_2Si and NiSi phases is rough (dashed line); (b) concentration profiles of Ni, Si, and Pt showing the presence of both Ni_2Si and NiSi phases (from left to right). The depth profiles were drawn by moving a small box (1 nm thick and 17.6 nm wide).

to the surface and decreases to 0.1 at% in the bulk of Ni_2Si. This latter value corresponds to the background noise and the concentration is thus certainly lower than 0.1 at%. Almost all Pt is found in the NiSi phase. Moreover, the Pt is not uniformly distributed in NiSi but is concentrated close to the middle of the NiSi layer. The maximum concentration of Pt in NiSi is around 12 at%.

Also, Fig. 3b shows that the concentration of Ni in NiSi decreases at the cost of Pt concentration whereas the Si concentration remains almost constant. This suggests that platinum substitutes for Ni in NiSi. Note that both NiSi and PtSi have the same ordered structure so that Pt is much likely to substitute for Ni in NiSi.

A very small amount of Pt was found at the NiSi/Si interface (not shown here). The Pt level in Si (not shown here) appears to be very low, close to zero (the background noise for Pt in mass spectrum was estimated to be 0.1 at%) in accordance with the solubility of Pt in Si [21].

The reconstruction in Fig. 3 shows a region where Ni_2Si is still present but APT analyses on some silicon posts of the same sample also revealed zones where the phase Ni_2Si was completely consumed. A typical LaWATAP (laser-assited wide-angle tomographic atom probe) reconstruction for a post where there is no further Ni_2Si is shown in Fig. 4. This is in accordance with TEM image (Fig. 2) where the thickness of Ni_2Si was found to vary. Indeed the typical extent of APT volume presented in Figs. 3 and 4 corresponds to the continuous line square and, respectively, dashed-line square drawn on the TEM image. The small volume analysed may feel in a region where the Ni_2Si layer is very thin (or even does not exist) or in a region where Ni_2Si is still present.

Note that the redistribution of Pt in Figs. 3 and 4 is similar. Pt is concentrated in the middle of the NiSi layer and the maximum concentration is around 12%. The Pt is also found to substitute for Ni.

Present results and previous studies make it possible to derive the evolution of the redistribution of Pt during the formation of Ni silicides. A compilation of results at RT, 290 and 350 °C is proposed in the schematic diagram shown in Fig. 5. The redistribution of Pt is intimately linked to silicide formation. Pt is shown to have very different behaviours when the temperature of annealing increases from RT to 350 °C. Increasing the temperature is thought to be equivalent to increasing the ageing time. The assumption is that the driving force for transformation does not change, only the mobility. This equivalence is to be kept in mind in the following.

Silicide formation after deposition was studied by Hoummada et al. [11]. The APT analyses showed the presence of two regions with different compositions between Si and $Ni_{1_x}Pt_x$. These two regions correspond, respectively, to a constant thickness layer of NiSi and to a particle of Ni_2Si. A weak accumulation of Pt was observed at the interface Ni/Ni_2Si and Pt is distributed homogenously in Ni, Ni_2Si, and NiSi. At 290 °C for 1 h, Ni_2Si and NiSi were found together with $Ni_{1_x}Pt_x$ [12]. The simultaneous presence of three phases during silicide growth is rarely observed in thin films. Usually phases appear sequentially [19]. The addition of 5% of Pt in Ni may favour this simultaneous formation. For example, Ma et al. [18] found that Ni_2Si and NiSi form simultaneously when Ni reacts with an amorphous film of Si contaminated with C. For this heat treatment (290 °C, 1 h), Pt was found to accumulate at the $Ni_{1_x}Pt_x/Ni_2Si$ and Ni_2Si/NiSi interfaces. The redistribution of Pt at the $Ni_{1_x}Pt_x/Ni_2Si$ interface

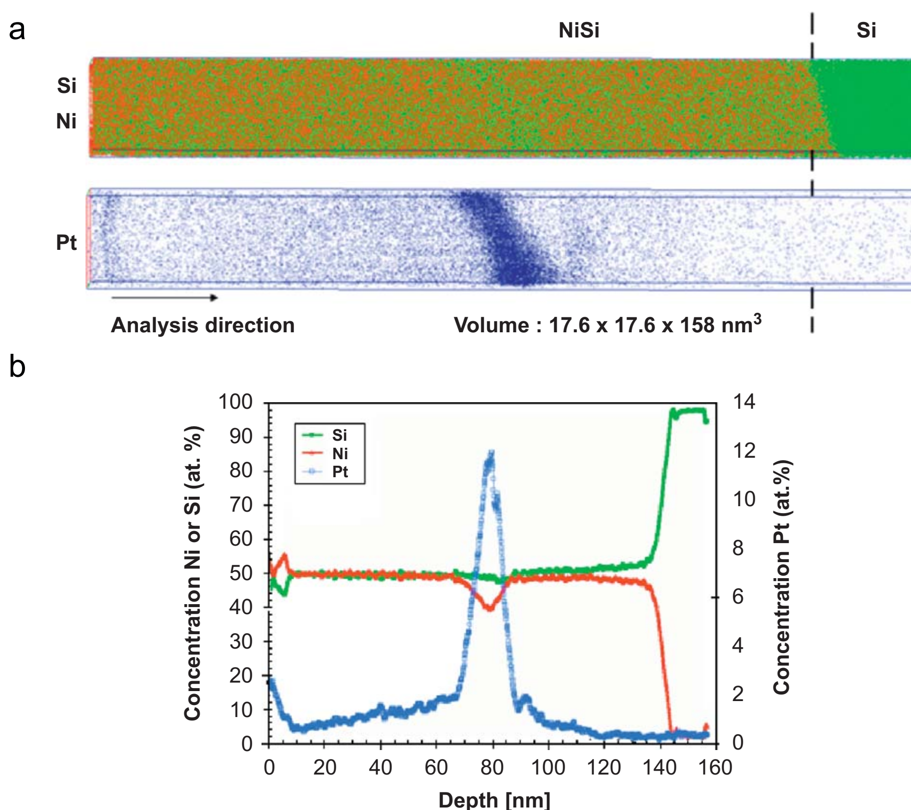

Fig. 4. (a) LAWATAP elemental maps of silicon (green), nickel (red), and platinum (blue) in a small selected volume ($17.6 \times 17.6 \times 158\,nm^3$). Pt enrichments in NiSi phase are clearly exhibited; (b) concentration profiles of Ni, Si, and Pt showing the presence NiSi and Si phases (from left to right). The depth profiles were drawn by moving a small box (1 nm thick and 17.6 nm wide).

Table 1
Concentration values of Ni, Si, and Pt in Ni_2Si and NiSi phases.

Phase	C_{Ni} (at%)	C_{Si} (at%)	C_{Pt} (at%)
Ni_2Si	63.0 ± 0.08	36.9 ± 0.08	0.11 ± 0.006
NiSi	43.0 ± 0.09	52.95 ± 0.09	4.05 ± 0.03

(Fig. 5b) is a clear illustration of the so-called "snowplow effect". This effect consists in rejecting an alloy element during the growth of a phase. Impurities are pushed away by the moving interface and accumulate at one side of the interface. The rejection of Pt in $Ni_{1_x}Pt_x$ when Ni_2Si grows means that the interface $Ni_{1_x}Pt_x/Ni_2Si$ moves towards the $Ni_{1_x}Pt_x$ phase. This rejection may be due to a limited solubility and/or to a limited diffusion in the growing phase. 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 (Ni_2Si has an orthorhombic structure and Pt_2Si has a rhomboedric structure). The accumulation of Pt at the Ni_2Si/NiSi interface is though to be due to interfacial segregation.

At 350 °C, Ni is consumed and NiSi starts growing at the expense of Ni_2Si. Our results show a weak enrichment of Pt at the surface of Ni_2Si. The most plausible explanation for this enrichment is that at temperatures between 290 and 350 °C, Pt, which is mainly at the $Ni_{1_x}Pt_x/Ni_2Si$ interface at 290 °C, diffuse through the grains and grain boundaries of Ni_2Si and accumulate at the Ni_2Si/NiSi interface. This process certainly occurs during the simultaneous growth of Ni_2Si and NiSi at the expense of $Ni_{1_x}Pt_x$. Indeed, when the very last $Ni_{1_x}Pt_x$ layer reacted, some of the Pt in the $Ni_{1_x}Pt_x$ layer stays at the surface and the other part reaches the Ni_2Si/NiSi interface. Experimental evidence for this process was

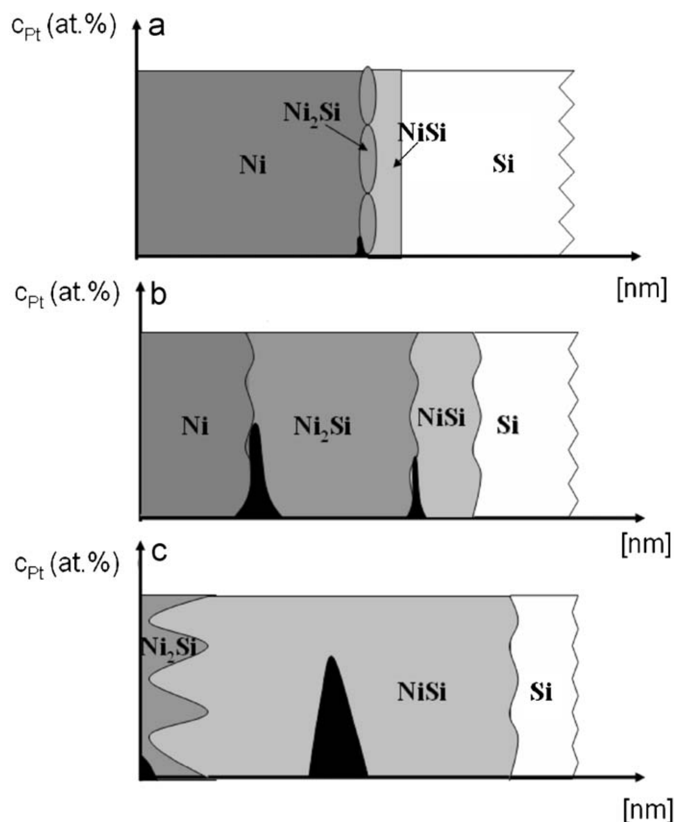

Fig. 5. Schema of platinum distribution in the presence of Ni_2Si and NiSi phases at: (a) RT; (b) 290 °C for 1 h, and (c) 350 °C for 48 min.

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obtained previously [23]. Another characteristic of Pt redistribution at 350 °C is that during NiSi formation, Pt is mainly located close to the middle of NiSi. This is valid during the consumption of Ni_2Si (Fig. 3) and also after the total consumption of Ni_2Si (Fig. 4). The high concentration of Pt in NiSi can be explained by the fact that NiSi and PtSi have the same orthorhombic structure (space group Pnma and structure type MnP) and their lattice dimensions are close (misfits less than 10%): NiSi and PtSi are thus expected to be miscible.

In order to understand why Pt is mainly located in the middle of NiSi, let us come back to the growth process of both Ni_2Si and NiSi films. Finstad [22] has shown using Xe atoms as Kirkendall markers that Ni is the most mobile species when the phase NiSi grows. The NiSi phase thus grows through two elementary processes: (i) consumption of Ni_2Si: $Ni_2Si \rightarrow NiSi+Ni$ (reaction 1) at the Ni_2Si/NiSi interface and (ii) formation of NiSi: $Ni+Si \rightarrow NiSi$ (reaction 2) at the NiSi/Si interface through the diffusion of Ni in NiSi towards this interface. In other words, the Ni_2Si phase is decomposed in NiSi and Ni (reaction 1): the free Ni diffuses in NiSi and reacts with silicon to form NiSi at the other interface (reaction 2). The Pt accumulation in the middle of NiSi is related to the low mobility of Pt in NiSi at 350 °C. The presence of this peak suggests a large growing rate of NiSi with respect to the mobility of Pt in NiSi. Pt thus acts like a marker for NiSi formation. The low diffusivity of Pt in NiSi is also evidenced by the high temperatures (700–800 °C) needed to obtain a homogenous redistribution of Pt in NiSi [23].

The roughness observed in our sample might be explained by the following arguments. The growth of silicide thin film is usually controlled by grain boundary diffusion. For example, Ciccariello et al. [20] showed that the growth of Ni_2Si occurs by Ni grain boundary diffusion. The same behaviour is thought to occur in NiSi. As the diffusion of Ni takes place at grain boundaries, one may thus expect that growth is more rapid when close to grain boundaries. The film thickness is thus larger in these regions (Fig. 3).

4. Conclusions

The redistribution of Pt associated with the formation of Ni silicides at 350 °C was investigated. The main results are the following:

- X-ray diffraction experiments performed on material aged at 350 °C for 48 min showed the complete consumption of the Ni (5 at% Pt) phase and the formation of NiSi phase at the expense of Ni_2Si.
- Pt distribution after this heat treatment was analysed by the APT technique. Platinum enrichment in middle of the phase NiSi suggests that Pt is almost immobile when NiSi grows at the Ni_2Si/NiSi and NiSi/Si interfaces.
- Platinum was found to substitute for Ni in the NiSi ordered phase. A small enrichment of Pt was found close to the surface of Ni_2Si phase and at the NiSi/Si interface.

These results lead us to a better understanding of the redistribution of alloying elements during diffusive Ni–Si reaction and its effect on silicide formation.

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References

[1] F.M. d'Heurle, P. Gas, J. Mater. Res. 1 (1986) 205–221.
[2] F.M. d'Heurle, J. Mater. Res. 3 (1988) 167.
[3] D. Mangelinck, J.Y. Dai, J. Pan, S.K. Lahiri, Appl. Phys. Lett. 75 (1999) 1736.
[4] P.S. Lee, K.L. Pey, D. Mangelinck, J. Ding, A.S.T. Wee, L. Chan, IEEE Electron Dev. Lett. 22 (2001) 568.
[5] C. Lavoie, C. Detavernier Jr., C. Cabral, F.M. d'Heurle, A.J. Kellock, J. Jordan-Sweet, J.M.E. Harper, Microelectron. Eng. 83 (2006) 2042.
[6] G.L. Kellogg, T.T. Tsong, J. Appl. Phys. 51 (2) (1980) 1184–1193.
[7] T.T. Tsong, S.B. McLane, T. Kinkus, Rev. Sci. Instrum. 53 (9) (1982) 1442–1448.
[8] B. Deconihout, F. Vurpillot, B. Gault, G. Da costa, M. Bouet, A. Bostel, A. Hideur, G. Martel, M. Brunel, D. Blavette, Surf. Interface Anal. 38 (2006).
[9] B. Gault, F. Vurpillot, M. Gilbert, A. Vella, A. Menand, D. Blavette, B. Deconihout, Rev. Sci. Instrum. 77 (2006) 043705.
[10] K. Thompson, J.H. Bunton, Th. Kelly, D.J. Larson, J. Vac. Sci. Technol. B 24 (2006) 421.
[11] K. Hoummada, E. Cadel, D. Mangelinck, C. Perrin, B. Deconihout, D. Blavette, Appl. Phys. Lett. 89 (2006) 181905.
[12] O. Cojocaru-Miredin, D. Mangelinck, K. Hoummada, E. Cadel, D. Blavette, B. Deconihout, C. Perrin-Pellegrino, Scr. Mater. 57 (2007) 373–376.
[13] M. Gross, S. Haaga, H. Fietzek, M. Herrmann, W. Engel, Mater. Sci. Forum 278–281 (1998) 242–247.
[14] D. Mangelinck, K. Hoummada, O. Cojocaru-Mirédin, E. Cadel, C. Perrin-Pellegrino, D. Blavette, Microelectron. Eng. (2008).
[15] R. Stull, G.C. Sinke, Thermodynamic Properties of the Elements Vol. 18, American Chemical Society, Washington, D.C., 1956.
[16] L.A. Clevenger, C.V. Thompson, J. Appl. Phys. 67 (1990) 1325.
[17] U. Gösele, K.N. Tu, J. Appl. Phys. 66 (1989) 2621.
[18] E. Ma, W.J. Meng, W.L. Johnson, M.-A. Nicolet, Appl. Phys. Lett. 53 (1988) 2033.
[19] F. Nemouchi, D. Mangelinck, C. Bergam, P. Gas, Appl. Phys. Lett. 86 (2005) 041903.
[20] J.C. Ciccariello, S. Poise, P. Gas, J. Appl. Phys. 67 (1990) 3315.
[21] H. Zimmermann, H. Ryssel, Appl. Phys. A 55 (1992) 121.
[22] T.G. Finstad, Phys. Status Solidi A 63 (1981) 223.
[23] D. Mangelinck, J.Y. Dai, S.K. Lahiri, C.S. Ho, T. Osipowicz, Mater. Res. Soc. 564 (1999) 163.

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