Functional Materials 20, No.3 (2013)

Formation and thermal stability of NiSi phase in Ni(30 nm)/Pt(2 nm; 6 nm)/$Si_{ep.}$ (50 nm)/Si(001) thin film systems

Iu.N.Makogon, E.P.Pavlova, S.I.Sidorenko, G.Beddies**, D.L.Beke*, A.Csik, T.I.Verbitska, E.V.Fihurna, R.A.Shkarban***

National Technical University of Ukraine "Kyiv Polytechnic Institute",
37 Prospect Peremogy, 03056 Kyiv, Ukraine
*University of Debrecen, Department of Solid State Physics,
H-4010 Debrecen, P.O. Box 2, Hungary
**Institute of Physics, Chemnitz University of Technology,
70 Reichenhainer Str., 09126, Germany
***Institute of Nuclear Research of the Hungarian Academy of Sciences
(ATOMKI), H-4001 Debrecen, P.O.Box 51, Hungary

Received February 20, 2013

The influence of Pt on solid state reactions in Ni(30 nm)/Pt(x)/$Si_{ep.}$(50 nm)/ Si(001) (x = 2 nm, 6 nm) nanodimensional films has been investigated. The layers of Pt and Ni were produced by magnetron sputtering technique on the epitaxially grown 50 nm Si layer on the top of the monocrystalline Si(001) substrate at the room temperature. Isochronal rapid thermal annealing of the samples was carried out in nitrogen atmosphere for 30 s in (450–900)°C temperature range. In the as-deposited films no phase formations were observed. During heat treatments thermally activated solid state reactions began by formation of intermediate silicide phase of Ni_2Si for x = 2 nm, but the formation of this Ni reach phase was hindered for x = 6 nm. Increasing the annealing temperature up to 600°C, independently from the thickness of the intermediate Pt layer, NiSi, PtSi compounds as well as $Ni_{1-x}Pt_xSi$ solid solution have been formed. Two-layered heterostructure has been observed for x = 6 nm: complex polycrystalline $Ni_{1-x}Pt_xSi$ phase formed close to the surface, below which the NiSi phase was situated. Decomposition of $Ni_{1-x}Pt_xSi$ silicide to the NiSi (and PtSi) phases was observed after annealing above 650°C and 850°C. Si enrichment at the surface of the $Ni_{1-x}Pt_xSi$, NiSi and $NiSi_2$ phases is clearly observed on secondary neutral mass spectrometry depth profiles, which is interpreted as a consequence of the fast diffusion of Si along the grain boundaries.

Исследовано влияние Pt на твердотельные реакции в наноразмерных пленках Ni(30 нм)/Pt(x)/ $Si_{эп}$.(50 нм)/Si(001) (где x = 2 нм, 6 нм). Слои Pt и Ni получены магнетронным осаждением на слой Si толщиной 50 нм, эпитаксиально выращенный на монокристаллической подложке Si(001) при комнатной температуре. Скоростной термический отжиг образцов проводился в атмосфере азота в интервале температур (450–900)°C в течение 30 с. В осажденных пленках фазообразование не наблюдалось. В процессе термической обработки термически активированные твердотельные реакции начинаются с образования промежуточной силицидной фазы Ni_2Si для x= 2 нм, но для x = 6 нм формирование этой обогащенной никелем фазы затруднено. Увеличение температуры отжига до 600°C, независимо от толщины промежуточного слоя Pt, приводит к формированию фаз NiSi и PtSi и твердого раствора $Ni_{1-x}Pt_xSi$. Для x = 6 нм наблюдалась двухслойная гетероструктура: ближе к поверхности формировалась сложная поликрис-

таллическая фаза $Ni_{1-x}Pt_xSi$, ниже которой располагалась фаза NiSi. После отжигов при температуре 650°C и 850°C силицид $Ni_{1-x}Pt_xSi$ распадался на фазы NiSi и PtSi. Концентрационные профили, полученные методом масс-спектрометрии вторичных нейтралей, продемонстрировали обогащение поверхностных слоев кремнием, что можно объяснить быстрой диффузией Si вдоль границ зерен.

Утворення і термічна стійкість фази NiSi у нанорозмірній плівковій композиції Ni(30 нм)/Pt(2 нм; 6 нм)/$Si_{еп.}$(50 нм)/Si(001). *Ю.М.Макогон, О.П.Павлова, С.І.Сидоренко, Г.Бедділс, Д.Л.Беке, А.Чик, Т.І.Вербицька, О.В.Фігурна, Р.А.Щкарбань.*

Досліджено вплив Pt на твердотільні реакції у нанорозмірних плівках Ni(30 нм)/Pt(x)/$Si_{еп.}$(50 нм)/ Si(001) (де x = 2 нм, 6 нм). Шари Pt і Ni отримано магнетронним осадженням на шар Si товщиною 50 нм, епітаксіально вирощений на монокристалічній підкладці Si(001) при кімнатній температурі. Швидкісний термічний відпал зразків проводився в атмосфері азоту в інтервалі температур (450–900)°C протягом 30 с. У осаджених плівках фазоутворення не спостерігалося. В процесі термічної обробки термічно активовані твердотільні реакції починаються з утворення проміжної силіцидної фази Ni_2Si для x = 2 нм, але для x = 6 нм формування цієї збагаченої нікелем фази утруднене. Збільшення температури відпалу до 600°C, незалежно від товщини проміжного шару Pt, призводить до формування фаз NiSi і PtSi і твердого розчину $Ni_{1-x}Pt_xSi$. Для x = 6 нм спостерігалася двошарова гетероструктура: ближче до поверхні формувалася складна полікристалічна фаза $Ni_{1-x}Pt_xSi$, нижче за яку розташовувалася фаза NiSi. Після відпалу при температурі 650°C і 850°C силіцид $Ni_{1-x}Pt_xSi$ розпадався на фази NiSi і PtSi. Концентраційні профілі, отримані методом мас-спектрометрії вторинних нейтралей, продемонстрували збагачення поверхневих шарів кремнієм, що можна пояснити швидкою дифузією Si уздовж меж зерен.

1. Introduction

Application of thermally stable, nanodimensional transition metal silicides as functional elements offers the solution of the following increase of degree of integration, miniaturization of electronic devices and their expected exploitation [1–3]. The silicides are formed in solid state reactions between the metallic film and the silicon substrate. In the case of Ni metallic film deposited on Si substrate, consecutive formation of three silicide phases takes place: Ni_2Si and NiSi at intermediate temperatures (200–350)°C and $NiSi_2$ at 750°C. The nickel monosilicide — NiSi, which is an intermediate phase in the solid state reaction between Ni and Si, appears to be the best, low resistive (~10 μΩ·cm) material in microelectronics for the transition to nanotechnology [1, 2]. The formation of NiSi is diffusion controlled process, which provides smooth planar interface. During its formation the consumption of the silicon substrate is about 30 % less than for the formation of other silicides, ($CoSi_2$ and $TiSi_2$), which, from the point of view of transition to nanodimensions, makes it acceptable for preparation of *p-n* contacts. The phase transformation of NiSi into $NiSi_2$, having higher electric resistivity, is a problem for the application of NiSi [4–7]. Since about 75 % of technological operations in the productions of microelectronic devices take place at relatively high temperatures after formation of the silicide layer we are faced with the topical requirement to increase the thermal stability of NiSi and avoid the transformation of this phase to the high resistivity $NiSi_2$ phase which is the end product of the solid state reaction between Ni and Si.

Solid state reactions between the film of Ni and Si substrate were investigated by different groups. It was shown that addition of few percent of Pt to Ni, besides the formation of $Ni_{0.95}Pt_{0.05}$ alloy, significantly enhanced the thermal stability of NiSi [7–12]. Decrease of the size of the electronic devices requires deeper understanding of processes related to the decrease of the thickness of the silicide film. In this article results on nanoscale solid state reactions in Ni(30 nm)/Pt(x)/$Si_{ep.}$(50 nm)/ Si(001) (x = 2 nm, 6 nm) multi-layered system as well as on the thermal stability of NiSi phase are described. The role of the intermediate 2 nm and 6 nm thick Pt layer is in the main focus; its effect on the diffusion, thermally activated phase formation processes is investigated. Indeed our work differs from the previous ones because we deposited Pt layer on the epitaxial, 50 nm thick Si layer, grown on the single crystalline (001) Si substrate.

2. Experimental

Epitaxial 50 nm thick Si layer was deposited first (at 800°C, 10^{-9} mbar), then it was

Table. Different phases in Ni(30 nm)/Pt(x)/$Si_{epit.}$(50 nm)/ Si(001) (x = 2 nm, 6 nm) films after the deposition and heat treatments in nitrogen in 450–900°C temperature interval

Sample	After deposition	Temperature of the heat treatment, °C					
		450–500	550	600	650–800	850	900
Ni(30 nm)/Pt(6 nm)/ $Si_{ep.}$(50 nm)/ Si(001)	Ni Pt	NiSi PtSi	NiSi PtSi	$Ni_{1-x}Pt_xSi$ NiSi	NiSi PtSi	NiSi PtSi	$NiSi_2$ PtSi
Ni(30 nm)/Pt(2 nm)/ $Si_{ep.}$(50 nm)/ Si(001)	Ni	Ni_2Si NiSi	NiSi PtSi	NiSi PtSi	$Ni_{1-x}Pt_xSi$ NiSi	$Ni_{1-x}Pt_xSi$ NiSi $NiSi_2$ PtSi	NiSi $NiSi_2$ PtSi

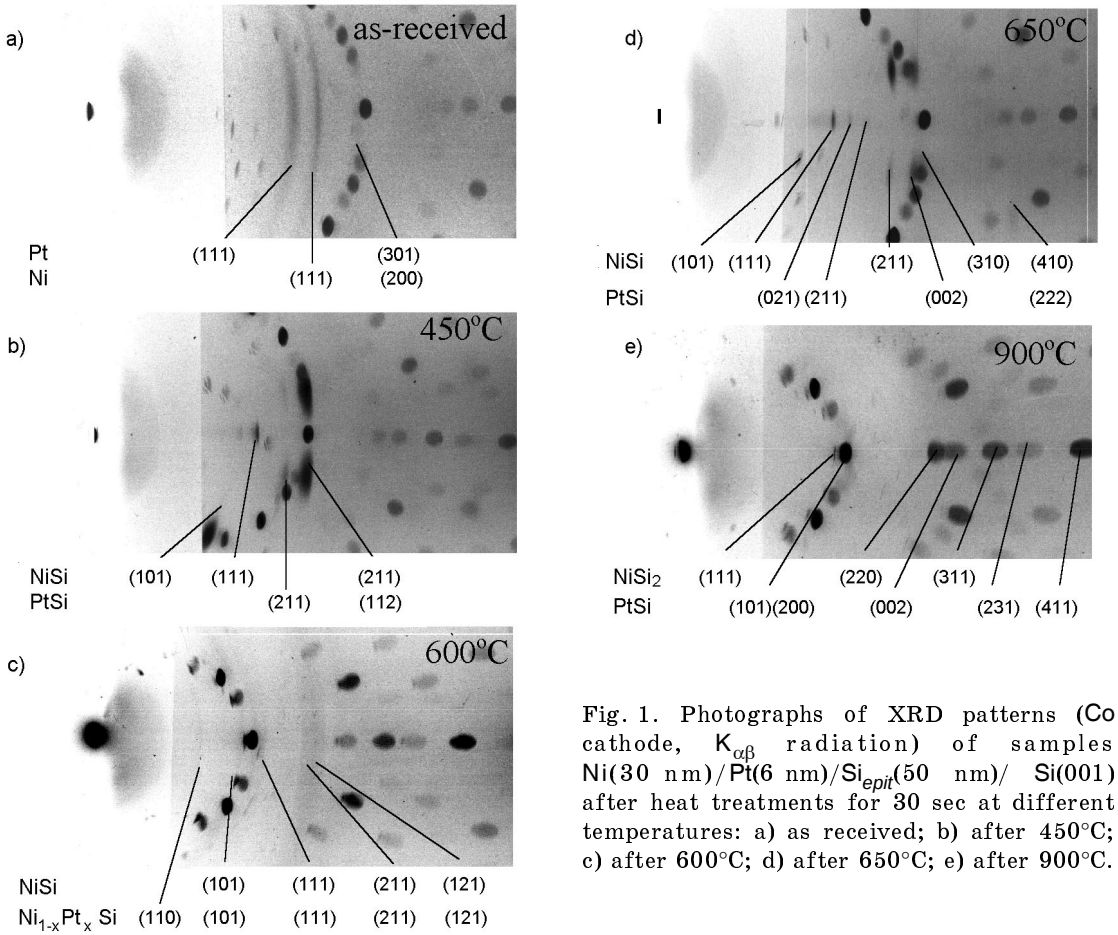

Fig. 1. Photographs of XRD patterns (Co cathode, $K_{\alpha\beta}$ radiation) of samples Ni(30 nm)/Pt(6 nm)/Si_{epit}(50 nm)/ Si(001) after heat treatments for 30 sec at different temperatures: a) as received; b) after 450°C; c) after 600°C; d) after 650°C; e) after 900°C.

exposed to ambient, etched in HF and put into the sputtering chamber. Nanosized Ni(30 nm)/Pt(x)/$Si_{ep.}$ (50 nm)/Si(001) films, x = 2 nm and 6 nm, were produced by magnetron sputtering technique depositing 30 nm Ni and 2 nm or 6 nm Pt layers on the epitaxially grown 50 nm thick Si layer at room temperature. The substrate was single crystalline (001)Si. Isochronal heat treatments of the samples in nitrogen atmosphere were carried out between 450°C and 900°C in 30 s steps. The solid state reactions were investigated by X-Ray Diffraction (XRD), and resistometry. Furthermore, it was shown recently that depth profiling by SNMS technique is a very suitable tool for the investigation of nanoscale solid state reactions [13]. Thus we investigated our samples by this technique too. The yield versus sputtering time SNMS functions were converted by a usual procedure to composition versus depth profiles [13].

For the determination of the phases Debye-Scherrer photographs of the XRD

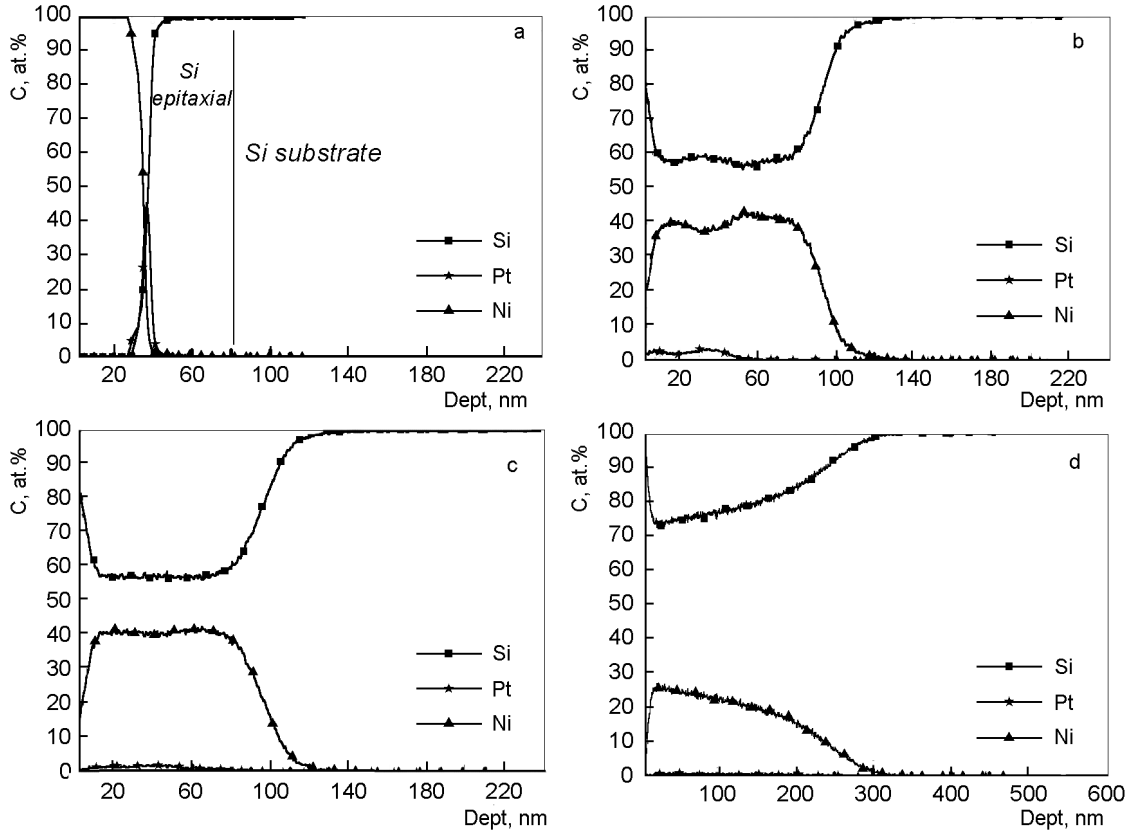

Fig. 2. Composition profiles of the components in Ni(30 nm)/Pt(6 nm)/$Si_{ep.}$(50 nm)/ Si(001) film after the deposition (a) and heat treatments at 450°C (b), 650°C (c) and 900°C (d) for 30 s.

patterns, obtained by using Co anode, were taken (with long exposition times of 36 h duration) and the electrical resistance was also measured by the four point method.

3. Results and discussion

The results of the phase analysis, carried out on the basis of the XRD data, are collected in Table. In the XRD patterns of the as-received samples the reflections of Ni, independently of the thickness of Pt layer, and the reflections of Pt (in samples with 6 nm thick Pt layer) could be identified (Fig. 1a). The results clearly indicate that there were no formations of new phase during the sample preparation. Sharp and smeared out Debye rings refer to a disperse structure of the films.

Composition depth profiles, obtained from SNMS show sharp interfaces between Ni and Pt confirming that there was no intermixing during deposition (Figs. 2a and 3a).

Fig. 1b shows that at 450°C textured NiSi and PtSi phases formed in system with 6 nm thick intermediate Pt layer. Heat treatment at 600°C leads to a qualitative change in the XRD picture (Fig. 1c): ternary polycrystalline $Ni_{1-x}Pt_xSi$ phase have been formed. The reflections of this phase in the XRD are continuous lines. By increasing the annealing temperature up to 650°C the ternary silicide $Ni_{1-x}Pt_xSi$ decomposes into NiSi and PtSi (Fig. 1d and see also Table). After further annealing in 650–800°C interval, only textured NiSi and PtSi phases can be identified. The phase transformation of NiSi silicide into the final product $NiSi_2$ can be observed after heat treatment at 850–900°C (Fig. 1e and Table). The amount of the PtSi phase, according to the weak reflections in Fig. 1, was always much less than the amount of the NiSi phase.

According to Fig. 2b, at 450°C interdiffusion of Ni, Pt and Si takes place and the reaction layer formed is about 80 nm thick. It is interesting that Pt is present in the first part of the reaction layer (closer to the free surface up to about 40–50 nm) and visibly replaces Ni atoms, as compared to the second part of the reaction layer. The average composition of the reaction layer corresponds to $Ni_{0.4}Si_{0.6}$. Furthermore there is an enrichment (segregation) of Si at the free surface.

From the composition depth profiles obtained after 650°C (Fig. 2c) it can be seen

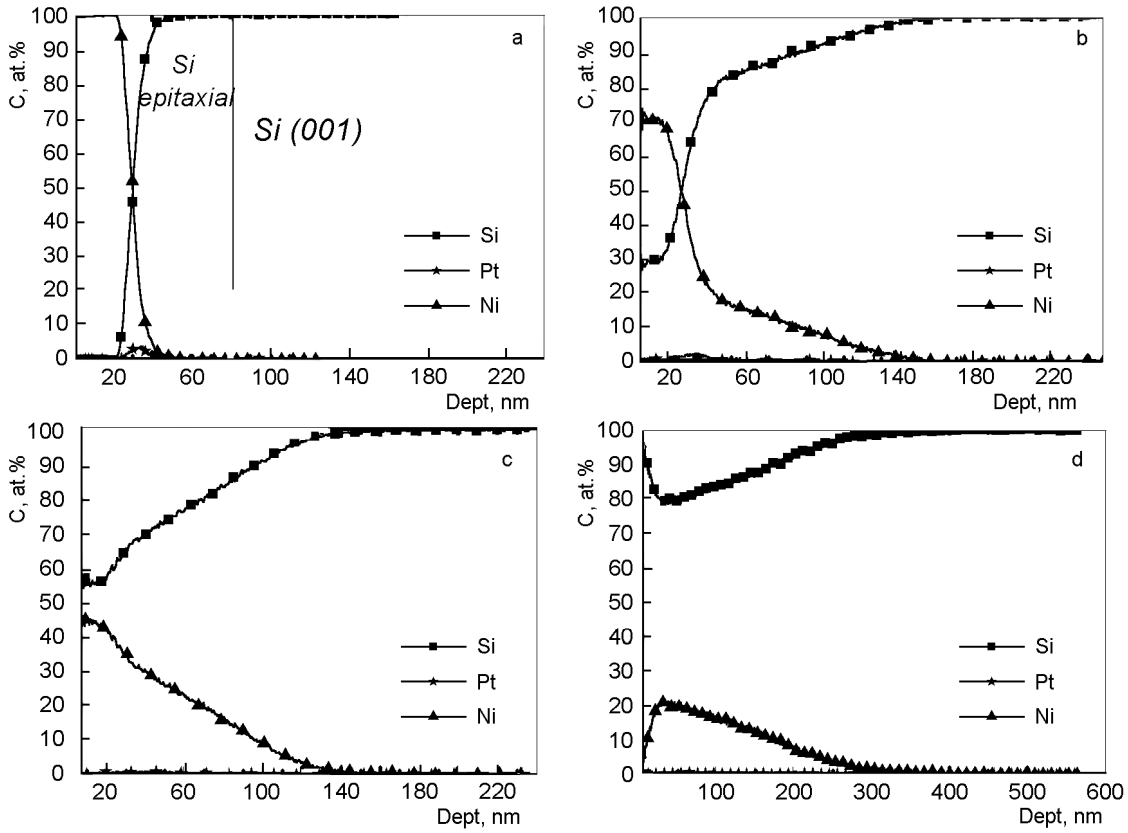

Fig. 3. Composition profiles of the components in Ni(30 nm)/Pt(2 nm)/$Si_{epit.}$(50 nm)/ Si(001) film after the deposition (a) and heat treatments at 450°C (b), 650°C (c) and 900°C (d) for 30 s.

that, besides the increase of the reaction layer thickness, Pt distribution became more homogeneous in it, but still there is a step in Pt composition at about 70 nm. From the SNMS profile taken after 650°C, the phase with a composition about $Ni_{0.41}Pt_{0.02}Si_{0.57}$ of 70 nm thick and Pt-free layer with the composition of about $Ni_{0.42}Si_{0.58}$ of 30 nm thick can be seen (Fig. 2c). Taking into account the accuracy of the determination of such a low Pt concentrations by SNMS, one can only conclude that the Pt content of the ternary phase is between 2 % and 5 %.

After heat treatment at 900°C, the depth profile shows that Si reach phase (with a composition corresponding to Si-rich $NiSi_2$) has been formed and diffusion of Ni can also be observed from the silicide layer into the Si one (Fig. 2d). This leads to increase of Si content in the silicide and to the change of its phase composition. The thickness of this Si reach phase is about 200 nm and Pt is homogeneously distributed in the reaction layer.

It can be seen in Fig. 4 that the electrical resistance of the samples remains constant in the interval of (450–550)°C, which is followed by a "peak" between 550°C and 650°C. According to the XRD data a peak in the electrical resistance can be attributed to the formation of a ternary polycrystalline $Ni_{1-x}Pt_xSi$ phase.

After annealing in (650–850)°C interval the electrical resistance becomes again equal to the resistance of the samples heat treated between 450–550°C. According to the XRD data only NiSi and PtSi phases are present and there is no detectable change in the electrical resistance. By increasing the annealing temperature up to 900°C a sharp increase in the electric resistance appears which could be the result of a formation of the high resistive $NiSi_2$ disilicide (Fig. 4) and/or the disintegration of the film.

It is worth noting that the formation of the above ternary $Ni_{1-x}Pt_xSi$ phase was also observed in [6–8] and [14–17]. For instance it was shown in [14] that before the formation of $Ni_{1-x}Pt_xSi$ ternary phase, during heat treatments at low temperatures, a two-layered heterostructure of $Ni_{1-x}Pt_xSi$–$Ni_{1-y}Pt_ySi$ forms, from which the homogeneous ternary phase develops at higher temperatures. The formation of this ternary phase can be explained by the Hume-Rothery's rules: in binary solid alloys extended solid solubility

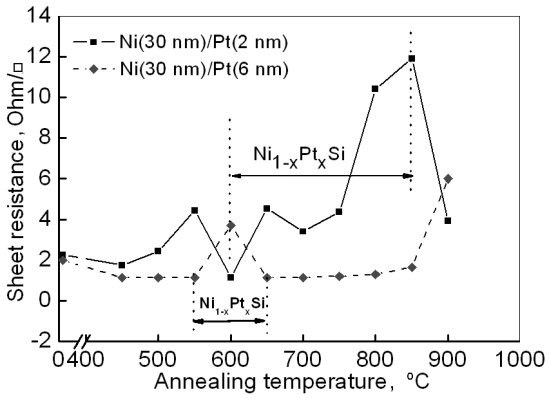

Fig. 4. Temperature dependences of the resistance of Ni(30 nm)/Pt(x)/$Si_{ep.}$(50 nm)/ Si(001) (x = 2 nm, 6 nm) samples.

exist only if the components have the same crystalline structure and parameters of their unit cells differs by less than 15 % [14, 15]. Pt with silicon forms PtSi phase which has the same crystalline structure (orthotombic MnP type with *Pnma* space group) as the NiSi silicide. Since both above silicides have identical crystalline structure and the difference in the lattice parameters is inside 15 % limit, thus NiSi–PtSi solid solution, with complete solute solubility, may form. The lattice parameter of this ternary $Ni_{1-x}Pt_xSi$ phase depends linearly on Pt concentration between the lattice parameters of NiSi and PtSi. The formation of the ternary phase can lead to increase of the electrical resistivity in (550–600)°C temperature interval (Fig. 4).

The phase transformations in the system with 2 nm thick intermediate Pt layer start under heat treatment at 450°C. As a result of interdiffusion, Ni_2Si and NiSi intermediate phases grow (Fig. 5a). Increasing the annealing temperature up to 500°C there were no changes in the diffraction pictures (Table). This indicates that the phases in the investigated films did not change. After heat treatment at 600°C polycrystalline NiSi and PtSi phases can be indentified with textured structure, as it is illustrated in Fig. 5b. The amount of the PtSi phase, according to the weak reflections in Fig. 5, was always much less than the amount of the NiSi phase.

Heat treatment at 650°C leads to a further change of the XRD pictures observed (Fig. 5c): polycrystalline ternary $Ni_{1-x}Pt_xSi$ phase, free of the texture, is detected. This coexists with the NiSi phase. In the XRD picture continuous lines as well dashed reflections correspond to $Ni_{1-x}Pt_xSi$ as well as NiSi phases, respectively.

After increasing the annealing temperature up to 850°C the $Ni_{1-x}Pt_xSi$ and NiSi phases were detected and the $NiSi_2$ phase was formed too i.e. NiSi silicide partially transformed to $NiSi_2$ disilicide. As it can be seen from Table $Ni_{1-x}Pt_xSi$ is present in (650–850)°C interval.

The results of SNMS depth profiling after annealing at 450°C, 650°C and 900°C

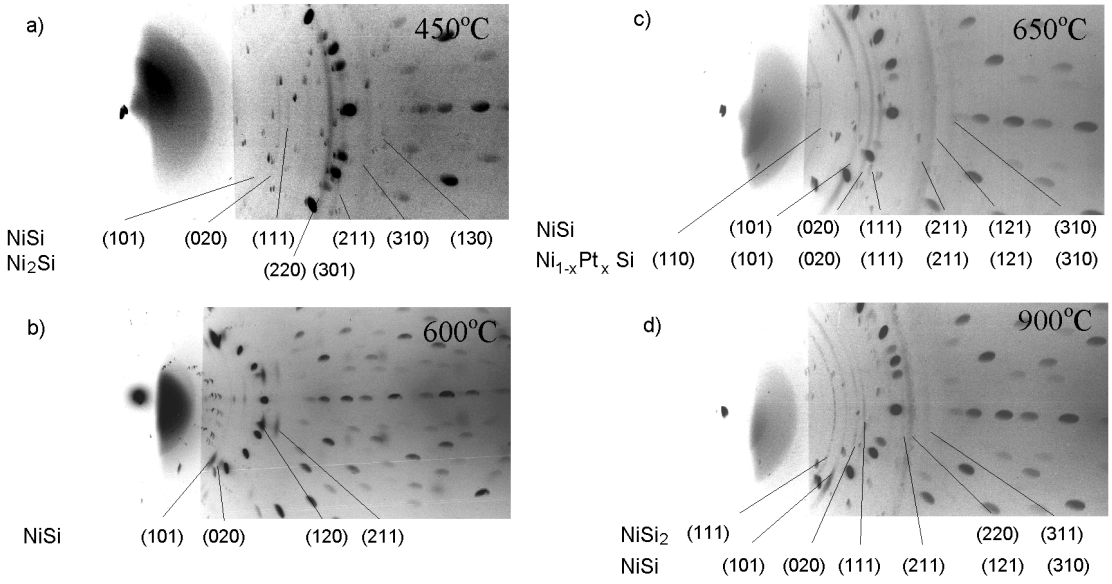

Fig. 5. Change of the phases in Ni(30 nm)/ Pt(2 nm)/$Si_{ep.}$(50 nm)/Si(001) films during heat treatments in nitrogen atmosphere at 450°C (a), 600°C (b), 650°C (c), 900°C (d).

are shown in Fig. 3 (3b, 3c and 3d, respectively). Fig. 3b illustrates that Ni_2Si layer (about 15 nm thick) has been formed at 450°C and there is a relatively long tail at deeper penetrations (similarly as in Figs. 3c and 3d). Fig. 3c shows that NiSi layer (with composition of $Ni_{0.45}Si_{0.55}$) is present close to the surface. After heat treatment at 900°C, the formation of $NiSi_2$ disilicide layer is observed. It is difficult to get a definite conclusion on Pt distribution (the amount of Pt is close to the detection limit) but it seems to be homogeneously distributed inside the reaction layer (Fig. 3b–3d).

It can be seen from Fig. 4 that there is an increase of the electric resistance, after the heat treatment at 500°C, reaching a peak at 550°C. This can be attributed to the formation of the ternary alloy (Table). At 600°C it drops down and then gradually increases up to 850°C. The drop of the resistivity above 850°C in Fig. 4 can be attributed to the disappearance of the ternary phase (see Table) which is in accordance with the results of [8].

The experimental results presented in this paper show that the presence of the intermediate Pt layer stabilizes the NiSi phase and hinders the formation of $NiSi_2$ phase in Ni(30 nm)/Pt(6 nm)/$Si_{ep.}$(50 nm)/Si(001) samples. The intermediate Pt layer of 6 nm thick, which is deposited on the silicon substrate, is five times less than the thickness of the 30 nm thick Ni layer, and thus the concentration of Pt, as an alloying component in the Ni, was not higher than 20 %. In [7, 8, 15–17] the increased thermal stability of NiSi has been discussed. For example the authors of [8] explained an increase of the thermal stability of the NiSi phase formed in the Ni layer alloyed by Pt, by two reasons: 1) formation of the high texture Ni(Pt)Si films considerably decreases the interface energy σ of (NiSi/Si) interface and increases the interface energy change $\Delta\sigma$ of $NiSi + Si \rightarrow NiSi_2$ reaction; 2) formation of the NiSi(PtSi) solid solution decreases the formation Gibbs free energy, ΔG(NiSi), and thus results in smaller absolute value of ΔG for $NiSi + Si \rightarrow NiSi_2$ reaction. Consequently Pt additions increase the activation energy of nucleation of $NiSi_2$, which is proportional to $\Delta\sigma^3/\Delta G^2$, and thus enhances the thermal stability of NiSi.

Our results suggest that in the nanolayered Ni/Pt/Si(001) system the role of Pt intermediate layer in the diffusional phase formation is analogous to the role of Pt in (Ni + Pt)/Si(001) system with Ni layer alloyed with Pt. The only difference is that in Ni/Pt/Si(001) system with the thicker (6 nm) Pt intermediate layer the textured NiSi and PtSi phases have been formed, having lower electrical resistivity and higher thermal stability than in the system with thinner (2 nm) Pt intermediate layer.

5. Conclusions

It was shown that the presence of the intermediate Pt layer stabilizes NiSi phase and hinders the formation of $NiSi_2$ phase. The complex $Ni_{1-x}Pt_xSi$ phase forms in the system with 6 nm thick Pt layer at 600°C, which is lower by 50°C than in the system with 2 nm thick Pt. The phase of $Ni_{1-x}Pt_xSi$ decomposes into NiSi and PtSi phases in the samples with 2 nm Pt after heat treatment at 850°C, while in the samples with 6 nm thick Pt this took place after heat treatment at 650°C. In the both cases (2 nm and 6 nm Pt layers) SNMS profiles show Si enrichment at the free sample surface (except the result obtained after 450°C for 2 nm intermediate Pt layer, where Ni_2Si phase was formed at the surface) and the increase of electrical resistance could be attributed to the presence of the ternary $Ni_{1-x}Pt_xSi$ phase. Introduction of the intermediate Pt layers between Ni and Si(001) substrate increases the thermal stability of NiSi as compared to the stability of this phase Ni/Si(001) system without Pt by 100°C (up to 850°C).

Acknowledgements. The authors gratefully acknowledge the support of the Hungarian Scientific Research Fund (OTKA) through Grant CK 80126 and the bilateral Hungarian-Ukrainian TeT project No.UA-4/2008. The work is also supported by TBMOP 4.2.1-08/1-2008-003 project. This project is implemented through the New Hungary Development Plan co-financed by the European Social Fund, and the European Regional Development Fund. Also this project is supported by the Ministry of Education and Science of Ukraine (Grant M84/2009).

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