The Reactive Formation of TiSi₂

in the Presence of Refractory Metals (from V to W)

By
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"But what ... is it good for?"

Engineer at the Advanced Computing Systems Division of IBM, 1968, commenting on the microchip.

---

Tout le monde savait que c'était impossible. Il est venu un imbécile qui ne le savait pas et qui l'a fait.

(Marcel Pagnol)
Mouroux, A.: The reactive formation of TiSi$_2$ in the presence of refractory metals (from V to W), Royal Institute of Technology, Department of Electronics, Solid State Electronics, Stockholm, Sweden 1997.

**ABSTRACT**

Titanium disilicide (TiSi$_2$) has been the favoured material for contact metallisation in recent Si devices. The formation of TiSi$_2$ usually begins with the high resistivity C49 phase as a result of the Ti-Si interaction at about 300-550 °C and finishes with the low resistivity C54 phase through the C49-C54 phase transformation at about 700 °C. The C49-C54 transformation becomes increasingly difficult as the device dimensions are scaled down and remains a technological challenge for dimensions below 0.5 µm. In this thesis, a thin layer of Mo deposited between Ti film and Si substrate is used to promote the formation of the C54 phase at temperature 100 °C lower than for the C49-C54 transformation. On narrow Si lines down to 0.25 µm width, the influence of Mo on the formation of TiSi$_2$ is even more pronounced than on blanket substrates; lower sheet resistance with smaller scatter is obtained in the presence of Mo than without. The enhancement in the formation of the C54 phase is interpreted as a consequence of epitaxial effects where the formation of C40 (Mo,Ti)Si$_2$ plays a key role. The validity of the template mechanism is verified by replacing Mo with Ta and Nb. The idea of using Ta and Nb comes from the fact that TaSi$_2$ and NbSi$_2$ have the same crystallographic structure and comparable lattice parameters as (Mo,Ti)Si$_2$. The epitaxial mechanism is confirmed by lattice imaging with a high-resolution microscope. In order to gain an insight into the thermodynamics of the ternary systems, the pseudo binary phase diagram of TiSi$_2$-NbSi$_2$ is studied. Three phase domains are identified, i.e. 1) C54 (Ti,Nb)Si$_2$ with Nb varying from 0 to 10 % at the metal sites, 2) a mixture of C54 and C40 (Ti,Nb)Si$_2$ with Nb being 10 to 25 % at the metal sites, and 3) C40 (Ti,Nb)Si$_2$ with Nb varying from 25 to 100 % at the metal sites. The resistivity of (Ti,Nb)Si$_2$ C54 increases by 1.2 μΩ cm per at. % Nb when the Nb concentration varies from 0 to 10 % at the metal sites. The presence of the refractory metals (Ta, Nb or Mo) at the Si/Ti interface modifies the energetic factors for the formation of C54 TiSi$_2$. The formation of C49 TiSi$_2$ is hindered and that of C54 is enhanced. With a Mo or Nb interposed layer, the phase of C54 TiSi$_2$ can be obtained at temperatures as low as 450 °C. Moreover, if a continuous silicide layer in the C40 structure is formed at the Si/TiSi$_2$ interface, it is the Si diffusion through this interfacial layer that is the controlling factor for the C54 TiSi$_2$ growth. Furthermore, the use of an interposed layer of Mo, Ta or Nb generally improves the surface morphology and morphological stability: the TiSi$_2$ formed has a smoother surface and interface and is more resistant to agglomeration.

**Key words:** Titanium disilicide TiSi$_2$, contact metallisation, phase formation, refractory metals, sub-micron technology, template growth, very large scale integration, VLSI, interconnection.
RESUME

Le disiliciure de titane (TiSi$_2$) est le composé le plus utilisé pour l’obtention de contacts ohmiques dans la technologie VLSI (Very Large Scale Integration). La formation de TiSi$_2$ se compose normalement de deux étapes. La première résulte de la reaction Ti-Si, à des températures comprises entre 300 et 550 °C, et produit la phase C49 à haute résistivité. La seconde est la transformation de phase C49-C54 qui a lieu à des températures voisines de 700 °C, elle produit la phase C54 à faible résistivité. Cette transformation de phase devient très difficile lorsque les dimensions des circuits intégrés sont diminuées. Réduire la température de cette transformation reste un problème technologique d’actualité pour des dimensions inférieures à 0.5 µm.

Lors de ce travail de thèse, une fine couche de Mo a été déposée entre la couche de Ti et le substrat de Si afin de favoriser la formation de la phase C54. Une couche tampon de (Mo,Ti)Si$_2$ de structure C40 est alors formée ce qui favorise l’apparition de la phase C54 de structure crystallographique similaire. Afin de confirmer cette explication basée sur l’épitaxie de deux phases, le même type d’expériences a été réalisé en remplaçant l’élément Mo par Nb ou Ta. En effet, TaSi$_2$ (ou NbSi$_2$) a une structure et des paramètres de maille voisins de ceux du (Mo,Ti)Si$_2$. Ces expériences complémentaires menées avec, notamment, l’aide de la microscopie électronique en haute résolution, ont validé le mécanisme épitaxique. Le diagramme de phase pseudo-binaire de Ti-Nb-Si a été étudié afin de mieux comprendre les phénomènes physiques qui interviennent. Trois domaines ont été identifiés : (1) C54 (Ti,Nb)Si$_2$ avec une concentration relative en NbSi$_2$ ($X_{Nb}$) variant de 0 à 10 % ; (2) une combinaison de phases C54 et C40 (Ti,Nb)Si$_2$ avec $X_{Nb}$ variant de 10 à 25 % et (3) C40 (Ti,Nb)Si$_2$ avec $X_{Nb}$ comprise entre 25 et 100 %. La résistivité de (Ti,Nb)Si$_2$ C54 augmente de 1.2 µΩ cm par pourcentage atomique de Nb lorsque $X_{Nb}$ est comprise entre 0 et 10 %. La présence de métal réfractaire (Ta, Nb ou Mo) à l’interface Si/Ti modifie l’énergie de nucléation de la phase C54 et favorise l’apparition de la phase C54 au détriment de la phase C49. Ainsi, avec une couche déposée de Mo ou de Nb, la phase C54 a pu être obtenue dès 450 °C. De plus, si une couche continue de siliciure réfractaire est formée à l’interface Si/TiSi$_2$, le facteur contrôlant la croissance de la phase C54 est la diffusion à travers cette couche. Par ailleurs, l’utilisation d’une couche déposée de Mo (ou Ta ou Nb) améliore la morphologie et la stabilité morphologique de la couche de siliciure : le TiSi$_2$ formé sur du Si monocristallin a une surface plus régulière et est plus résistant à l’agglomération. Alors que TaSi$_2$ n’affecte pas la stabilité morphologique des couches de TiSi$_2$ formées sur du Si polycristallin, la présence de (Mo,Ti)Si$_2$ semble la déteriorer en abaissant la température d’agglomération d’environ 75 °C. Sur des bandes étroites de Si poly-cristallin (jusqu’à 0,25 µm de largeur), l’influence de Mo sur la formation de TiSi$_2$ est encore plus marquée ; une résistance plus basse et un écart type réduit ont été obtenus grâce à l’interposition d’une couche de Mo.
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4. **Formation of the C54-TiSi$_2$ at Record Low Temperature (525°C) with a Refractory Metal Bilayer Deposited on <100> Si**, A. Mouroux, B. Reynard, and S.-L. Zhang, “Advanced Metallisation and Interconnect Systems for ULSI Applications in 1997” in San Diego (California) p. 605.


Other paper related to TiSi$_2$ not included in the thesis


Other papers not related to TiSi$_2$ and not included in the thesis


# Alieette Mouroux's contributions in the appended papers

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<td>70 %</td>
<td>90 %</td>
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Aliette Mouroux
1 Introduction

After the birth of the integrated circuits in 1962, the number of transistors on a chip initially doubled every year. Moore pointed out this interesting behaviour in 1965, and this trend is referred to as the Moore’s law (see Fig. 1). Moore also predicted that the pace of doubling would slow down. Indeed, since 1975, the number of transistors doubled every 18 months instead of 12 months. The driving force of the miniaturisation and integration has always been the same: enhanced performances and functionality, improved reliability, decreased power dissipation, increased throughput, and reduced cost. For each new generation of chips, new technologies are developed to achieve higher degree of integration. More than 20 years ago, the down scaling of integrated circuits already introduced limitations due to the contact resistance in the electronic components. New materials were then brought into the interconnection level in order to preserve the circuit performance. The choice of a new material to be used in the integrated circuits is determined by its intrinsic properties as well as its compatibility with the fabrication process used.

Figure 1: Moore's Law.
The properties required for interconnection materials are, among others, low resistivity and good thermal stability, i.e. the material can stand high process temperatures without changing phase or morphology. Those are properties of most metal silicides, and the refractory metal silicides, in particular, have a very good thermal stability. The silicides can be processed in oxidising atmosphere without suffering serious deterioration. In addition, metal silicides possess an outstanding advantage from the processing point of view; they form selectively on Si substrate and not on dielectric materials such as SiO$_2$ when annealed. This property leads to the selective formation of silicides; the process is known as self-aligned silicide (salicide) (Fig. 2). In such a process, the metal film is deposited on top of the whole surface of a wafer. After appropriate heat treatment, the silicide is formed only in the areas where the metal is in direct contact with Si. The unreacted metal is then removed with a selective wet etch leaving the silicide in the contact area. The use of the salicide process reduces the total number of process steps, optimises the alignment of the metal contact to the active layer and helps miniaturisation of the device dimensions. Moreover, the contact resistivity between the silicide and Si can be made low.\(^3\)

Since the introduction of the salicide process, titanium disilicide (TiSi$_2$) has been the favoured material.\(^4\) Titanium disilicide has a low resistivity, good chemical stability, self-passivation property in O$_2$, good selective formation when using the salicide process and it can stand high temperature treatment without changing phase or morphology. As the dimensions of the integrated circuits decrease, the performances of the integrated circuits have become more dependent on the interconnections.\(^5\) The requirements on the interconnections including silicides are then more stringent. In the case of silicides, not only the sheet resistance but also the contact resistance are crucial for low RC time constants and low voltage drops.\(^6\) The scaling of the integrated circuits results in higher demands for the intrinsic properties of the material. The fabrication process is subject to limitations such as reduction of the thermal budget. Since the beginning of the use of silicides in integrated circuits, the number of silicides able to fulfil the requirements has been reduced. Nowadays, only TiSi$_2$ and CoSi$_2$ are considered as acceptable.\(^7,8\) Nickel monosilicide (NiSi) in spite of its poor thermal stability is also considered as a new candidate for the salicide process in sub-0.5 μm circuits.\(^9\) Because TiSi$_2$ has been used for almost two decades, the TiSi$_2$ process is well mature and used in all fabrication lines. Economically, it is beneficial to keep using TiSi$_2$. This,
However, requires improvement of the TiSi$_2$ salicide process. Chemical vapour deposition (CVD) of TiSi$_2$ has been proposed as a possible technique for CMOS devices with dimensions below 0.2 µm. However, in view of the problems associated with the selective deposition of TiSi$_2$ by CVD and with the introduction of a new process, a standard salicide process is still preferable.

(a) Basic MOSFET structure fabricated

(b) Metal deposition

(c) First annealing in N$_2$ at 700 °C (Formation of C49 TiSi$_2$)

(d) Selective etch and second annealing at 800 °C (Formation of C54 TiSi$_2$)

Figure 2: Schematic of the standard salicide process using TiSi$_2$.

This thesis is focused on the formation of TiSi$_2$ via the standard salicide process. In Chapter 2, a description of TiSi$_2$, as well as of its basic properties is given and the problems attached to its formation are discussed. The crystallographic structure of a number of refractory metal silicides is presented in Chapter 3, showing the similarities between them and TiSi$_2$. The refractory metals concerned are V, Nb, Ta, Cr, Mo or W, they will be noted RM in the text. In Chapter 4, the fundamental aspects of the formation of TiSi$_2$ in the presence of RM are discussed in conjunction with the presentation of the appended papers. The mechanism of the enhanced formation of TiSi$_2$ and the modifications of its growth kinetics are summarised. The effects of a thin RM interposed layer on the process related properties of TiSi$_2$ such as surface morphology, thermal stability, resistivity and dopant redistribution are described in Chapter 5. The salicide process with the deposition of Mo/Ti instead of Ti is shown to function well in submicron lines down to 0.25 µm linewidth. Finally, a summary of the thesis and future trends are presented in Chapter 6.
2 TiSi$_2$, the silicide of choice

2.1 Basic properties

Titanium disilicide may exist in two different crystallographic phases$^{11}$ (Fig. 3). One is orthorhombic face centred with a low resistivity. The other one is orthorhombic base centred with a high resistivity. They are referred to as C54 and C49, respectively, and are described in the crystallographic nomenclature of Ewald and Hermann.$^{12-14}$ The letter ‘C’ in C49 and C54 means that the molecule consists of three atoms (one Ti and two Si). The C49 TiSi$_2$ is known to be highly faulted.$^{15,16}$ The phase diagram of the Ti-Si system indicates that at the composition Ti 0.33 and Si 0.66, i.e. TiSi$_2$, the compound crystallises in the C54 phase.$^{17}$ In fact, recent calculations by F. Bonoli et al.$^{18}$ show that the heat of formation of C54 TiSi$_2$ is slightly lower than that of C49 TiSi$_2$. As a consequence, when the C49 TiSi$_2$ forms, it is metastable. Therefore, the desirable phase for the metallisation of the integrated circuits is the low resistivity and stable C54 phase. Various properties and characteristics of the TiSi$_2$ phase are given in Table I.$^{11,19-21}$

Table I: Basic properties of the two phases of TiSi$_2$

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystallographic structure</th>
<th>Lattice parameters$^{16,17}$ (nm)</th>
<th>Density$^{21}$ (gr/cm$^3$)</th>
<th>Resistivity$^{11}$ (µΩ cm)</th>
<th>Energy of formation kJ/mol at$^{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>C54</td>
<td>Orthorhombic face centred (Fig. 3)</td>
<td>0.827</td>
<td>0.855</td>
<td>0.480</td>
<td>4.07</td>
</tr>
<tr>
<td>C49</td>
<td>Orthorhombic base centred (Fig. 3)</td>
<td>0.3562</td>
<td>1.3531</td>
<td>0.3550</td>
<td>4.04</td>
</tr>
</tbody>
</table>
Figure 3: Crystallographic structures of the two types of TiSi₂.
2.2 Issues of formation

When a film of Ti deposited on Si is heated at temperatures above 500 °C, the high resistivity C49 phase forms. Annealing at higher temperature is needed to transform the C49 phase into the C54 phase.\textsuperscript{11,22} In spite of much effort, the sequence of formation of Ti\textsubscript{Si\textsubscript{2}} passing through the formation of the metastable C49 phase is not clearly understood. Jeon et al.\textsuperscript{23} suggested that a lower energy barrier induced by a lower surface energy leads to the initial nucleation of the metastable C49 phase. On the other hand, the faster diffusion of Si in C49 than in C54\textsuperscript{24} may also lead to the preferential formation of the C49 phase.\textsuperscript{25} Once the C49 is formed, the driving force for the C54 formation, which is the difference between the free energy of C49 and C54, is small (about 2 kJ/mol).\textsuperscript{26} The C49 to C54 transformation is then nucleation controlled.\textsuperscript{27,28} As usually observed in such cases, the C54 seems to nucleate preferentially at the triple grain junctions of the C49 phase.\textsuperscript{15}

Therefore, the usual route leading to the formation of the C54 phase, i.e. the standard salicide process (Fig. 2), includes the C49 to C54 phase transformation. After the metal deposition, a first anneal at 300-600 °C induces the C49 formation as a result of the Ti-Si interaction. The C54 phase is obtained after a second anneal at about 700 °C. The transformation of C49 to C54 constitutes one of the main problems in the salicide process using Ti\textsubscript{Si\textsubscript{2}}: higher doping level,\textsuperscript{29-31} thinner Ti film,\textsuperscript{23,32} and/or narrower line width\textsuperscript{33-37} increases the transformation temperature. The C54 Ti\textsubscript{Si\textsubscript{2}} growth is also affected by the dimensions of the interconnection lines.\textsuperscript{38-40} In thin films, the C54 Ti\textsubscript{Si\textsubscript{2}} grows isotropically in two dimensions, while in narrow lines, its growth is dominated by one dimensional growth along the lines if the linewidth is much smaller than the average distance between two nuclei (Fig 4). A consequence of this one dimensional growth is increases in line resistivity and resistance scattering. Reduction of the device dimensions also decreases the temperature at which the Ti\textsubscript{Si\textsubscript{2}} film begins to agglomerate,\textsuperscript{41-43} which results in reduction or even disappearance of the process temperature window. The process temperature window is determined, at the high end, by the film stability and, at the low end, by the temperature for the C49-C54 transformation. The highest process temperatures should also be kept low to preserve the electrical characteristics of the shallow junctions.
Figure 4: Schematic representation of two dimensional growth on blanket substrate leading to complete transformation (a), and one dimensional growth in narrow lines with
- three C54 nuclei leading to complete transformation (b),
- one C54 nucleus leading to partial transformation (c),
- no C54 nucleus resulting in no C49-C54 transformation (d).
A number of different approaches have been used to lower the temperature of the C54 formation. Ion bombardment of the C49 TiSi$_2$ with Ar or N$_2$ failed to promote the C49 to C54 transformation. Xenon implantation in the poly-Si substrate prior to Ti deposition lowered the transformation temperature by 150 °C, but Ar implantation in the C49 TiSi$_2$ increased it. It has also been reported that the presence of Sb impurities in amorphous TiSi$_2$ decreases the activation energy of the C49 to C54 transformation. Preamorphisation of the Si surface with As before Ti deposition enhanced the C54 TiSi$_2$ formation. In spite of the diverse studies, a reliable process for the formation of C54 TiSi$_2$ on devices with very narrow lines (<0.3 µm) remains to be confirmed. The C49 phase forms first independently of the fabrication process (deposition of Ti, Ti-Si alloys or Si/Ti multilayers), and of the surface treatment (amorphisation). Kinetic factors instead of thermodynamic factors seem to play an important role in the formation of TiSi$_2$ leading always to the formation of the C49 phase and then to the transformation into C54.

An important breakthrough has been made by Mann et al. The implantation of Mo or W at doses as small as 1×10$^{13}$-1×10$^{14}$ ions/cm$^2$ (at 45 keV) into the substrate prior to Ti deposition lowers the temperature for the C54 formation by 100-150°C. Mann et al. suggested that the implantation enhances the nucleation of the C54 at the triple junctions of the C49 grains. The density of triple junctions of the C49 phase would be a controlling factor for the C54 nucleation, smaller C49 grains should lead to an easier C49-C54 transformation. However, an interposed layer of Al between Ti and Si results in smaller C49 grains but it increases the temperature of the C49-C54 transformation. The disilicides formed with Mo and W have a crystallographic structure very similar to that of C54 TiSi$_2$. This particularity could explain why the implantation of Mo or W enhances the C54 formation, whereas implantation of other atoms, like Ar or As, dependent on the dose, does not affect or even hinders the C54 formation.

The work of Mann et al. extends the usefulness of TiSi$_2$ in the ULSI technology and presents new opportunities to investigate the formation of TiSi$_2$. In the next chapter, the crystallographic structure and the kinetics of formation of RMSi$_2$ will be examined.
3 Silicides sharing a crystallographic structure similar to that of C54 TiSi₂

3.1 Crystallographic structure

The disilicides formed with Cr, V, Mo, W, Ta, Nb and Ti have very similar crystallographic structures referred as C40, C11b and C54 in the Ewald and Hermann’s nomenclature (see Table II). The fundamental building block of those disilicides is a close-packed hexagonal plane of atoms (Fig. 5). The environment of both Si and metal atoms is equivalent in the three types of disilicides. The crystallographic cell of the disilicide is built with the stacking of the hexagonal plane shown in Fig. 5. Figure 6 illustrates the position of a metal atom in the different layers of the hexagonal planes. In the first layer, the metal atom is at A, in the second layer, it is at B, etc… The structure is tetragonal C11b if the stacking order is …ABA… It is the hexagonal C40 for the stacking …ABCA… and orthorhombic C54 for the stacking …ABCDA… (see Fig. 7). For the latter, it is the slightly distorted hexagonal plane that makes the structure orthorhombic. In fact, the angle between hexagonal axes in the stacking plane is 121°, instead of 120°. It can be pointed out that, in all those structures, the metallic atoms are surrounded by Si atoms and do not touch other metallic atoms. The diffusion of Si atoms is then easier than that of metallic atoms.

![Figure 5: Two-dimensional atomic arrangements in the stacking plane for the C54, C40 and C11b. The axis $a'_{C11b}$ in the C11b cell is the parallel of the (110) planes in the C11b structure.](image-url)
Table II: Crystallographic properties of the RM disilicides.\textsuperscript{54,55}

<table>
<thead>
<tr>
<th>Silicide</th>
<th>Crystallographic structure</th>
<th>Angle between hexagonal axes in the stacking plane</th>
<th>Interatomic distance in the stacking plane (nm)</th>
<th>Distance between the stacking planes (nm)</th>
<th>limit of solubility of Ti in RMSi\textsubscript{2} at 1300 °C (%)</th>
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<tbody>
<tr>
<td>TiSi\textsubscript{2}</td>
<td>C54</td>
<td>121°</td>
<td>0.276</td>
<td>0.2138</td>
<td></td>
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<tr>
<td>TiSi\textsubscript{2} (metastable)</td>
<td>C49</td>
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<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>VSi\textsubscript{2}</td>
<td>C40</td>
<td>120°</td>
<td>0.264</td>
<td>0.2124</td>
<td>85</td>
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<tr>
<td>NbSi\textsubscript{2}</td>
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<td>?</td>
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<tr>
<td>CrSi\textsubscript{2}</td>
<td>C40</td>
<td>120°</td>
<td>0.256</td>
<td>0.2121</td>
<td>88</td>
</tr>
<tr>
<td>MoSi\textsubscript{2}</td>
<td>C11</td>
<td>120°</td>
<td>0.261</td>
<td>0.227</td>
<td>0</td>
</tr>
<tr>
<td>MoSi\textsubscript{2} (metastable)</td>
<td>C40</td>
<td>120°</td>
<td>0.266</td>
<td>0.21416</td>
<td>80</td>
</tr>
<tr>
<td>WSi\textsubscript{2}</td>
<td>C11</td>
<td>120°</td>
<td>0.262</td>
<td>0.228</td>
<td>0</td>
</tr>
<tr>
<td>WSi\textsubscript{2} (metastable)</td>
<td>C40</td>
<td>120°</td>
<td>0.266</td>
<td>0.2138</td>
<td>60</td>
</tr>
</tbody>
</table>

Figure 6: Position of the metal atom in the stacking of the hexagonal planes. The metal atom is at position A in the first layer, at B in the second layer, etc...
In these various silicides, the crystallographic structures are similar, and the interatomic distances in the stacking plane are comparable within 8%. Figure 8 shows the area of one hexagon (i.e. one metal and six Si atoms) for the different RM silicides. Ternary silicides can form with a mixture of Ti and RM at the metal sites. In the pseudo binary systems of TiSi$_2$-RMSi$_2$, the composition in atomic percent for the metal atoms only (RM/(RM+Ti)) is the same as the molar composition if one considers the system TiSi$_2$-RMSi$_2$. In what follows one shall quote the composition in percentage referring to either one of these equal quantities without any further definition. One may note that in all of the similar structures considered here, where the metallic atoms do not touch each other, the percentage thus given corresponds to the relative occupation of the metal sites. The solubility limit of Ti in the RMSi$_2$ at 1300 °C varies from 50 % at the metal site in C40 TaSi$_2$ up to 88 % in CrSi$_2$. The ternary silicide (Ti,RM)Si$_2$ has a C40 structure and in the case of (Ti,Mo)Si$_2$ at least, the interatomic distance in the stacking plane lies between those of MoSi$_2$ and TiSi$_2$.56,57
Figure 8: Area of one hexagon in the stacking plane for the RM silicides.
### 3.2 Formation of the silicides

When a film of RM is deposited on Si and heated, the thickness of the RM silicides has been reported to vary linearly with time (see Table III).\textsuperscript{2,21} It indicates, in general, that the nucleation of the RM silicides is not rate limiting. The growth may be interpreted as controlled by the reaction at the silicide/metal interface since Si is the dominant diffusive species.\textsuperscript{21} This type of growth is often regarded as “ill-behaved”,\textsuperscript{58} because it is difficult to reproduce the results, as the reaction seems to be dependent on external factors such as native oxide, stress, etc...

As the growth of these disilicides is mediated by Si diffusion, it is important to have the knowledge of Si diffusion coefficient in the silicides. The activation energy of the Si diffusion in a silicide is proportional to the silicide melting point in Kelvin. Hence, depending on temperature, the Si diffusion can differ by a factor of 1000 among the various silicides. It is faster in TiSi\textsubscript{2} than in MoSi\textsubscript{2}, NbSi\textsubscript{2}, TaSi\textsubscript{2} or WSi\textsubscript{2}.

The aim of this work was first to investigate the influence of Mo on the TiSi\textsubscript{2} formation. Later on, other RMs such as Ta and Nb instead of Mo were introduced in the Ti-Si system before silicidation. The results are discussed in the next chapter, where the appended papers are presented.

#### Table III: Formation and melting temperatures and growth kinetics of RM disilicides\textsuperscript{2,21}

<table>
<thead>
<tr>
<th>Silicide</th>
<th>Formation Temperature (°C)</th>
<th>Time dependent growth</th>
<th>Melting temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSi\textsubscript{2}</td>
<td>600</td>
<td>-</td>
<td>1500</td>
</tr>
<tr>
<td>VSi\textsubscript{2}</td>
<td>600</td>
<td>$t, t^{1/2}$</td>
<td>1677</td>
</tr>
<tr>
<td>NbSi\textsubscript{2}</td>
<td>650</td>
<td>?</td>
<td>1940</td>
</tr>
<tr>
<td>TaSi\textsubscript{2}</td>
<td>650</td>
<td>$t$</td>
<td>2040</td>
</tr>
<tr>
<td>CrSi\textsubscript{2}</td>
<td>450</td>
<td>$t$</td>
<td>1490</td>
</tr>
<tr>
<td>MoSi\textsubscript{2}</td>
<td>525</td>
<td>$t$</td>
<td>2020</td>
</tr>
<tr>
<td>WSi\textsubscript{2}</td>
<td>650</td>
<td>$t, t^{1/2}$</td>
<td>2160</td>
</tr>
</tbody>
</table>
4 TiSi$_2$ formation in the presence of refractory metal

4.1 Experimental

For more detailed information, readers should refer to the appended papers. A brief summary of the sample preparation and characterisation is presented below. In order to study the effects of RM on the TiSi$_2$ formation, various types of samples were prepared (Fig. 9). The concentration of RM versus depth is different depending on how the RM is introduced in the Ti-Si system. How the sample preparation can affect the TiSi$_2$ formation will be shown later.

Figure 9: The various types of samples, with the concentration of the RM versus depth.
At first, the RM was introduced as a thin interposed layer (0.1 to 2 nm thick) between the Si substrate and the Ti films. The metals were deposited consecutively without breaking the vacuum with a dual source e-beam evaporator. The base pressure in the deposition chamber was $3 \times 10^{-5}$ Pa. The deposition rates were 0.5 nm/s for Ti and between 0.01 and 0.5 nm/s for the RM. It was pointed out in paper 3 that purging the chamber with N$_2$ prior to the deposition affects substantially the silicidation. Samples with a TiN cap about 60 nm thick on top of Ti were also prepared for kinetics studies. In that case an MRC 643 sputter deposition chamber with a load lock system was used (IBM Thomas J. Watson Research Center, Yorktown Height, USA). The films (TiN, Ti and RM) were deposited consecutively without breaking the vacuum. The base pressure in the chamber was $10^{-5}$ Pa.

Samples with Mo implantation were prepared at INSA-Lyon. After the studies with the interposed layer of Mo, the presence of Mo at the Si/Ti interface seems to be important. Therefore, to obtain a shallow depth profile, a low implantation energy was used (45 KeV). The maximum implantation dose was $5 \times 10^{14}$ at/cm$^2$. The subsequent Ti deposition was then carried out in Kista with the same evaporator as mentioned above.

From the process point of view, the deposition of a thin interposed layer below 2 nm can be somewhat difficult to control, and the Mo implantation is not desirable. The use of Ti-RM alloys appears as the best solution for the introduction of the RM in the Ti-Si system. Such samples were prepared at IBM. The alloy films were deposited in an ultra high vacuum (UHV) magnetron cosputtering system. The base pressure was about $1 \times 10^{-7}$ Pa.

A variety of ex situ analyses was carried out in this work. They include the routinely used sheet resistance measurement with a linear 4 point probe, X-Ray diffraction (XRD) with the $\theta$–$2\theta$ (Bragg-Brentano) geometry using Cu K$\alpha$ radiation and Rutherford backscattering spectrometry (RBS) with $^6$He ions at 2.4 eV to obtain the first set of information about the silicidation, i.e. phase formation, morphology, film texture, layer configuration and composition. For some experiments, more specific analysis tools were used. Transmission Electron Microscopy (TEM) was carried out in Kista and at INSA-Lyon to get the cross-sectional morphology and lattice imaging. The redistribution of impurities was monitored with Secondary Ion Mass Spectrometry (SIMS), also in Kista and at INSA-Lyon. Finally, atomic force microscopy (AFM) was used to study the surface morphology in Kista. Thanks
to the collaboration with IBM Watson Research Center, I had also the access to in situ analyses. The in situ analyses were carried out at the IBM/MIT beam line X20C, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). In situ XRD and resistance measurements were performed simultaneously to monitor phase formation as a function of temperature or time. Synchrotron radiation with a wavelength of 0.1797 nm was used in the in situ XRD analysis.
4.2 Interposed layer

Mann et al.\textsuperscript{51} have shown that Mo implantation in Si prior to Ti deposition enhances greatly the formation of C54 TiSi\textsubscript{2}. However, ion implantation of Mo is not a desirable process. Therefore, a different approach was used in this work: a Mo layer was deposited between the Ti layer and the Si substrate. Hence, the salicide process can still be used in the same way as is described in Fig. 1, but with the modification of replacing the deposition of Ti with that of Mo/Ti bilayer. The use of the Mo interposed layer is simpler than Mo implantation that introduces an additional process step. Furthermore, a post-annealing step at elevated temperature is required if the dose of Mo is above $10^{14}$ at/cm\textsuperscript{2} because implantation damage has to be removed.

The study of the role of the Mo interposed layer was initiated on bare monocrystalline (mono) Si wafers with different thicknesses of Mo (\textbf{paper 1}). The presence of the Mo interlayer apparently slows down the Si diffusion and consequently controls the thickness of TiSi\textsubscript{2} grown in a given interval of time. The C54 TiSi\textsubscript{2} formed is more textured with Mo than without, and an additional phase, C40 (Mo,Ti)Si\textsubscript{2}, is found. On the basis of XRD and RBS results, an epitaxial mechanism called template mechanism is proposed in \textbf{paper 1}. The (Mo,Ti)Si\textsubscript{2} identified on the XRD spectra is situated at the Si/TiSi\textsubscript{2} interface. If the initial Mo is thick enough, a continuous (Mo,Ti)Si\textsubscript{2} layer forms as can be seen on the TEM picture in Fig. 10. The XRD spectra indicate also that the C54 TiSi\textsubscript{2} grows preferentially oriented to the <010> crystallographic direction on top of the (Mo,Ti)Si\textsubscript{2} that is oriented to the <001> crystallographic direction. The ternary alloy (Mo,Ti)Si\textsubscript{2} has a hexagonal crystallographic structure referred to as C40. The similarities between the hexagonal C40 and the orthorhombic C54 structures have already been discussed in \S3. Furthermore, the in-plane lattice mismatch between the basal planes (003) of the (Mo,Ti)Si\textsubscript{2} and the (040) planes of the C54 TiSi\textsubscript{2} is within 3\%. Consequently, epitaxial growth of C54 TiSi\textsubscript{2} is anticipated to occur on top of the C40 (Mo,Ti)Si\textsubscript{2}. In other words, the enhanced formation of C54 is the result of a template mechanism, i.e. epitaxial growth of C54 TiSi\textsubscript{2} on C40 (Mo,Ti)Si\textsubscript{2}. With the Mo interlayer, the formation of C54 occurs at lower temperatures, and no C49 phase is detected, instead, direct formation of the C54 phase is observed.
Since the formation of TiSi$_2$ on polycrystalline (poly) Si has been the major technological concern, the logical continuation was to study the influence of Mo on TiSi$_2$ formation on poly-Si substrates (paper 2). The presence of Mo results also in the direct formation of C54 phase. However, the TiSi$_2$ formation occurs at a slightly higher temperature, 700 °C on poly-Si as compared to 650°C on mono-Si. This difference in the TiSi$_2$ formation temperature due to different substrates used, has been reported by others. The TiSi$_2$ is found less textured on poly-Si than on mono-Si. The influence of the dopant level on the TiSi$_2$ formation with a Mo interposed layer was also studied. A high level of doping concentration in poly-Si does not affect the C54 formation. The template mechanism for the enhanced formation of C54 TiSi$_2$ with a Mo interposed layer proves to be valid on poly-Si as well.

In order to confirm that this mechanism is operative, Mo was replaced with another metal which could, upon annealing, leads to the formation of a compound having the same crystallographic characteristics as (Mo,Ti)Si$_2$. This is the main theme developed in papers 3 & 4 where Ta and Nb, respectively, were used as the interposed layer between Si and Ti. Silicon is the dominant diffusion species in both Si-metal diffusion couples. The formation of the template layer should then occur at the Si/TiSi$_2$ interface where the RM is originally situated. In fact, the in-plane lattice match between the (040) planes of the C54 and the basal

\[ \text{TiSi}_2 \]
planes of TaSi$_2$ or of NbSi$_2$ TiSi$_2$ is even better (<0.3%) than between the C54 (040) and the (Mo,Ti)Si$_2$ (003) (Fig. 8). Indeed, the Ta and Nb interlayers are found to be as effective as the Mo interlayer in enhancing the C54 phase formation.

Further work was carried out to investigate how the template mechanism takes place at the atomic level (paper 5). After annealing of the Si/Ta/Ti structure at 650 °C, two different (Ti,Ta)Si$_2$ phases are found at the Si/silicide interface. Figure 11 summarises the various phases and their orientation observed by TEM. The Ta to Ti ratio changes rapidly from 0.11-0.12 at the interface to zero at about 35 nm from the interface. One of the (Ti,Ta)Si$_2$ phases has a C40 structure (Fig. 11a) and the other one has a C54 structure (Fig. 11b). At such low temperature, the composition of these two phases indicates that neither of them is in thermodynamic equilibrium, according to Kudielka et al. Inside one grain, the C54 crystal can be rotated in such a way that two regions are found with different orientations. Yet the two types of orientations have the C54 <010> axis in common (b and c in Fig. 11). In fact in all grains observed by TEM, the <010> axis of the C54 or the <001> axis of the C40 is always at 20 ° off the surface normal. This off-orientation is in good agreement with the finding in paper 3. In addition, staking faults are observed in the <010> stacking direction of the C54 phase. Further away from the Si-silicide interface, only C54 grains are found. Those observations illustrate the epitaxial relationship between the C40 and C54 phases. After annealing at a higher temperature (i.e. 750 °C), no C40 was detected either by TEM or by XRD. Thus, the formation at 650 °C of C40 and C54 (Ti,Ta)Si$_2$ in non-thermodynamic equilibrium confirms the existence of the template mechanism between the C40 phase and the C54 phase.
Figure 11: The different phases and their orientation observed by TEM.

(a) C40 (Ta,Ti)Si$_2$ with <001> direction 20° off the surface normal,
(b) C54 (Ti,Ta)Si$_2$ with its <010> direction aligned with the <001> of the C40 phase,
(c) C54 (Ti,Ta)Si$_2$ with a rotation about surface normal in its <010> planes as compared to (b), and
(d) C54 (Ti,Ta)Si$_2$ as in (b) but with stacking faults in the <010> direction.

The gray scale represents the concentration of Ta, with black as maximum (i.e. Ta/Ti=0.11 right at the Si/silicide interface).
4.3 Implantation

The samples with an interposed layer of Mo, Nb or Ta, as analysed by ex situ means, always show the direct formation of C54 TiSi$_2$. However, a more systematic study using in situ analyses indicates that with a very thin Mo interposed layer (0.06 nm) the C49 phase does form. It was in fact suggested in paper 3 that it is not a prerequisite to have a continuous layer of (Mo,Ti)Si$_2$ for the enhanced formation of C54 TiSi$_2$ to occur. In this regard, Mo introduced in Si by implantation enhances the formation the C54 TiSi$_2$ at those specific locations in the neighbourhood of Mo atoms. Nucleation of the C49 phase could be observed in the regions not in contact with Mo atoms. It has been demonstrated that Mo implantation increases the number of C54 nucleation sites. In fact C49 and C54 phases can coexist under certain conditions of annealing. Figure 12 illustrates schematically how the amounts of RM in the Ti-Si system may influence the nucleation and the subsequent growth of TiSi$_2$. Once formed, the crystallites of the C54 phase being the stable one in TiSi$_2$, grows rapidly at the expenses of C49. Thus, a non-continuous layer of Mo can also induce the enhanced formation of C54 TiSi$_2$.

At this point, the study of the effect of Mo implantation as compared to that of Mo interposed layers was considered to be a logical continuation of my thesis work (paper 6). The preferential orientation of C54 TiSi$_2$ is dependent on the thickness of the interposed layer as also shown by Zhang et al. For a “thick” interposed layer (0.7 nm), the C54 structure has a <010> orientation that is a consequence of the template mechanism (papers 1-3). In the presence of a "thin" interposed layer (0.09 nm), the preferential orientation of the C54 TiSi$_2$ grown is the same as that of C54 TiSi$_2$ formed with implanted Mo, the orientation is <110> as in the C54 TiSi$_2$ layer formed without Mo additions. This variation in preferential orientation indicates that as long as the (Mo,Ti)Si$_2$ does not form a continuous layer, it does not dominate the preferential orientation of C54 TiSi$_2$. However, the formation temperature of the C54 is consistently lowered by the presence of Mo in the Ti-Si system, independently of the deposition mode. For the same amount of Mo introduced at the Si/Ti interface, the Mo implantation induces the TiSi$_2$ C54 formation at a lower temperature than when the Mo is deposited as an interposed layer. This difference in the formation temperature of C54 TiSi$_2$ is
attributed to the formation of C11b MoSi2 during the post implantation anneal in the case of Mo implantation. Small crystallites of C11b MoSi2 formed in the vicinity of the interface and act as seeds for the nucleation of the C54 TiSi2 as soon as silicidation starts.

Figure 12: Models for the formation and the growth of TiSi2 in the presence of
(a) a thick (i.e. continuous) interposed layer of RM,
(b) implanted or thin (i.e. non-continuous) layer of RM, and
(c) Ti-RM alloys.
4.4 Alloy

From the process point of view, neither implantation nor the interposition of a thin RM layer is desirable. The deposition of a thin interposed layer is difficult to reproduce, and ion implantation of RM presents compatibility problems. Titanium alloys were chosen by IBM scientists as an alternative solution to introduce RM in the Ti-Si system. With the help of the IBM group, it was possible to study the Ti-Nb-Si ternary system (paper 7). The pseudo-binary diagram of NbSi$_2$-TiSi$_2$, as that of TaSi$_2$-TiSi$_2$, is composed of three phase domains: 1) C54 (Ti,Nb)Si$_2$, 2) C54 (Ti,Nb)Si$_2$+C40 (Ti,Nb)Si$_2$ and 3) C40 (Ti,Nb)Si$_2$. At 1000 °C, the solubility limit of Nb in TiSi$_2$ lies between 10 and 16 % of Nb and that of Ti in NbSi$_2$ lies between 76 and 79.6 % of Ti. Increasing the Nb content in either C40 (Ti,Nb)Si$_2$ or C54 (Ti,Nb)Si$_2$ increases the unit cell dimensions by about 0.035 % per at.% Nb. The existence of C40 (Ti,Nb)Si$_2$ with up to 76 % of Ti and interatomic distances lying between those of C54 TiSi$_2$ and C40 NbSi$_2$ confirm that a Nb interposed layer can play the same role as a Mo interposed layer in the enhancement of the formation of the C54 phase (paper 4).
4.5 New growth kinetics

All the various experiments discussed so far show the enhanced formation of C54 TiSi$_2$ in the presence of RM. The formation of silicides can be governed by different mechanisms\textsuperscript{27,58}. The phase formation, in general, starts with the nucleation of a new phase followed by its growth (Fig. 13). The nucleation rate is dependent on the changes in volumetric free energy and surface energy due to the formation of the nucleus, and on atomic transport. The atomic supply of species involved, Si or metal or both through the growing silicide control the growth of the new phase. If the nucleation is easy and fast, the growth is controlled by diffusion. On the contrary, if the nucleation is difficult and the diffusion rapid, the formation is nucleation controlled. With the standard process, the C49 TiSi$_2$ forms first, followed by the C49-C54 transformation. The latter process driven by a small free energy change is nucleation controlled. As a consequence, the C54 phase cannot be obtained below a threshold C54 temperature (about 700 °C) and prolonging the annealing time does little to cause the C49-C54 transformation to happen. In paper 4, it is shown that the formation of TiSi$_2$ with a Nb interposed layer is more dependent on the annealing time than without interposed layer.

\[
\rho^* = K \exp \left( \frac{-\Delta G^*}{kT} \right) \Delta G^* = \gamma \frac{\Delta \sigma}{\Delta G^2} + Q
\]

\[
\frac{dl}{dt} = \Omega \left( \frac{1}{l^3} + \frac{1}{D} \right)
\]

\(\rho^*\) Nucleation rate  
\(\Delta G^*\) Critical energy of a nucleus  
\(\gamma\) Geometrical factor  
\(K\) Proportionality factor  
\(\Delta \sigma\) Change in surface energy  
\(\Delta G\) Change in free energy  
\(Q\) Activation energy of diffusion  
\(l\) Thickness of the growing phase  
\(\Omega\) Volumetric constant  
\(D\) Diffusion coefficient of Si in the new phase  
\(k\) Rate constant of interfacial reaction

Figure 13: Schematic of phase formation with first nucleation and then phase growth.
By using a Nb or Mo interposed layer, the C54 phase was obtained at 450 °C, a temperature well below the threshold temperature of the C49-C54 transformation without RM additions (paper 8). Once again, this demonstrates that the usual route of the C54 formation is modified by the presence of the interposed layer. The C54 formation is not a result of the phase transformation. Rather it depends on the formation of a template layer of C40 RM silicide. Consequently the C54 formation is controlled by other kinetics than nucleation. The effect of RM is at least two fold. By forming silicide crystallites with a C40 structure at the Si/Ti interface, it provides seeds for the growth of C54 TiSi$_2$ and thus lowers the surface energy needed to form the C54 TiSi$_2$ (Fig. 13). As discussed earlier, the activation energy of diffusion scales with the melting point of the silicide. For example, Si diffusion is 1000 times slower in MoSi$_2$ than in TiSi$_2$ at 600 °C. Thus the presence of interfacial RM can lower the Si diffusion coefficient substantially and also affect the activation energy of diffusion for nucleation (Fig. 13). On the other hand, the stable phase in TiSi$_2$ shifts successively from C49 to C54 and then to C40 as the electron to atom ratio (e/a) increases.$^{18}$ Replacing Ti by Ta, Nb, W or Mo increases the e/a ratio; the formation of C49 becomes then more difficult whereas that of C54 or even C40 becomes easier.

In the absence of RM, the growth of C54 TiSi$_2$ initiated by the C49-C54 transformation is lateral and dependent on the formation of C54 nuclei, thus on a critical temperature (Fig. 14a). In the Ti-RM alloy (Fig. 9c), Nb (or Ta or Mo) is uniformly distributed, and the formation of C49 TiSi$_2$ may not be suppressed if the Nb content is below 10 at.% (paper 7). As the C40 (Nb,Ti)Si$_2$ is formed uniformly throughout the layer (fast Si diffusion), a rather homogeneous C49-C54 transformation can take place within the entire layer. The growth kinetics will remain the same, nucleation controlled, but with a much greater rate because of a higher density of nuclei (i.e. C40 (Nb,Ti)Si$_2$). This phenomenon is what can be inferred from the in situ XRD and resistance measurements in Cabral et al.$^{63}$ Indeed the Nb does not prevent the C49 TiSi$_2$ from forming. Nor does it change the resistance characteristic corresponding to the C49-C54 transformation.
In the case of Mo implantation, the C54 TiSi$_2$ growth is reported to be controlled by the Si diffusion through the growing TiSi$_2$. The growth is planar (Fig. 14b) and the thickness of the C54 TiSi$_2$ layer is proportional to the square root of time.$^{64}$

Figure 14: Two different types of growth
(a) lateral growth, and
(b) planar growth.
Not to scale, the films drawn are much thicker than in reality
Similarly to the case of Mo implantation the growth kinetics is expected to change when the RM is introduced as an interposed layer. In order to study the effect of Mo interlayer on growth kinetics, samples with 2 nm Mo/128 nm Ti/60 nm TiN were prepared. The inclusion of the surface TiN was to avoid oxidation during silicide formation. Figure 15a shows a cross-sectional TEM picture obtained on a sample annealed at 620 °C for 1200 s. The four distinct layers found in the figure are, according to XRD results and counting from the top, TiN, Ti-rich phase TiSi$_x$, C54 TiSi$_2$ (+ C40 (Ti,Mo)Si$_2$), and poly-Si. All interfaces between each two adjacent layers are rather sharp and follow well the surface morphology of the Si substrate, as also found in other samples annealed for different lengths of time (not shown here). The results indicate that the silicide growth in the presence of Mo is indeed planar along the direction of surface normal. The measured thickness of the TiSi$_2$ layer is plotted in Fig. 15b as a function of annealing time. The growth of C54 TiSi$_2$ seems to follow a more complex law than pure parabolic$^{64}$ governed by Si diffusion through the growing TiSi$_2$ itself. The low magnification used in the TEM analysis prevents us from separating the interfacial C40 (Ti,Mo)Si$_2$ layer from the C54 TiSi$_2$ layer bulk, although the XRD results show its
presence. Therefore, the thickness values obtained are comprised of two contributions, one from the C54 TiSi$_2$ layer and one from the interfacial C40 (Ti,Mo)Si$_2$ layer. The thickness of the interfacial C40 (Ti,Mo)Si$_2$ layer depends not only on the initial Mo thickness but also on the composition of the final ternary alloy. Since the Ti-to-Mo ratio in the C40 structure can vary from 0 to 4, the thickness of this C40 (Ti,Mo)Si$_2$ interfacial layer can be anywhere between 5 and 25 nm (a factor of about 2.5 should be multiplied to the initial metal thickness to get the disilicide thickness). According to the RBS results of a similar sample annealed by RTA at 650 °C for 30 s (Fig. 16), 40 nm C54 TiSi$_2$ is formed on top of 15 nm C40 (Ti$_{0.66}$Mo$_{0.33}$)Si$_2$. The fact that the C40 (Ti,Mo)Si$_2$ layer remains at the interface between the Si substrate and the growing C54 TiSi$_2$, in agreement with the results in papers 1-3&5, allows for a relatively simple analysis of the experimental results in Fig. 15b. In the model presented below the interfacial C40 (Ti,Mo)Si$_2$ layer is assumed to quickly grow to 15 nm with a Ti-to-Mo ratio of 2 and remains unchanged during the subsequent annealing.

![RBS Spectrum](image)

**Figure 16:** RBS spectrum showing the formation of 40 nm TiSi$_2$ on top of 15 nm (Ti$_{0.66}$Mo$_{0.33}$)Si$_2$ after annealing a sample with a 2 nm Mo interlayer, at 650 °C for 30 s.

The different kinetic factors, i.e. interfacial reaction, Si diffusion through the interfacial C40 (Ti,Mo)Si$_2$ layer, and Si diffusion through the growing C54 TiSi$_2$ layer, are considered in order to account for the growth of C54 TiSi$_2$ in the presence of a Mo interposed layer.
silicide growth is sustained by Si diffusion from the Si/silicide interface to the reaction interface that is the one between the growing C54 TiSi₂ and Ti-rich phase (TiSiₓ). The steady-state growth is schematically shown in Fig. 17, with a flux for Si diffusion from the Si substrate towards the TiSi₂/TiSiₓ interface. The Si activity is shown at the respective interfaces, a₀ (= 1), a₁ and aᵢ. At the interface (Ti,Mo)Si₂/TiSi₂, the system is at equilibrium, the Si activity is then continuous. The diffusion of Si proceeds from the substrate first through the C40 (Ti,Mo)Si₂ layer (diffusion coefficient \( D_{\text{Si}}^{(\text{Ti,Mo})\text{Si}_2} \)), and then through the C54 TiSi₂ (diffusion coefficient \( D_{\text{TiSi}_2}^{\text{Si}} \)) to the reaction interface. The reaction at the TiSi₂/TiSiₓ interface can be characterized by a phenomenological reaction rate constant \( k_γ \).

The rate of thickening of the C54 TiSi₂ layer \( (l_{\text{TiSi}_2}) \) can now be expressed as:

\[
\frac{dl_{\text{TiSi}_2}}{dt} = \Omega \frac{1}{\frac{1}{k_γ} + \frac{l_{(\text{Ti,Mo})\text{Si}_2}}{D_{\text{TiSi}_2}^{\text{Si}}} + \frac{l_{\text{TiSi}_2}}{D_{\text{TiSi}_2}^{\text{Si}}}}
\]  

(1)

where, \( \Omega \) is a volumetric factor equal to 2.5.\(^{65} \) It should be noted that the Si diffusion through the interfacial (Ti₀.₆₆Mo₀.₃₃)Si₂ layer of invariant thickness (15 nm) with a constant diffusion coefficient \( D_{(\text{Ti,Mo})\text{Si}_2}^{\text{Si}} \) contributes in the same way as the interfacial reaction rate constant \( k_γ \) does to limit the interfacial reaction, i.e. both give rise to a linear growth kinetics. In fact, this formula is similar to that in Fig. 13 describing the phase growth where both linear growth terms are contained in \( k \). Once the C54 TiSi₂ layer becomes sufficiently thick, the growth enters the region where the diffusion through it is rate-limiting. Then, the variation of its thickness will follow the usual parabolic growth law.

Since all parameters in the denominator of Eq. 1 are constant except \( l_{\text{TiSi}_2} \), integration of Eq. 1 results in the well known linear-parabolic growth law once devised by Deal and Grove for the oxidation of Si:\(^{66} \)

\[
l_{\text{TiSi}_2}^2 + Al_{\text{TiSi}_2} = Bt
\]

(2)
with the linear and parabolic rate constants being equal to

\[
\frac{B}{A} = \frac{\Omega}{1 + \frac{l_{(Ti,Mo)Si_2}}{k_\gamma D_{(Ti,Mo)Si_2}^{Si}}} \quad (3)
\]

and

\[
B = 2\Omega D_{TiSi_2}^{Si} \quad (4)
\]

respectively. Thus, the experimental results in Fig. 15b are fitted using Eq. 2 with \(B=19\) \(\text{nm}^2/\text{s}\) and \(B/A=0.24\) \(\text{nm}/\text{s}\), after subtracting 15 nm from all data points. Since \(k_\gamma\) is usually big but not accessible, its contribution to the linear growth kinetics is neglected for estimating \(D_{(Ti,Mo)Si_2}^{Si}\). Therefore, the comparison between experiment and model gives \(D_{(Ti,Mo)Si_2}^{Si} = 1.4 \text{ nm}^2/\text{s}\) and \(D_{TiSi_2}^{Si} = 3.8 \text{ nm}^2/\text{s}\) at 620 \(^\circ\)C. Thus, Si diffusion in \((Ti_{0.66}Mo_{0.33})Si_2\) is about 2.5 times slower than in TiSi\(_2\) at this temperature.

Figure 17: Schematic of the steady-state planar growth of C54 TiSi\(_2\) in the presence of a \((Ti,Mo)Si_2\) interfacial layer. The layer thicknesses, the Si diffusion coefficients, and the interfacial Si activity are indicated.
5 Effects of refractory metal

5.1 On blanket substrates

It has been demonstrated that the formation of C54 TiSi$_2$ can be enhanced by the presence of a specific RM (Mo, Ta and Nb for example). The presence of RM can also affect other properties of TiSi$_2$, which is described below.

5.1.1 Thermal stability and morphology

Among the different properties that are important for advanced Si device technology, thermal stability and morphology of the silicides are investigated (papers 4&10).

In general, on mono-Si substrate, grooving leading to agglomeration (Fig. 18) causes the film disintegration. Small grain size and thicker film should improve the resistance to agglomeration. The interposed layer promotes the epitaxial growth of C54 TiSi$_2$, and increased the number of nuclei. Hence, the TiSi$_2$ is smoother, with smaller grains and more resistant to grooving.

![Figure 18: Schematic view of grooving mechanism, (a) energy balance at upper and lower grain boundary, (b) grain morphology for different grain size.](image-url)
The Si diffusion is sufficiently high in a TiSi$_2$ film to allow Si grain growth.\textsuperscript{68} Therefore, the presence of a TiSi$_2$ film on top of the poly-Si substrate promotes the Si grain growth leading to the break-up of the TiSi$_2$ film (Fig. 19). When TiSi$_2$ is formed with a Mo interlayer, C40 (Ti,Mo)Si$_2$ forms at the interface. The properties of this ternary phase are not known. However, it may be expected that its behaviour should be very similar to that of the hexagonal MoSi$_2$. Thus, (Mo,Ti)Si$_2$ is susceptible to phase transformation (hexagonal to tetragonal) in the temperature range 800-1000°C or to decomposition into C54 TiSi$_2$ and C11b MoSi$_2$. This phase transformation occurs in a very similar system, Ti-W-Si, in the same range of temperature.\textsuperscript{69} These processes could stimulate the grain growth in the underlying poly-Si, thus cause the TiSi$_2$ film to break at lower temperature. In contrast, the presence of TaSi$_2$ at the poly-Si/ TiSi$_2$ interface does not affect the thermal stability of the TiSi$_2$ film.

![Figure 19: Schematic of the mechanism leading to film break down on poly-Si substrate.](image)

(a) initial film structure,  
(b) enhance diffusion of Si in silicide film, and  
(c) resulting structure.
Another important parameter for applications is the morphology of the Si-TiSi$_2$ interface. For the formation of shallow junctions, a smooth interface is of prime importance. In order to study the Si/TiSi$_2$ interface with AFM, the TiSi$_2$ was removed with a selective chemical etch. The root-mean-square (RMS) was chosen as a figure of merit for characterising the roughness of the Si/TiSi$_2$ interface. The presence of an interposed layer consistently results in a smoother Si/TiSi$_2$ interface when the substrate is mono-Si (Fig. 20). The interface with the lowest RMS value is obtained with a Nb interposed layer. Although on poly-Si substrate the interposed layer does not affect the roughness of the interface, the thermal and morphological properties of TiSi$_2$ are improved by interposing a layer of Ta or Nb.

![Graph showing RMS values of Si/TiSi$_2$ interface](image)

**Figure 20:** RMS values of the Si/TiSi$_2$ interface obtained according to AFM analysis.

- **Ti:** 60 nm Ti, (nominal thickness, same below)
- **Ta/Ti:** 60 nm Ti on 0.5 nm Ta
- **Mo/Ti:** 60 nm Ti on 0.5 nm Mo
- **Nb/Ti:** 60 nm Ti on 0.5 nm Nb
5.1.2 Resistivity

Titanium disilicide is the silicide of choice because, among other physical properties, it has a low resistivity. Adding an interposed layer between Si and TiSi₂ may modify the contact resistance (under investigation). It can also increase the total resistivity of the silicide. As the ternary silicide layer is typically between 5 and 10 nm, about 10-20 % of the whole silicide layer, its contribution to the overall sheet resistance can be neglected. On the other hand, the use of Ti-RM alloys can modify significantly the resistivity of the resulting silicide. It appears that among Ta, Nb and Mo, Nb affects the least the resistivity of the C54 TiSi₂ when the amount of RM in the C54 phase is under 12 % at the metal sites. In paper 7, the dependence of the resistivity on the metal composition of the silicide is studied from pure TiSi₂ to pure NbSi₂. The resistivity of C54 (Ti,Nb)Si₂ increases by 1.2 µΩ cm per at. % Nb at the metal site. In contrast, the resistivity of the C40 (Ti,Nb)Si₂ remains mostly insensitive to the alloy composition. The average resistivity value of this silicide is about 55 µΩ cm.
5.1.3 Dopant redistribution

The distribution of the dopants after the silicidation is important for shallow junctions and contact properties. In the salicide process, the formation of TiSi$_2$ proceeds as a solid phase reaction between the Si substrate and the deposited Ti. Thus, this leads to Si consumption and possibly dopant redistribution in the Si. Dopant redistribution during the silicidation was investigated for both p (B) and n (As) type. The dopants were introduced in the poly-Si substrate by ion implantation prior to Ti or Mo/Ti deposition. The implantation dose was $1 \times 10^{16}$ at/cm$^2$ and the energy 80 KeV for both dopants. The control samples without the Mo interlayer were annealed following the conventional salicide process: two step annealing at 700°C and 850°C, respectively, with a selective chemical etch in between (see Fig. 1). For comparison, the samples with a Mo interlayer were annealed at 800 °C for 30 s. The unreacted Ti and the TiN were removed by selective etch. The dopant profiles analysed by SIMS are shown in Fig. 21. It is clear that the presence of Mo does not affect the redistribution of either As or B. The rapid diffusion of As into the TiSi$_2$ layer (Fig. 21a) is well known. The segregation of B at the Si/silicide interface is the result of the formation of titanium boride (Fig. 21b).
Figure 21: SIMS depth profiling showing the (a) As and (b) B distribution in the sample with (filled symbols) and without (open symbols) a Mo interposed layer. The arrows indicate the position of Si/TiSi$_2$ and SiO$_2$/Si.
5.2 On patterned substrates

The formation of C54 TiSi2 with the standard salicide process becomes increasingly difficult as the device dimensions are scaled down, as shown schematically in Fig. 4. Since a Mo interposed layer enhances the formation of the C54 TiSi2 on blanket Si substrates, it is desirable to study its formation on patterned poly-Si. Titanium disilicide formation with a Mo interposed layer was investigated on narrow lines down to 0.25 µm.72

The samples were made as follow. Poly-Si films of about 300 nm thickness were deposited on oxidised Si wafers. The poly-Si films were patterned into narrow lines by photolithography and the photoresist ashing method. The linewidth obtained ranged from 0.2 to 1 µm. Two types of metal depositions were then carried out, one with 60 nm Ti and the other with a Mo/Ti bilayer (0.5 nm/60 nm). The silicidation was carried out in N2 at 700 or 800 °C for 30 s by RTA. Additional annealing at 850 °C was performed on the sample with only Ti after the first 700 °C anneal (i.e. standard Ti salicide process). After selective etch, the sheet resistance of the poly-Si lines was measured on the van der Pauw structures made. About 35 chips on each wafer lines were produced to determine the standard deviation of the resistance measurement.

Figure 22a presents the sheet resistance measured on the various samples as a function of the linewidth. On the reference sample (i.e. pure Ti and two step annealing process), the sheet resistance increases with decreasing linewidth. It is the direct consequence of the C49-C54 transformation being dependent on the linewidth: the smaller the patterned dimensions the more difficult the transformation. After only the first step annealing, the sheet resistance of the Ti sample is high but independent of linewidth, because the silicide formed is the high resistivity C49 whose formation is not controlled by nucleation. In the presence of Mo, the sheet resistance is low and mostly independent of linewidth after the 800 °C anneal. Perhaps of more technological importance is the standard deviation of the sheet resistance as shown in Fig. 22b. The sample with Mo/Ti annealed at 800 °C, and that with only Ti annealed at 700 °C have a very low standard deviation. The diffusion controlled growth of C54 TiSi2 in the presence of Mo interlayer (paper 9) is the key factor for a small scattering in the sheet resistance in the narrow Si runners. Similarly, the non-nucleation controlled growth of C49 TiSi2 in the control sample with Ti also leads to small scattering in sheet resistance in the
narrow runners. The low standard deviation found on these two samples also provides evidence to the formation of single phases, C49 on the sample with only Ti, C54 on the sample with the Mo/Ti bilayer. In contrast, the reference sample with TiSi$_2$ formed using the standard salicide process shows a large scatter in sheet resistance which can be described clearly with the assistance of the schematic diagrams in Fig. 4.

To summarise, the TiSi$_2$ films formed in the presence of Mo show better sheet resistance characteristics, i.e. low sheet resistance and small scatter in the sheet resistance values.
Figure 22: Sheet resistance (a) and standard deviation in sheet resistance (b) as a function of the linewidth of poly-Si runners (lines).
6 Summary and future trends

In the work leading to this thesis, a method to enhance the C54 TiSi\textsubscript{2} formation has been presented. A simple modification of the salicide process results in the direct formation of the C54 phase. Hence the difficult C49 to C54 transformation is avoided. The modification consists of adding an RM layer deposited between Si and Ti. At the beginning of the silicidation anneal, (RM,Ti)Si\textsubscript{2} with a C40 crystallographic structure forms and acts as a template layer for the direct formation of the C54 TiSi\textsubscript{2}. This is a consequence of the similarities between the C40 and C54 crystallographic structures. It was demonstrated that the enhanced formation of the C54 TiSi\textsubscript{2} through the template mechanism takes place with an interposed layer of either Mo, Ta or Nb. Evidences of the template mechanism were also shown at the atomic level with HRTEM. An interposed layer of Mo enhances the formation of C54 TiSi\textsubscript{2} on lines with width smaller than 0.3 µm. The presence of RM in the Ti-Si modifies the kinetics of the C54 formation. With a thick (1-2 nm) layer of Mo, the formation of C54 TiSi\textsubscript{2} is controlled by Si diffusion through the (RM,Ti)Si\textsubscript{2} and the TiSi\textsubscript{2} layer, resulting in a TiSi\textsubscript{2} film with smooth surface and interface. In fact, TiSi\textsubscript{2} formed with a Ta, Mo or Nb interposed layer on mono-Si has a smoother surface and an enhanced resistance to agglomeration. On poly-Si substrate, TiSi\textsubscript{2} films formed with Mo break up at a lower temperature than TiSi\textsubscript{2} films formed with Ta or without interlayer.

This method to enhance the formation of C54 TiSi\textsubscript{2} might be used for the sub-0.1 µm technology. Processes involving the presence of RM in the Ti-Si system for the formation of TiSi\textsubscript{2} have already been proposed. Preamorphisation and Mo implantation in Si prior to Ti deposition lead to low sheet resistance of the TiSi\textsubscript{2} formed on gates of 0.06 µm length. These processes are rather complicated and add at least three steps to the conventional process but result in the formation of low resistivity TiSi\textsubscript{2}. Low resistivity TiSi\textsubscript{2} was also formed on narrow lines using Ti-Nb alloys instead of Ti. This simple technological solution does not solve the nucleation problem of the C54 phase. The presence of Nb increases the number of nucleation centres for the C54 formation, but still C49 forms first. By using alloys, the C54 phase can form on submicron lines because of the increase of nucleus density. But the
problem of limited number of nuclei will come up again for the next generation of process
(0.15 or 0.13 µm). In order to solve the problem of the C54 formation, the C49 formation
must be prohibited. The use of a Nb interposed layer of 0.5 nm thickness shows that the C54
phase can form directly. The difficulties of the C49 to C54 transformation can then be
avoided. However, the controlled deposition of such thin layer is difficult to use at the
industrial level and necessitates further optimisation.

Another way to overcome the problems attached to TiSi$_2$ is to replace it by its strongest
concurrent CoSi$_2$. The formation of CoSi$_2$ is relatively easy to form on small device
features (below 0.18 µm) and from ultra thin Co layers (below 30 nm). However, the
formation of CoSi$_2$ also presents some difficulties. Because Co, unlike Ti, does not reduce
the native oxide on the Si surface, the formation of CoSi$_2$ is vulnerable to oxygen
contamination either from the native oxide or from the annealing atmosphere. The formation
of CoSi$_2$ is nucleation controlled leading to rough surface and interface. Moreover, CoSi$_2$
films agglomerate at 800 °C, a temperature 120 °C lower than for TiSi$_2$ films. Whereas
the consumption of Si must be limited or even reduced, the formation of CoSi$_2$ using a larger
amount of Si than that of TiSi$_2$ (by a factor of 1.6) might become an issue. For this aspect,
NiSi is very attractive; the formation of NiSi consumes about half of the Si amount consumed
by the formation of CoSi$_2$. The formation of NiSi occurs at 400 °C, 300 °C lower than that
of TiSi$_2$ and CoSi$_2$. Moreover, the NiSi formation is diffusion controlled resulting in NiSi
films with smooth interface and surface. The main disadvantage of NiSi is its poor thermal
stability: NiSi films agglomerate at 550 °C, and NiSi reacts with Si to form the high resistivity
NiSi$_2$ through a nucleation controlled process at about 800 °C.

In fact, among those three silicides, none presents strong advantages that would make it
indisputably the best possible choice. Titanium disilicide is still widely used in the Si
technology. The works presented at the MAM’99 in Leuven or at the MRS Spring Meeting 99
in San Francisco show the increasing interest of the industry (IBM, Texas Instrument,
Applied Materials) as well as of the universities for the formation of TiSi$_2$ in the presence of
RM. However, to keep TiSi$_2$ as the preferred silicide, a viable solution must be offered to the
semiconductor industry in the very near future.
7 References

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8 Appended papers


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