



HAL
open science

Lateral growth of NiSi at the θ -Ni₂Si/Si(100) interface: Experiments and modelling

Dominique Mangelinck, M. El Kousseifi, K. Hoummada, F. Panciera, T.
Epicier

► To cite this version:

Dominique Mangelinck, M. El Kousseifi, K. Hoummada, F. Panciera, T. Epicier. Lateral growth of NiSi at the θ -Ni₂Si/Si(100) interface: Experiments and modelling. *Microelectronic Engineering*, 2018, 199, pp.45-51. 10.1016/j.mee.2018.07.014 . hal-01916302

HAL Id: hal-01916302

<https://hal.science/hal-01916302v1>

Submitted on 14 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Lateral growth of NiSi at the θ -Ni₂Si/Si(100) interface: experiments and modelling

D. Mangelinck¹, M. El Kousseifi¹, K. Hoummada¹, F. Panciera¹, T. Epicier²

1) CNRS, Aix Marseille Univ., IM2NP, service 142, Faculté de saint Jérôme, 13397 Marseille, France

2) Univ. Lyon, INSA de Lyon, MATEIS, UMR 5510, Bât. B. Pascal, F-69621 Villeurbanne

Corresponding author: dominique.mangelinck@im2np.fr

Abstract

Nucleation and lateral growth become more and more important steps for the growth of a phase (silicide, intermetallic...) when its thickness is in the range or below 10 nm. It might become crucial for contact in microelectronics that are in this range of thickness for actual devices and affect the properties contacts in different part of devices. For reaction between 10 nm Ni(10%Pt) and (100)Si, it was shown that NiSi grows by nucleation and lateral growth at the epitaxial θ -Ni₂Si/Si interface and forms precipitates having a large aspect ratio (large diameter and small thickness) were observed. In this work, the precipitate shape as well as the shape of the different interfaces close to the triple line are reproduced by using the model of Pasichnyy and Gusak for θ -Ni₂Si/Si interfaces that are either curved or straight. The deduced interfacial energies and kinetic parameters enabling to obtain the characteristics of the precipitates are discussed and compared to the ones obtained by the model of El Kousseifi et al. The conditions for mechanical equilibrium and the implication for the contact formation are discussed.

Keywords

Lateral growth; interfacial energy; triple line; model; kinetics;

1. Introduction

In thin film, the formation of a single product phase by solid state reaction occurs in several steps: the thickening by growth perpendicular to the interface usually controls the later stages but it has been shown that the first step corresponds to nucleation and lateral growth [1]. Indeed two peaks were found by differential scanning calorimetry (DSC) for the formation of a single product phase revealing a two steps growth, (i) nucleation/lateral growth and (ii) thickening, for silicides [1] [2] [3] [4] and other compounds [5] [6]. A few other experimental evidence for lateral growth were also found. Using transmission electron microscopy (TEM) and in situ X-ray diffraction (XRD) experiments with high-intensity synchrotron radiation, Lucadamo *et al.* [7] evidenced a two-stage reaction mechanism in Nb/Al multilayer thin-films. By TEM analysis, Delattre *et al.* [8] found that CoSi_2 precipitates at the CoSi/Si interface. Precipitates of Al_9Co_2 that quickly grow to form a dense layer were observed by atom probe tomography (APT) as the first product of the Al/Co reaction [9]. A Ni_2Si precipitate attributed to lateral growth was found by APT after deposition of a Ni film on a Si substrate, [10]. In most cases, the precipitates height was found to be limited (in the order of 10 nm) but the full shape of the precipitates was not determined and thus it could not be compared to the models developed for the lateral growth [1] [9] [11] [12] [13].

Among these models, Coffey *et al.* [1] proposed a general description that takes into account the nucleation, the two-dimensional in plane growth up to the coalescence of the cylindrical precipitates and their thickening by growth perpendicular to the interface plane. This models allows to well reproduce global kinetics such as DSC or in situ XRD experiment. Other models were proposed to simulate mainly the lateral growth along the interfaces during solid state reaction [9] [11] [12] [13]. Although these models use different approximations and different phenomena, they all conclude that the product phase should reach a stationary thickness in accordance with the experimental results [1] [2] [3] [4] [5] [6] [9], this thickness being slightly dependent on the kinetics parameters. Even if relatively similar particle shapes are obtained in these models, difference are present especially at the triple line. A comparison between experiments on the first stages of the phase formation along the interfaces and the models is thus important to validate mechanisms and this required to determine the full shape of the precipitate during its lateral growth. This also required a "model" system..

The Ni thin film reaction with silicon can be considered as a characteristic system for reactive diffusion and presents a large interest for application in microelectronics. Most of the studies on the reaction between a pure Ni thin film and the Si substrate have shown the following sequence of phases during the reaction [14]: δ -Ni₂Si appears as the first phase and grows at low temperature (from 250°C) until full consumption of the Ni metallic film. NiSi then grows at the expense of the δ -Ni₂Si phase and is stable up to 700–800°C when NiSi₂ nucleates [15]. With the downscaling of microelectronic devices, NiSi is widely used as contacts in complementary-metal-oxide-semiconductor (CMOS) transistors because of its low resistivity, low Si consumption and Ni diffusion controlled reaction [16]. However, this application is limited by the agglomeration of NiSi and the formation of the high resistivity NiSi₂ that degrades the contact resistance. A solution was found through the addition of 5 at. % Pt in the Ni film that increases the temperature of NiSi₂ nucleation and delays the agglomeration of NiSi by more than 100°C [17]. Therefore Ni with 5 at.% Pt replaced pure Ni and the Pt content has then been increased from 5 at.% to 10 at.% in microelectronics industry to enhance the stability of the monosilicide. However for this content of Pt, the phase sequence is changed and θ -Ni₂Si is the first phase to form and it grows [19] in epitaxy on (100)Si [20]. Since NiSi will grow at the expense of the θ -Ni₂Si silicide for the Ni(10 at.%Pt) alloy films used nowadays in microelectronic devices, the formation of NiSi may change as already reported [21] [22] [23] [24]. Therefore, a better understanding of the mechanisms responsible for the NiSi growth is needed for a better control of the quality of NiSi contacts. As the thickness of NiSi for the contacts is in the order of 15-20 nm in actual devices, most of the NiSi growth may be controlled by lateral growth. A good understanding of lateral growth is thus crucial for process control. In a former paper [25], we found clear evidence for the lateral growth of NiSi at the θ -Ni₂Si/Si interface by Transmission Electron Microscopy (TEM). These analyses allow us determining the full shape of the particle and to compare it with a model developed by Klinger *et al.* and modified in order to take into account the change in atomic volumes during the reaction. A good agreement was obtained between the TEM images and the simulation but the precise shape at the triple line was not well reproduced.

In this paper, we extend the results of our former paper [25] and we evaluate another model for the lateral growth developed by Pasichnyy and Gusak [12]. This model allows to better reproduce the shape around the triple line. The kinetics parameters and the conditions for mechanical equilibrium are discussed.

2. Experimental procedure

A Ni (10 at.% Pt) film with a 10 nm thickness was deposited at room temperature by magnetron sputtering on (100) Si substrates from a 99.99% Ni(Pt) target. The (100) Si substrate was immersed into a 5% dilute HF solution for 1 min to remove the native oxide prior loading into the sputtering chamber. The deposition was performed in a sputtering deposition setup with a base pressure of (10^{-8}) Torr using 99.99% pure Ar gas flow and the wafer was rotating during deposition to improve the uniformity and the homogeneity of the films. Two types of in-situ XRD measurements were performed using a Cu K α source, a rapid detector and a chamber equipped with a heating stage under a vacuum of $\sim 10^{-5}$ mbar. In the first type, after ramping from room temperature to 150°C with a rate of 30 °C/min, the temperature was increased by step of 5°C and kept constant during the XRD measurements that lasted typically to six minutes. For isothermal measurements, the temperature was increased from room temperature to a given temperature at a rate of 30°C/min and XRD scans of 6 min were then recorded continuously during various time at this temperature. TEM measurements (microscope TITAN equipped with an image C_s-corrector and operated at 300 kV) were performed by cross-sectional view on samples prepared by FIB (Focused Ion Beam Dual Beam instrument FEI Helios600 NanoLab) along the direction (110) of Si, after deposition of a protection layer. The same FIB system was used to prepare tip-shaped specimen in the direction perpendicular to the sample surface. The APT analyses were carried out in a LEAP 3000X HR instrument. The specimen temperature and the laser energies were set between 20 and 50 K and between 0.3-0.6 nJ respectively. Data reconstruction and analysis were done with the commercial IVAS software.

3. Results

The sample corresponding to the first stage of the NiSi was selected using in-situ XRD (not shown here) that allows determining the beginning of the NiSi formation from the XRD peaks evolution. The procedure is explained in details in [25] and consists of performing a first in situ XRD measurement with increasing temperatures to select the temperature of the first appearance of the characteristic peak of

NiSi ($2\theta \sim 56^\circ$). The same in situ experiment is then repeated but stopped at the temperature of interest (250°C) and ex-situ analyses can be performed. Figure 1 shows low magnification TEM cross section views where different layers can be seen. The continuous thin layer of Ni silicide observed on the Si substrate was identified as the θ -Ni₂Si phase. At the θ -Ni₂Si/Si interface, some precipitates appear with an elliptical shape: they are marked with numbers in Fig. 1 and a zoom of some of them is shown in Fig. 2.

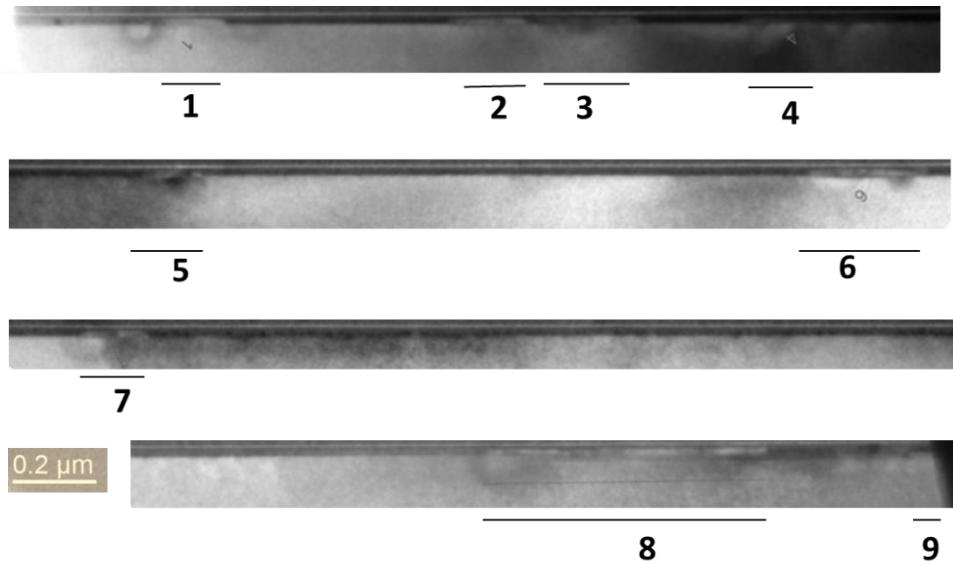


Figure 1: Low magnification conventional TEM micrographs of the 250°C annealed Ni(10%Pt) sample observed in cross-section along a $\langle 110 \rangle$ -Si direction.

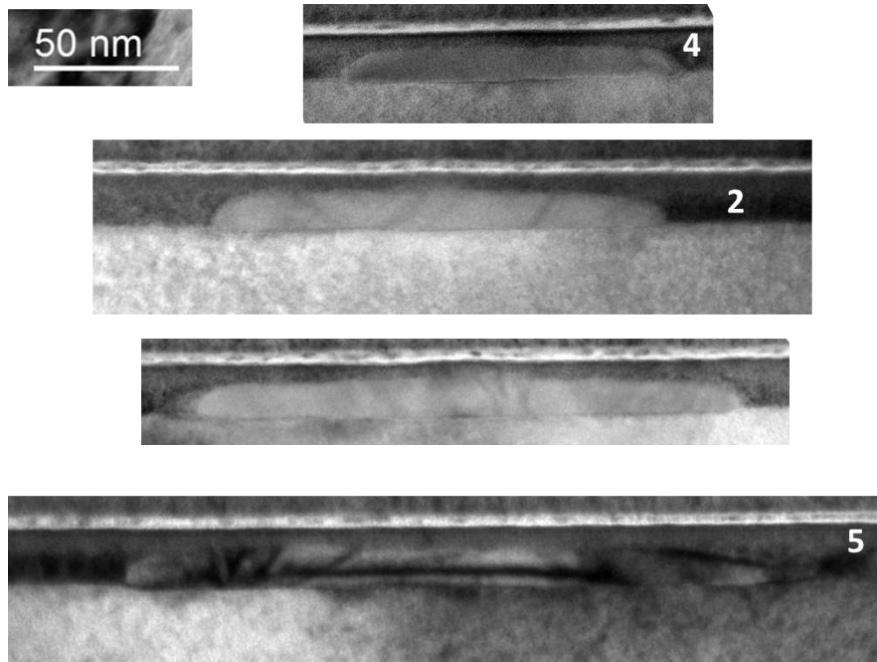


Figure 2: High magnification conventional TEM micrographs of the 250°C annealed Ni(10%Pt) sample observed in cross-section along a $\langle 110 \rangle$ Si direction.

From these TEM observations, the precipitates are separated by distances ranging from 0.8 to 1.2 μm and the average distance between them is about 1.1 μm . The density of the NiSi precipitates is relatively low (around 1 nucleus/ μm^2). Figure 2 shows that they are slightly different but their overall shape is similar. They have roughly the shape of cylinders with a high aspect ratio since their diameter vary from 120 to 380 nm while their thickness ranges from 13 to 17 nm. Their edges have an asymmetrical lens shape and correspond to the triple line between the three phases (θ -Ni₂Si/NiSi/Si).

Figure 3 and 4 show that the triple junction between θ -Ni₂Si, NiSi, and Si are not always the same. The exact shape of the triple junction is difficult to determine because TEM is not a real 3 dimensional (3D) technique but rather a 2D projection of a 3D volume. However two main type of triple junction were observed. Indeed the θ -Ni₂Si/Si interface is straight in Fig. 3 while it is curved in Fig. 4.

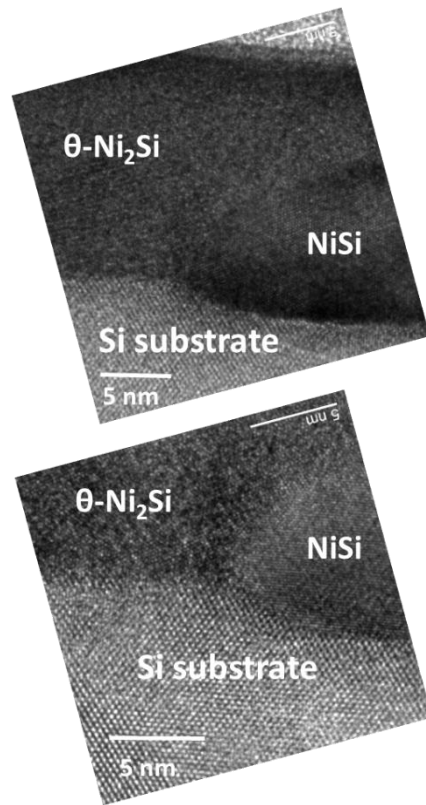


Figure 3: HR-TEM image of NiSi precipitate with a **straight** θ -Ni₂Si/Si interface after annealing at 250°C of the 10 nm Ni(10%Pt) film on (100)Si: the sample was observed in cross-section along a $\langle 110 \rangle$ Si direction.

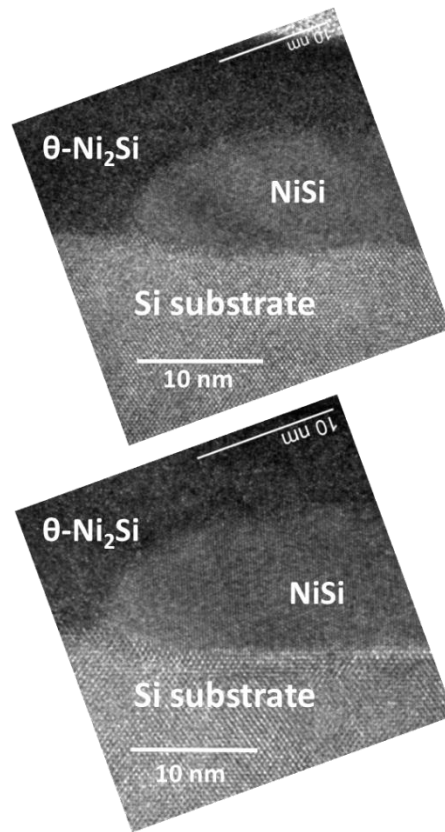


Figure 4: HR-TEM image of NiSi precipitate with a **curved** θ -Ni₂Si/Si interface after annealing at 250°C of the 10 nm Ni(10%Pt) film on (100)Si: the sample was observed in cross-section along a $\langle 110 \rangle$ Si direction.

4. Discussion

As mentioned before, the first stages of the formation during reactive diffusion in thin film are associated to nucleation and lateral growth. The NiSi precipitates observed in this study should correspond to the lateral growth mechanism since (i) their volume is much larger than the typical critical size of a nucleus (a few nm³), (ii) their aspect ratio is large, and (iii) they have not consumed the whole θ -Ni₂Si phase in thickness. These characteristics indicate a fast lateral growth as compared to the normal growth of the NiSi nuclei. They also highlight that the formation of the NiSi phase starts by nucleation and lateral growth at the θ -Ni₂Si/Si interface during the reaction of Ni(10 at.% Pt) films with Si. Our TEM results provide thus a direct observation of the shape of the precipitates associated to the lateral growth phenomenon in contrast to former experimental results [14-19] where only partial view of

lateral growth were observed. They also allow to compare experiment with models that were developed for lateral growth [1] [11] [9] [13] [25] [12] .

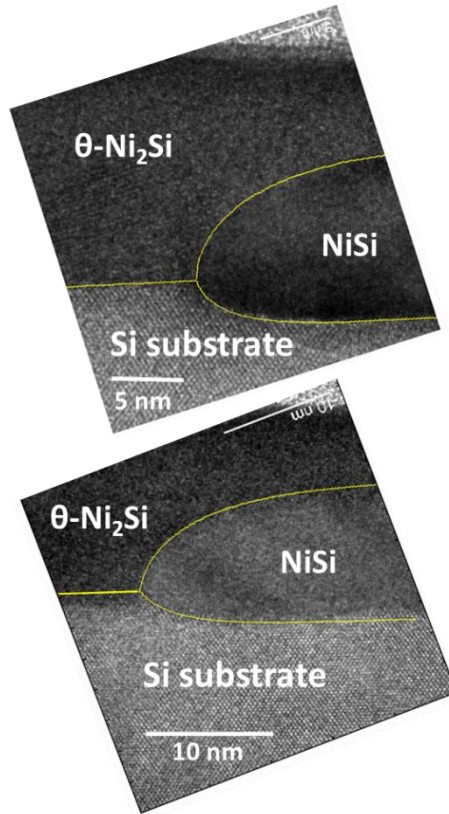


Figure 5: Fit of the HR-TEM image of NiSi precipitate using the model of El Kousseifi et al [25] for (a) the **straight** θ -Ni₂Si/Si interface, (b) the **curved** θ -Ni₂Si/Si interface.

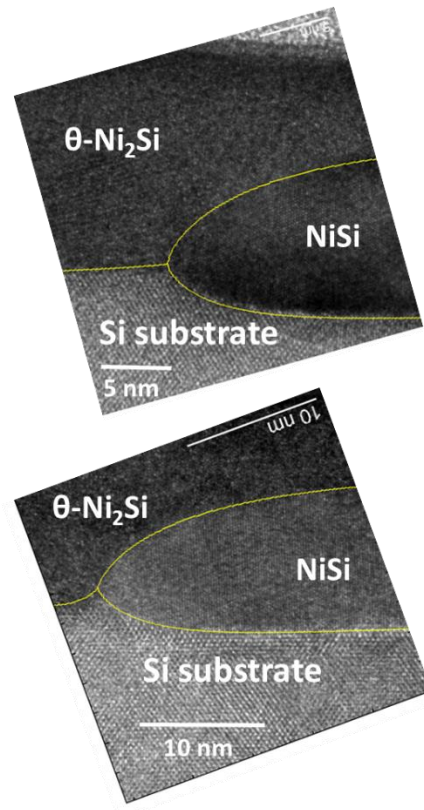


Figure 6: Fit of the HR-TEM image of NiSi precipitate using the model of Pasichnyy and Gusak [12] for (a) the **straight** θ -Ni₂Si/Si interface, (b) the **curved** θ -Ni₂Si/Si interface.

The shape of precipitates as well as their dimensions are in accordance with the existing models that are presented in Fig. 5. Indeed these models predict a roughly elliptical or cylindrical shape with a large aspect ratio between the diameter of the precipitates and their thickness. Among these models we selected the analytical ones instead of the numerical simulation developed by Lucenko et al [11] and Vovk et al [9].

In our former paper [25], we extended the model of Klinger *et al.* [13] to take into account the volume change associated to the formation of θ -Ni₂Si. This was needed because Fig. 1 to 4 show that the position of the NiSi particle is not symmetrical with respect to the θ -Ni₂Si/Si interface and that the NiSi precipitates are more developed on the θ -Ni₂Si side. This asymmetrical shape can be explained by matter conservation during the reaction (θ -Ni₂Si + Si \rightarrow 2NiSi) taking into account the atomic volumes of the different phases.

The main assumptions of our model, based on the Klinger's model, are: (1) the asymmetrical position of the NiSi particle with respect to the θ -Ni₂Si/Si interface is due to the matter conservation and to the

volume change during the reaction between θ -Ni₂Si and Si, (2) the mechanical equilibrium of the interfacial energies is responsible for the particle shape, and (3) the Ni and Si interdiffusion along interfaces is assumed to drive the kinetics of the fast lateral growth; the elements Ni and Si are thus considered to diffuse in opposite directions along the Si/NiSi and θ -Ni₂Si/NiSi interfaces. The driving force for the flux of the diffusing element along the interface is the gradient of the chemical potential difference due to the gradient of curvature. The steady state shape of the moving interface and its velocity are calculated from the flux and the mass conservation condition across the moving interface and the boundaries. The details of the model can be found in refs. [13] [25] [26].

Figure 5 shows the fit obtained with the model of El Kousseiffi et al. [25] for the two types of triple junction. The value used for the fit are reported in table 1 for the phases (θ -Ni₂Si, NiSi, or Si) and in table 2 for the interphases (NiSi/ θ -Ni₂Si, NiSi/ θ -Ni₂Si, or NiSi/ θ -Ni₂Si). In these tables, Ω is the atomic volume of either a phase or an interface, γ is the interface energy, x is the atomic percentage and L is the atomic mobility. The composition of θ -Ni₂Si that is not a stoichiometric phase was chosen to be 40 at% Si in accordance with former APT results [27]. The atomic volume was determined from the asymmetrical shape of NiSi and the mass conservation to be approximately 11 Å³ [25]. With these values, there is almost no change in volume during the formation of NiSi phase from the θ -Ni₂Si and Si. This relative non-variation of volume can also be seen on the TEM images where there is almost no deformation at the sample surface (as attested by the absence of typical 'lobes' of diffraction contrast). From this small change in volume, the stress during the reaction should be low and should not have a strong impact on the precipitates. The driving force was estimated to -5 kJ/mol [25] although the exact value is not known since the effect of Pt on the energy of the silicide are not known. For the diffusion, the mobility for both elements Si and Ni at the interface were considered equal to 10²² at/(s.J).

« Phase »	x [%]	Ω [nm ³]
NiSi	50	0.12
θ -Ni ₂ Si	40	0.11

Si	100	0.2
----	-----	-----

Table 1: Parameters used for the phases in both models.

Interface	γ [J/m ²]	L [at/(s.J)]	Ω [nm ³]
NiSi/Si	1.2	10 ²²	0.15
NiSi/ θ -Ni ₂ Si	2.5	10 ²²	0.11
Si/ θ -Ni ₂ Si	0.3		

Table 2: Parameters used in the models for the interfaces in the model of El Kousseifi et al [25].

Concerning the interface energies, the fit leads to values within the same order of magnitude (typically a few mJ/m²) for all interfaces. However the epitaxial θ -Ni₂Si/Si interface is coherent or at least semicoherent and should have a much lower energy than the ones for the NiSi/Si and NiSi/ θ -Ni₂Si interfaces. This point will be discussed in more details later. An important point of this model is that the mechanical equilibrium is assumed only along the initial θ -Ni₂Si/Si the interface and not in the direction perpendicular to this interface. Moreover this model supposes that the θ -Ni₂Si/Si interface is imposed to be straight that is in contradiction with the experimental observations and thus cannot fit the second type of triple line (Fig. 5.b).

The model developed by Pasichnyy and Gusak [12] allows the initial interface to be deformed and to become curved. The assumptions of this model are relatively similar to our model [25]: (1) asymmetrical position of the growing particle due to the matter conservation and to the volume change during the reaction, (2) mechanical equilibrium of the interfacial energies is responsible for the particle shape and (3) Ni and Si interdiffusion along interfaces with a Darken diffusion coefficient (D) However the diffusion is not driven by the gradient of curvature but by a gradient of concentration along the

interface. The displacement speed of the interface $V_n^{\alpha\omega}$ is also assumed to be proportional to the difference of concentration across the interface :

$$V_n^{\alpha\omega} = k_{\alpha\omega}(x - x_{\alpha\omega}^{eq}) \quad \text{Eq. 1}$$

Figure 6 shows that with this model, a good fit is obtained for both types of triple line. The model developed by Pasichnyy and Gusak [12] is thus more general than the other models since it allows to reproduce more experimental observations.

Interface	γ [J/m ²]	K [nm/s]	D _c [nm ² /s]	D _s [nm ² /s]
NiSi/Si	1	100	200	200
NiSi/ θ -Ni ₂ Si	1	100	100	100
Si/ θ -Ni ₂ Si	0.1	100	5	100

Table 3: Parameters used in the model of Pasichnyy and Gusak [12]. The values D_c and D_s correspond to the interdiffusion coefficients in the case of the curved θ -Ni₂Si/Si interface and the straight θ -Ni₂Si/Si interface respectively.

The best fitting parameters are reported in table 3. In order to be representative of expected interface energies, the energy of the θ -Ni₂Si/Si interface was set to a low value. However this imposes almost equal values for the θ -Ni₂Si/NiSi interface and the NiSi/Si interface since in the Pasichnyy and Gusak model, a true (i.e. vectors) mechanical equilibrium is assumed:

$$\vec{\gamma}_{\alpha\beta} + \vec{\gamma}_{\alpha\omega} + \vec{\gamma}_{\beta\omega} = \vec{0} \quad \text{Eq. 2}$$

In order to fit both types of triple line, one thus has to change the change the kinetics factor (either k or D). As the mobility of interface are difficult to measure, they were supposed to be equal for all interface

and only the diffusion coefficients were changed. Change of the interdiffusion coefficient for the NiSi/Si and NiSi/ θ -Ni₂Si interfaces were first tried as one expects more change in these interfaces for NiSi precipitates with different orientations than for the θ -Ni₂Si/Si interface. However only a variation of interdiffusion coefficient along the θ -Ni₂Si/Si interface is able to fit the shape of the whole precipitates including the triple line and to give reasonable values for height (~ 10 nm) and growth speed (1 nm/s) of the precipitates. Indeed with a change from a low value (5 nm²/s) to a value (100 nm²/s) similar to the other interfaces, one can pass from a θ -Ni₂Si/Si interface curved in the vicinity of the triple line to a straight one while keeping similar height and growth speed of the precipitates. To confirm this finding and obtain a better understanding, it would be interesting to measure the diffusion along the different interfaces even if these measurements are difficult.

As already mentioned before, there is concern with the mechanical equilibrium and the expected values of the interface energies. Indeed as the θ -Ni₂Si is in epitaxy on Si, the θ -Ni₂Si/Si interface should have a much lower energy than the ones of the incoherent NiSi/Si and NiSi/ θ -Ni₂Si interfaces. If one applies the classical equation for the mechanical equilibrium (Eq. 2), the forces should be almost equal and opposite $\vec{\gamma}_{\alpha\omega} \sim \vec{\gamma}_{\beta\omega}$ since $\vec{\gamma}_{\alpha\beta} \ll \vec{\gamma}_{\alpha\omega}, \vec{\gamma}_{\beta\omega}$. However, there is no reasons why the two interface energies, $\vec{\gamma}_{\alpha\omega}$ and $\vec{\gamma}_{\beta\omega}$, are equal since these interfaces are different. In order to explain this paradox, one should remember that the classical equation is an approximation and neglects the torque term. Indeed the Herring's equation that is valid when interfacial energies are orientation dependent can be expressed as [28] [29]:

$$\sum_{j=1}^3 \left(\gamma_j \vec{b}_j + \frac{\partial \gamma_j}{\partial \theta_j} \vec{n}_j \right) = \vec{0} \quad \text{Eq. 3}$$

where the sum is conducted over the three interfaces intersecting at the triple junction, γ_j is the excess free energy of the j^{th} boundary, \vec{n}_j is the unit boundary normal of the j^{th} boundary, \vec{b}_j is a unit vector lying in the j^{th} boundary and perpendicular to the triple line, $\vec{l} = \vec{b}_j \otimes \vec{n}_j$, which is common to all three adjacent boundaries and θ_j is defined to be the right handed angle of rotation about \vec{l} of the j^{th} boundary from a reference direction. The derivative terms are referred to as torque terms and reflect the dependence of

interface energy on orientation or the resistance of an interface to rotation about the triple junction at fixed \vec{l} (Fig. 7).

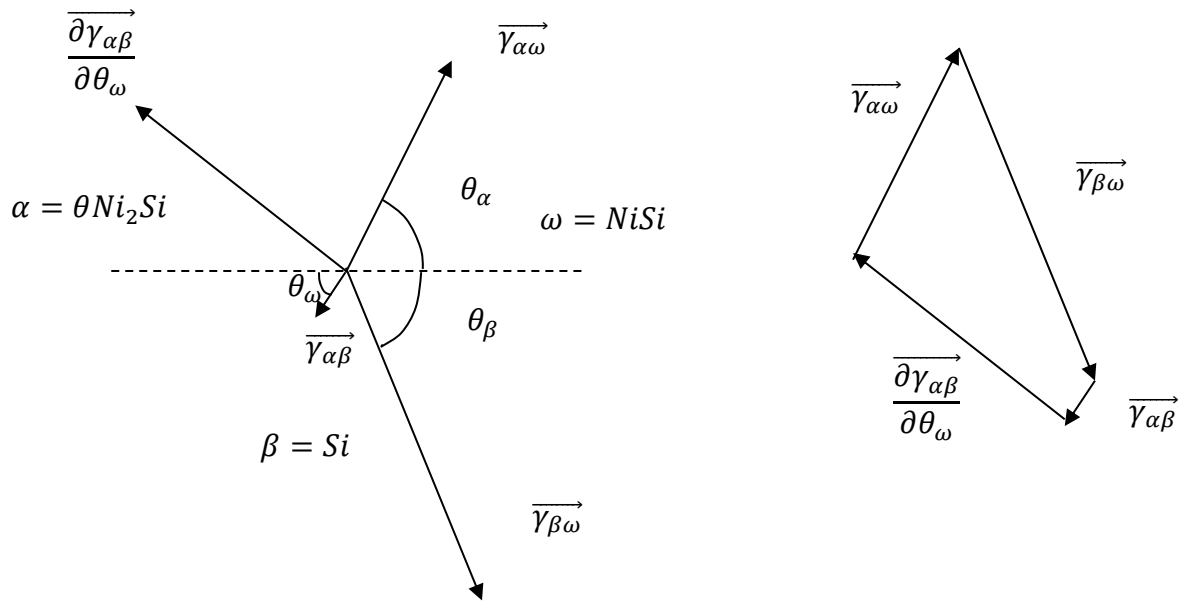


Figure 7: Schematics of the interfacial energies in the presence of a torque term for the epitaxial θ -Ni₂Si/Si interface: (a) interfacial energies at the triple junction (b) verification of the Herring's equation (Eq. 3).

As pointed by Aaronson et al [30], the torque terms can be quite high for coherent interfaces and may explain this apparent paradox. Indeed Figure 6 shows that one can construct a configuration that respects the observed angles and different values of the interfacial energies expected for the different interfaces if one assumed a large torque term for the epitaxial interface between θ -Ni₂Si and Si. The presence of this large torque term may also explain to some extent why the θ -Ni₂Si/Si interface is curved close to the triple line since the torque term exerts a force perpendicular to this interface. In order to fully understand the lateral growth, one may thus have to take into account the torque term.

The comparison between experiments and models allows to highlight the important parameters for the lateral growth even if there are still some points to clarify. Further analysis and models may be needed in order to gain a better understanding of the parameters and the phenomena responsible for the lateral growth. This should be important for the actual microelectronics devices in which the thickness of the silicide used as contact is in the order of 10 nm and thus the formation of silicide should be controlled

by nucleation and lateral growth. In order to have reproducible and reliable process, i.e. the silicide process used for the contact formation by solid state reaction, these phenomena should be understood and controlled because they can impact the behaviour and the properties of the contacts

The lateral growth may be involved in the “piping”, i.e. the formation of silicide in the transistor channel, that is a detrimental behaviour. Although the exact mechanisms behind this behaviour are not known, lateral growth of NiSi could be at the origin of the piping. Indeed lateral growth can expand the silicide laterally from the source and drain zone into the channel instead to grow in thickness. To avoid this undesirable behaviour, one should thus limit lateral growth.

Another characteristic that might be affected by nucleation and lateral growth and that is of importance for devices is the grain size of the silicide. Indeed when a grain nucleates, it will spread laterally until it meets another grain and this will fix the grain size. The grain size should thus depend on the density of nucleation sites, the nucleation kinetics and the lateral growth speed. If the lateral growth is fast, the grain size should thus be larger. Accordingly to Nolan et al [31], for a given thickness, film with larger grains will be more prone to agglomeration. On the other hand, one might use lateral growth to obtain single grain as a contact which may result in an increase of thermal stability.

The nucleation and lateral growth should also influence the texture of the silicide contact. In particular lateral growth depends on the interfacial energy that depends on the orientation of the growing grain with respect to the parent phase. Grains with special orientation may thus laterally grow faster and thus induce a change of texture that is also of importance for the stability of the contact.

The precipitate thickness and the speed of lateral growth are complex function of the driving force, the interfacial energy and the diffusion of the two elements [12] [13] [25] . They have a reverse behaviour: i.e. when the speed is large, the thickness is small. The speed is high for large driving force, fast diffusion and high change in interfacial energy ($\Delta\gamma = \gamma_{\alpha\omega} + \gamma_{\beta\omega} - \gamma_{\alpha\beta}$). In order to change the lateral growth, one can thus try to modify these parameters. Alloy element may change the driving force to some extent. Interfacial energy may be modified by segregation at the interface but this is difficult to control. A more efficient way might be to use segregating element to modify the diffusion at interface. Even if it might be difficult to verify the effect of segregating element, the beneficial effect of C for agglomeration [32] might be partly due to modification in lateral growth. As the experimental determination of lateral growth is difficult, only a few studies have been performed on lateral growth and it is difficult to have precise

information on its kinetics especially as a function of temperature. However as the activation energy for lateral growth and thickening should be different [3], this offers in principle the possibility to tune the shape of precipitates and the relative contribution of lateral growth and thickening.

6. Conclusion

To conclude, in situ XRD and TEM were used to characterize NiSi precipitates formed by nucleation and lateral growth at the epitaxial θ -Ni₂Si/Si interface. The shape of NiSi precipitates is in good accordance with the existing models. A comparison between two models (El Kousseiffi et al / Pasicchnyy and Gusak) and the experimental shape of the precipitates determined by TEM is performed. In particular the model of Pasicchnyy and Gusak is able to better reproduce the shape of the interfaces close to the triple line as well as the other characteristics of the precipitates. Estimation of the parameters governing lateral growth (interfacial energies, kinetics parameters...) are obtained. The conditions for mechanical equilibrium are presented and the torque term has to be taken into account for realistic interfacial energies. The implications of lateral growth on the stability, behavior, and properties of contacts in microelectronics are also discussed.

Acknowledgements

"The authors acknowledge financial support from the CNRS-CEA "METSA" French network (FR CNRS 3507) for the TEM experiments at CLYM (www.clym.fr) which is also acknowledged for the access to the microscopes. M. Descoins and M. Bertoglio are greatly acknowledged for technical assistance.

References

- [1] K. Coffey, L. Clevenger, K. Barmak, D. Rudman, C. Thompson, Experimental-Evidence for Nucleation During Thin-Film Reactions, *Appl. Phys. Lett.* 55 (1989) 852–854.
doi:10.1063/1.102447.

- [2] F. Nemouchi, D. Mangelinck, C. Bergman, P. Gas, U. Smith, Differential scanning calorimetry analysis of the linear parabolic growth of nanometric Ni silicide thin films on a Si substrate, *Appl. Phys. Lett.* 86 (2005) 041903. doi:10.1063/1.1852727.
- [3] K. Hoummada, D. Mangelinck, A. Portavoce, Kinetic of Formation of Ni and Pd Silicides: Determination of Interfacial Mobility and Interdiffusion Coefficient by *In Situ* Techniques, *Solid State Phenom.* 172–174 (2011) 640–645. doi:10.4028/www.scientific.net/SSP.172-174.640.
- [4] K. Hoummada, A. Portavoce, C. Perrin-Pellegrino, D. Mangelinck, C. Bergman, Differential scanning calorimetry measurements of kinetic factors involved in silicide process, *Appl. Phys. Lett.* 92 (2008) 133109. doi:10.1063/1.2905293.
- [5] K. Coffey, K. Barmak, D. Rudman, S. Foner, Thin-Film Reaction-Kinetics of Niobium Aluminum Multilayers, *J. Appl. Phys.* 72 (1992) 1341–1349. doi:10.1063/1.351744.
- [6] C. Bergman, J.L. Joulaud, M. Capitan, G. Clugnet, P. Gas, In situ real-time analysis of the formation of a quasicrystalline phase in Al-Co multilayers by solid-state reaction, *J. Non-Cryst. Solids.* 287 (2001) 193–196. doi:10.1016/S0022-3093(01)00558-0.
- [7] G. Lucadamo, K. Barmak, S. Hyun, C. Cabral Jr., C. Lavoie, Evidence of a two-stage reaction mechanism in sputter deposited Nb/Al multilayer thin-films studied by in situ synchrotron X-ray diffraction, *Mater. Lett.* 39 (1999) 268–273. doi:10.1016/S0167-577X(99)00017-8.
- [8] R. Delattre, O. Thomas, C. Perrin-Pellegrino, C. Rivero, R. Simola, First stage of CoSi₂ formation during a solid-state reaction, *J. Appl. Phys.* 116 (2014) 245301. doi:10.1063/1.4904852.
- [9] V. Vovk, G. Schmitz, R. Kirchheim, Nucleation of product phase in reactive diffusion of Al/Co, *Phys. Rev. B.* 69 (2004). doi:10.1103/PhysRevB.69.104102.
- [10] K. Hoummada, E. Cadel, D. Mangelinck, C. Perrin-Pellegrino, D. Blavette, B. Deconihout, First stages of the formation of Ni silicide by atom probe tomography, *Appl. Phys. Lett.* 89 (2006) 181905. doi:10.1063/1.2370501.

- [11] G. Lucenko, A. Gusak, A model of the growth of intermediate phase islands in multilayers, *Microelectron. Eng.* 70 (2003) 529–532. doi:10.1016/S0167-9317(03)00432-5.
- [12] M. Pasichnyy, A. Gusak, Model of Lateral Growth Stage during Reactive Phase Formation, *Defect Diffus. Forum.* 277 (2008) 47–52. doi:10.4028/www.scientific.net/DDF.277.47.
- [13] L. Klinger, Y. Bréchet, G. Purdy, On the kinetics of interface-diffusion-controlled peritectoid reactions, *Acta Mater.* 46 (1998) 2617–2621. doi:10.1016/S1359-6454(97)00471-0.
- [14] S.S.L. M. A. Nicolet, *Formation and Characterization of Transition-Metal Silicides*, Academic Press, NY, 1983.
- [15] F.M. d’Heurle, Nucleation of a new phase from the interaction of two adjacent phases: Some silicides, *J. Mater. Res.* 3 (1988) 167–195. doi:10.1557/JMR.1988.0167.
- [16] C. Lavoie, F.M. d’Heurle, C. Detavernier, C. Cabral, Towards implementation of a nickel silicide process for CMOS technologies, *Microelectron. Eng.* 70 (2003) 144–157. doi:10.1016/S0167-9317(03)00380-0.
- [17] D. Mangelinck, J.Y. Dai, J.S. Pan, S.K. Lahiri, Enhancement of thermal stability of NiSi films on (100)Si and (111)Si by Pt addition, *Appl. Phys. Lett.* 75 (1999) 1736–1738. doi:10.1063/1.124803.
- [18] D. Mangelinck, J.Y. Dai, S.K. Lahiri, C.S. Ho, T. Osipowicz, Formation and Stability of Ni(Pt) Silicide on (100)Si and (111)Si, *MRS Online Proc. Libr. Arch.* 564 (1999). doi:10.1557/PROC-564-163.
- [19] M. Putero, L. Ehouarne, E. Ziegler, D. Mangelinck, First silicide formed by reaction of Ni(13%Pt) films with Si(1 0 0): Nature and kinetics by in-situ X-ray reflectivity and diffraction, *Scr. Mater.* 63 (2010) 24–27. doi:10.1016/j.scriptamat.2010.02.040.
- [20] F. Panciera, D. Mangelinck, K. Hoummada, M. Texier, M. Bertoglio, A. De Luca, M. Gregoire, M. Juhel, Direct epitaxial growth of θ -Ni₂Si by reaction of a thin Ni(10 at.% Pt) film with Si(1 0 0) substrate, *Scr. Mater.* 78–79 (2014) 9–12. doi:10.1016/j.scriptamat.2014.01.010.
- [21] C. Van Bockstael, *silicide*, Gent University, 2009.

- [22] C. Van Bockstael, K. De Keyser, R.L. Van Meirhaeghe, C. Detavernier, J.L. Jordan-Sweet, C. Lavoie, Influence of a transient hexagonal phase on the microstructure and morphological stability of NiSi films, *Appl. Phys. Lett.* 94 (2009) 033504. doi:10.1063/1.3073750.
- [23] S. Gaudet, *Silicide*, Ecole Polytechnique de Montreal, 2011.
- [24] S. Gaudet, C. Coia, P. Desjardins, C. Lavoie, Metastable phase formation during the reaction of Ni films with Si(001): The role of texture inheritance, *J. Appl. Phys.* 107 (2010) 093515. doi:10.1063/1.3327451.
- [25] M. El Kousseifi, K. Hoummada, T. Epicier, D. Mangelinck, Direct observation of NiSi lateral growth at the epitaxial θ -Ni₂Si/Si(1 0 0) interface, *Acta Mater.* 99 (2015) 1–6. doi:10.1016/j.actamat.2015.07.062.
- [26] C. T'e-Jer, J.R. Rice, The shape of intergranular creep cracks growing by surface diffusion, *Acta Metall.* 21 (1973) 1625–1628. doi:10.1016/0001-6160(73)90105-3.
- [27] K. Hoummada, I. Blum, D. Mangelinck, A. Portavoce, Composition measurement of the Ni-silicide transient phase by atom probe tomography, *Appl. Phys. Lett.* 96 (2010) 261904. doi:10.1063/1.3457995.
- [28] C. Herring, Surface tension as a motivation for sintering, in: *Phys. Powder Metall.*, McGraw-Hill Book Co., W.E. Kingston, New York, 1951: p. 143.
- [29] B.L. Adams, S. Ta'Asan, D. Kinderlehrer, I. Livshits, D.E. Mason, C.-T. Wu, W.W. Mullins, G.S. Rohrer, A.D. Rollett, D.M. Saylor, Extracting Grain Boundary and Surface Energy from Measurement of Triple Junction Geometry, *Interface Sci.* 7 (1999) 321–337. doi:10.1023/A:1008733728830.
- [30] H.I. Aaronson, M. Enomoto, J.K. Lee, *Mechanisms of Diffusional Phase Transformations in Metals and Alloys*, CRC Press, 2016.
- [31] T.P. Nolan, R. Sinclair, R. Beyers, Modeling of agglomeration in polycrystalline thin films: Application to TiSi₂ on a silicon substrate, *J. Appl. Phys.* 71 (1992) 720. doi:10.1063/1.351333.

- [32] R.T.P. Lee, L.T. Yang, T.Y. Liow, K.M. Tan, A.E.J. Lim, K.W. Ang, D.M.Y. Lai, K.M. Hoe, G.Q. Lo, G.S. Samudra, D.Z. Chi, Y.C. Yeo, Nickel-Silicide:Carbon Contact Technology for N-Channel MOSFETs With Silicon $\times 2013$;Carbon Source/Drain, IEEE Electron Device Lett. 29 (2008) 89–92. doi:10.1109/LED.2007.910793.