INVESTIGATIONS OF TRANSIENT PHASE FORMATION IN Ti/Si THIN FILM REACTION

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Abstract

The analysis of temperature and time dependence of the Ti film microstructure evolution in Ti/Si thin films indicates Si diffusion occurs before any crystal phase is formed. Diffusion occurs first in Ti grain boundaries and then, within the grains. Ti_5Si_3 has been identified as a transient phase forming before C49 TiSi_2 grows. Ti_5Si_3 only grows in isothermal runs in a narrow range of annealing temperatures (412-434°C in our study). It has not been observed in temperature runs in which C49 TiSi_2 forms. The mechanisms of Ti_5Si_3 formation and transformation into C49 have been found to be diffusion limited. Phases of alloyed Ti, amorphous silicide, Ti_5Si_3 and C49 TiSi_2 have been simultaneously observed. The lifetime and the volume fraction of the initial metal layer transformed into Ti_5Si_3 are naturally tightly temperature dependent.

Keywords: silicidation, transient phase, Ti_5Si_3 , X-ray diffraction

1. Introduction

The formation of TiSi_2 by annealing Ti films deposited on Si substrates has been extensively studied upon thermal treatment. Successive transient structural phases are formed before more stable phases, C49 and C54 TiSi_2 , can be obtained above 600°C . The first one, formed at annealing temperature close to 600°C , has the metastable and high resistivity C49 ZrSi_2 structure-type. Annealing above 800°C gives rise to the stable low-resistivity C54 structure¹⁻³.

Below 600°C , the reactivity of the Ti/Si system or, more generally of refractory metal/Si systems has been investigated in many studies to identify the reaction process leading to silicide formation. Two main superimposed processes can be retained, one proceeding by interfacial reaction between Si and Ti, one by Si diffusion in Ti grain boundaries□

1- Interfacial silicide formation was clearly reported in the Ti/Si system⁴ as well as in Ti/Si multilayers⁵. Whatever the Si substrate - amorphous or single crystal - a thin amorphous or very fine grain silicide layer, about 2 nm thick, was observed in as-deposited transition metal films, as reported in other papers (Ti⁶⁻⁷, Zr⁸⁻¹⁰, V⁸, Hf⁹). The more plausible origin of this layer is intermixing of metal and Si resulting from ballistic energy during the sputter deposition process. The layer can be further grown by low temperature annealing ($T \leq 450^\circ\text{C}$) up to about 15-20 nm of thickness, following a diffusion-controlled growth law. Voids were observed to be formed at the amorphous phase/Si interface in the case of Ti/amorphous substrate⁴. The growth process of the amorphous interlayer in the Zr/Si and Hf/Si systems, investigated by Cheng⁹ and Tanaka¹⁰, first consists of a rapid and linear increase up to a critical thickness: the amorphous layer grows into the metal layer by diffusion of Si in the amorphous layer. The growth rate then slows down and deviates from a linear growth law until a maximum thickness is reached: both Si and metal atoms are released from the respective interfaces to diffuse into the amorphous layer¹⁰. This causes a gradual increase in thickness to both sides of the amorphous layer. The growth is faster at the amorphous layer/Si interface than at the amorphous layer/metal interface. This may be related to the fact that Si is reported to be the dominant diffusing species in the Ti/Si system^{4, 11}. At each stage, the thickness increases with annealing temperature T. Saturation occurs in the final stage with the start of crystallization. The growth kinetics of amorphous interlayers in the Ti/Si¹², $\text{Ti/Si}_{1-x}\text{Ge}_x/\text{Si}$ or $\text{Ti/Si}_{1-x}\text{Ge}_x/\text{Ge}$ ¹³ systems was found to follow a similar growth behavior.

2- A grain boundary diffusion process was proposed by Rubloff et al¹⁴⁻¹⁵ to account for experimental results obtained at very low temperatures with Ti/(111) Si thin films, 2.5 nm thick, by using the high depth resolution of medium energy ion scattering. Extensive Ti-Si intermixing across the interface was observed from $250\text{--}300^\circ\text{C}$ with considerable spatial extent: the increased intensity of the Si signal at the film surface has shown that Si has already reached the Ti film surface from these

low temperatures. From excellent fits of their data, the authors have suggested that during intermediate reaction stages, the overlayer consists of two phases, one essentially unreacted and one fully reacted at the final stage. In this stage, the composition is close to TiSi and an extremely fine grain microstructure is observed (1-3 nm grains). Once reaction has proceeded at low temperature, growth of much larger silicide grains (~ 100 nm) is mostly prevented up to very high temperature ($\geq 800^\circ\text{C}$) is attained. Thus, in the case of very thin Ti film, this intermediate reaction stage can markedly change the kinetics and structure for subsequent high temperature formation of silicides.

Controversy about the composition of the amorphous silicide layer appears in literature. Raaijmakers and Kim suggested a composition close to TiSi ⁴; Ogawa et al showed the existence of a gradient, from about 70% Si near the substrate (i.e. close to TiSi_2) to about 30% Si close to the Ti interface and that TiSi_2 crystallites grow locally at the amorphous alloy/Si interface from temperature close to 460°C ⁷. For Cocchi et al, the amorphous phase has a graded composition between Ti_5Si_3 and TiSi ¹⁶. Many authors conclude that the formation and growth of amorphous interlayers may be seen as a precursor to crystallization and then, to the growth of epitaxial silicides^{7, 9}.

The formation of multiphases is quite general in the initial stages of interfacial reactions of refractory metal thin films on silicon. Not all the equilibrium phases may appear in the thin film interactions between metal films and Si substrate; the amorphous or crystalline state of the Si substrate as well as kinetic factors can play a critical role in determining the phase formation and the sequence of formed phases. As a consequence the nature of the first crystalline phase is still controversial. Some authors reported the nucleation of ZrSi_2 from 400°C ^{10, 17} and of C49 TiSi_2 between 450 and 500°C ^{4, 6, 7}, as first crystalline phases. Others related the formation of metal-rich silicide crystallites which are recrystallized before C49 formation is completed. They were identified as MSi , M_5Si_3 , M_5Si_4 . In the case of $\text{M}=\text{Zr}$, the corresponding annealing temperatures were in the range $440\text{--}480^\circ\text{C}$ ^{8, 9}. For $\text{M}=\text{Ti}$, they were reported to appear at $500 \leq T \leq 560^\circ\text{C}$, i.e. at temperatures just below the formation temperature of C49 TiSi_2 in the range $575\text{--}600^\circ\text{C}$ ¹⁸⁻²⁰. Ti_5Si_3 was reported to be the first nucleated phase in²⁰⁻²¹; it was found to locate at the amorphous layer/Ti interface whereas Ti_5Si_4 , TiSi and C49 TiSi_2 were found to distribute at the amorphous layer/Si interface²⁰.

The purpose of this work is a contribution to the understanding of the reaction process leading to silicide formation in the Ti/Si solid phase reaction. As previous works obviously indicate that multiple interfaces are present and have their own temperature dependence or kinetic evolution, the investigation was expected to be particularly difficult. However, we wanted to propose a comprehensive description of the microstructure evolution. Significant efforts have been specifically made to understand how silicon diffusion was taking place before crystallized phase seeding. To reach our purpose, in-situ X-ray diffraction (XRD) experiments were performed on Ti/Si films in a high-temperature diffraction stage. XRD results were correlated with Transmission Electron Microscopy (TEM) observations.

2. Experimental details

As-deposited samples were obtained by sputtering 100 nm-thick Ti on (100) Si substrates capped with a 250 nm-thick amorphous Si film. During deposition, substrates were kept at 100 °C to prevent samples from reaching temperatures at which the metal-silicon reaction could be started. Indeed, the energy transferred from the incoming atoms during deposition contributes to raise the substrate temperature. To protect the films from oxidation, the Ti films were then capped with a nominal 25 nm-thick TiN film.

Ti crystallizes in the hexagonal structure, space group $P6_3/mmc$. The lattice constants are $a=0.29505$ nm and $c=0.46826$ nm²². X-ray analysis indicated that the initial Ti metal films exhibit a high degree of (002) and (101) preferred orientation of fiber type with no in-plane orientation, according to X-ray analysis. TEM observations showed a pronounced columnar texture characterised by a high density of grain boundaries extending from the Si-metal interface to the TiN surface²³. From the measured 002/101 intensity ratio (≈ 3) and the diffraction powder data ($I_{002}/I_{101} \approx 0.4$), the estimated volume fractions were roughly 90% (002) and 10% (101). The TiN film had a columnar texture and (111) preferred orientation. The 111 TiN reflection did not show any marked change aside from the expected thermoelastic shift. The grain misalignments, evaluated from the full width at half maximum (FWHM) of ω scans recorded from the 002 Ti, 101 Ti and 111 TiN reflections are 4°, 5.1° and 8.2°, respectively.

To conduct in-situ experiments, the samples were annealed in a high-temperature diffraction stage used for in-situ XRD experiments. The hot stage allowed to heat samples up to 900°C, in slightly reducing gaseous atmosphere to preserve the samples from oxidation. As possible shifts from the diffractometer center are very critical in 2θ measurements, the apparatus was equipped with cooling liquid circulating in closed cycle up to the sample holder. This temperature control permits to minimize the shifts of the sample surface from the diffractometer center. A position-sensitive detector (INEL, CPS 120) spanning a 120° aperture and a conventional X-ray tube ($\lambda_{Fe K\alpha}=0.1936$ nm) were used. This combination allowed us to obtain, from a single pattern, reliable angular positions of the diffraction lines, and therefore, accurate values for thermal expansion coefficients of the investigated material. The crystal mosaicity estimated from the Ti 002 and 101 rocking curves was large enough to optimize the 002 and 101 $\theta/2\theta$ profiles by fixing the incident angle at $(\theta_{002} + \theta_{101})/2$.

The thermal expansion investigations have been done from samples at room temperature progressively annealed by applying repeated sequences of temperature ramps followed by stabilization. The typical temperature range between two stabilizations was 10 °C. The samples were

heated following this protocol up to a temperature where first tiny signals from the C49 phase started to be detected. This occurs near 540°C. Diffraction patterns were recorded for 200 s at each stabilization step (300 s for the highest temperatures).

The time evolution of the diffraction pattern was followed at three different temperatures (412, 422, 434°C) to characterize the Si diffusion process. For each experiment, the sample was heated following the same protocol - temperature ramp (14°C/mn) + stabilization - by steps of 100°C then, of some tens of degrees, from room temperature up to the desired temperature. As soon as temperature stabilized, data recording is started for 500 s.

TEM cross-section observations were made from a JEOL 200CX microscope. To prepare TEM specimen, a piece of sample was firstly mechanically thinned down to ~50 µm and then finally ion-milled from both sides, down to electron beam transparency by using a BALTEC RES010 ion-milling device.

3. Results and discussion

Data were recorded as a function of temperature or time (at constant temperature). The analysis showed the following:

- as temperature changes, the simple Ti-Si stacking gives rise to several interfaces that move up or down apparently independently. The resulting diffraction patterns then contain several contributions that possibly overlap.
- various interfaces are embedded at different levels.
- in the case of a metal-rich component, two interfaces are concerned with specific behaviors.

To overcome these difficulties, a very careful examination of the patterns was necessary. From these efforts, a set of new results can be presented.

3.1 Ti evolution as a function of temperature

The Ti 002 and 101 diffraction profiles were analyzed as a function of annealing temperature in the whole temperature domain where no other crystalline phase was observed in the diffraction pattern. The results were reported in a recent paper²⁴. We will summarize them briefly for convenience in the following. As seen in Fig. 1, three regimes can be distinguished in the thermal evolution of the angular positions:

I- A conventional thermal expansion is observed up to about 360°C, as seen from the d-spacing evolution in Fig. 1a. At the same time, reflection intensities slightly decrease (Fig. 1b). The resulting 'effective' perpendicular thermal expansion coefficients along the normal to the film were found to be

$(\alpha_{002}^{\text{perp}})_{\text{eff}} = 12.6 \times 10^{-6} \text{ K}^{-1}$ for (001) oriented grains and $(\alpha_{101}^{\text{perp}})_{\text{eff}} = 15.8 \times 10^{-6} \text{ K}^{-1}$ for (101) oriented grains. The FWHM of both reflections is nearly constant in this temperature range (Fig. 1c).

II- Above 360°C, a large shift of the reflections towards lower angles is observed, corresponding to a rapid increase of the d-spacing values (Fig. 1a), i.e. to a Ti expansion higher than the thermal expansion itself.

III- From a temperature close to 450°C, the expansion slows down (Fig. 1a) and the FWHM increases drastically (Fig. 1c). At the same time, the reflection intensities fall down.

At this stage of the reaction, no crystalline phase such as metal-rich silicide is observed, as mentioned above. Changes occurring at 360°C and 450°C are assigned to Si diffusion²⁴: first, it proceeds by Ti grain-boundary diffusion which develops a very compressive stress on Ti grains (≈ 1 GPa) and upon further annealing, intragrain diffusion is detected from the observed broadening of the diffraction profiles. The stress/strain analysis of the film reported in²⁴ shows that the maximum Si content in Ti grains is close to 4.5%. Such titanium is designed as alloyed Ti labeled Ti_{al} in the following.

3.2 Coexisting crystal phases

3.2-1 Crystal phase identification

Phase identification has been performed by combining TEM cross-section images (Fig. 2) and X-ray data (Fig. 3) obtained from Ti films in the as-deposited state and at different typical stages of the Ti-Si reaction. The typical stages were analyzed at room temperature from quenched samples. The quenched state was obtained by rapid cooling performed by suppressing the power onto the heating stage. Only Ti, TiN, Ti_3Si_3 , C49 TiSi_2 crystal phases and an amorphous component have been identified in the selected samples. Similar results are reported in literature. In addition, it was possible to locate the various layers as a function of the film depth from the TEM images.

As-deposited samples: The TEM image in Fig. 2a shows the as-deposited Ti film, about 90 nm thick, underlying a 25 nm TiN top layer, as measured from the image. The corresponding Ti and TiN reflections are observed in Fig. 3a. The image reveals a thin interfacial amorphous layer, 2 nm of thickness, at the amorphous Si / Ti interface. As seen in Section 1, it was recognized by many authors as coming from Ti-Si intermixing during the sputter deposition process.

Annealed samples: Three typical phase coexistences are depicted in Fig. 2.

Coexistence 1: The film microstructure results from a progressive heating up to $T=427^\circ\text{C}$, stabilization at this temperature for 53 min and then, heating again up to 433°C . An amorphous layer was grown under the Ti film (Fig. 2b). The maximum thickness of this layer is 20 nm at all

investigated temperature before C49 TiSi_2 formation. Similar maximum thickness values are reported in literature in the Zr/Si system¹⁰. This suggests that both Si and Ti atoms were released from the respective interfaces to diffuse into the amorphous layer. As in the TEM figures the SiO_2/Si interface can serve as a reference for interface position, it can be seen from the asymmetric shift from the initial Ti/Si interface that the growth was faster towards Si. The composition of the amorphous layer has not been determined. A thin crystalline layer, several nm thick, is observed at the amorphous layer/Ti interface. It was identified as Ti_5Si_3 by TEM-HRTEM in regions where lattice fringes could be clearly observed; the d-spacing is 0.25 nm close to $d_{210}(\text{Ti}_5\text{Si}_3) = 0.2436$ nm. This result is consistent with Wang and Chen TEM results²⁰ and is also found from our X-ray data (Fig. 3b). In the pattern, the 002 single diffraction line characteristic of Ti_5Si_3 is visible at $2\theta = 44.46^\circ$. In addition to this line, the 111 TiN and 002 Ti profiles are clearly overlapped. The resolution of the overlap is improved by adding a third line in the fitting process. The third line can be identified as 102 Ti_5Si_3 ($2\theta_{\text{meas}} = 48.3^\circ$, $2\theta_{\text{exp}} = 47.7^\circ$ ²⁵, where $2\theta_{\text{meas}}$ and $2\theta_{\text{exp}}$ are measured and expected angle values) with a possible contribution of 210 Ti_5Si_3 ($2\theta_{\text{exp}} = 46.7^\circ$ ²⁵). The latter is overlapped with the 111 TiN line slightly shifted at higher angle ($2\theta_{\text{meas}} = 46.95^\circ$, $2\theta_{\text{exp}} = 46.56^\circ$ ²⁶). As the layers are thin, the observed shifts from the positions come from residual stresses. The Ti_5Si_3 crystallized phase detected in this analysis is not expected at such a low temperature (433°C) if we refer to the temperature domains defined in Fig. 1. However, the step at 427°C (i.e. in domain II) before reaching 433°C permitted to increase locally Si concentration in Ti grains and thus initiate Ti_5Si_3 crystallization. If the constant step is skipped and temperature is monotonously increased to 433°C, Ti_5Si_3 crystallization is not observed. This will be detailed in a following section.

Coexistence 2: A phase coexistence was observed during an isothermal study at 434°C for 45 min. Very similar features can be observed concerning the amorphous layer (see Fig. 2b and Fig. 2c). However, the 002 Ti_5Si_3 reflection intensity is drastically increased in the diffraction pattern (Fig. 3c). It is likely related with the slight 002 preferred orientation detected from the FWHM of a 002 rocking-curve: 6.5° . Thus, the constant step at 434°C allowed a Ti_5Si_3 intermediate textured phase to develop. It has been quenched after 45 min to allow the TEM observation.

Coexistence 3: A kinetic run performed at 422°C for 420 min resulted in the nearly complete transformation of the initial amorphous layer into a crystallized layer made of large grains. This layer is much thicker - 40 nm - than the initial amorphous layer and the position of the initial interface has moved preferentially towards Si (Fig. 2d). The crystallized phase was identified as C49 TiSi_2 both by TEM and XRD²⁷: 131 and 002 C49 reflections appear in the X-ray diffraction pattern near $52^\circ 2\theta$ (Fig. 3d) and $66^\circ 2\theta$ (not shown) in addition to Ti_{al} , TiN and Ti_5Si_3 reflections. Similar location of C49 growth at the Si/amorphous layer interface has been reported by Wang and Chen TEM observations²⁰. Let us note that a 8-10 nm thick remaining fraction of the amorphous layer is still observable on top of the C49 grains.

All these observations performed at typical stages of the Ti-Si reaction suggest the various layers involved in the silicidation process are very sensitive to temperature and kinetics conditions. Such dependences will be described in detail in the next sections.

3.2-2 Temperature dependence of the phase sequence

Fig. 4a-4f show selected diffraction patterns of Ti/Si films annealed between 435 and 567°C, i.e. in temperature domains related to Si diffusion in Ti grain boundaries, in Ti grains and formation of long range crystallized phase. Despite the difficulty in the line assignment, the pattern evolution gives evidence of successive phase formation. In the following, 101 Ti, 002 Ti and 111 TiN lines will be labelled as A, B and C lines.

The shifted Ti lines in Fig. 4a (T=435°C) are characteristic of the stage of Si diffusion in Ti grain boundaries (see Section 3.1). A small temperature increase up to 444°C greatly affects the diffraction pattern (Fig. 4b) which reveals the beginning of Si diffusion into the Ti grains: A vanishes as B transforms into a broadened, less intense line, shifted towards lower angles. The latter may be fitted into two components B and B' (Fig. 4b, 2θ close to 47.7 and 47.2, respectively), considered as related to Ti and Ti_{al} , respectively. Both types of grains are 002-oriented at this stage.

By increasing temperature up to T=472°C, a new line (A') is observed in the diffraction pattern (Fig. 4c). It is located at an angle very close to the 101 Ti line position in Fig. 4a and is identified as 101 Ti_{al} line.

Further diagrams, measured from samples annealed from T=529°C (Fig. 4d-f), show that two additional lines (labeled E and F in the following) located at 45.5 and 52° 2θ are present. F is unambiguously identified as 131 C49 $TiSi_2$. The thermal dependence of E and F intensities has been considered to identify the E line origin. At this stage, it is not possible to give a single interpretation of the existence of the E line. From the observed correlation between both phases, it is however possible to think as follows:

- the unique possible assignment among the $TiSi$ ²⁸, Ti_5Si_3 ²⁵, Ti_5Si_4 ²⁹, $TiSi_2$ ²⁷ silicide candidates would be the 111 C49 $TiSi_2$ line expected at 45.3° 2θ . The C49 phase could be formed first as a textured phase which recrystallizes in a second step to give rise to the usual powder structure phase (131 line). A texture component of this type has never been reported.

- another transient silicide, whose Ti/Si ranges between 1 and 0.5, is stabilized by stresses. This would be made possible by residual stresses. Indeed, as mentioned earlier, layers are highly stressed in the films obtained in Metal-Si reactions and it is well known that stresses are crucial to obtain C49 $TiSi_2$. No such silicide phase has been reported yet.

It is also very important to note here that no Ti_5Si_3 reflection has ever been observed in all diffraction patterns recorded as a function of temperature. Finally, note that the 111 TiN line (C) is quite stable at any investigated temperature.

3.2-3 Time dependence of the phase sequence

To precise the kinetic evolution of the various crystal phases, three experiments at constant temperature have been performed between 412 and 434°C. Selected diffraction patterns recorded at 422°C are given in Fig. 5. As temperature increases up to 422°C, both Ti lines are first shifted to lower 2θ angles. Then, temperature is kept constant. The Ti line behaviour is nearly similar to the evolution observed in temperature runs: the Ti lines vanish (see the first step of the kinetics shown in Fig. 5); the Ti_{al} lines grow and remain observable up to the final step after 420 min. However, the major difference with temperature run is the formation of the intermediate transient Ti_5Si_3 phase as indicated by the 002 Ti_5Si_3 line at $2\theta = 44.5^\circ$ (G line in Fig. 5b). As described in Section 3.2-1, a possible contribution of 210 and 102 Ti_5Si_3 lines to 111 TiN (C) and 002 Ti_{al} (B'), respectively, is also to be considered. Then, the Ti_{al} lines are slightly shifted towards higher angles (Fig. 5c-e). The F (131 C49) and G (002 Ti_5Si_3) lines have very weak intensity in the final diffraction pattern measured in-situ (Fig. 5e, $T=422^\circ\text{C}$ during 420 min). As previously seen, the corresponding ex-situ diffraction pattern in Fig. 3d as well as the corresponding TEM image in Fig. 2d indicate more clearly the simultaneous presence of C49 $TiSi_2$ and Ti_5Si_3 in addition to the remaining Ti_{al} and amorphous layer. Fig. 2d gives evidence of the successive stages occurring during the reaction from Ti to C49 $TiSi_2$. Ti_5Si_3 is probably a textured phase which would explain the very weak intensity of the 002 line recorded in-situ in the diffraction chamber (Fig. 5e). The 131 C49 line is still weaker. Note that the C49 line intensities are always weak due to the slightest Ti contribution in the structure factor calculation than in Ti_5Si_3 .

The reflection shift towards higher angles can be explained by a partially stress relaxation on the Ti grains as a result of Si diffusion into the Ti grains. This effect is easily observed during measurements performed at selected annealing temperatures as just seen, but the signal is dimmed by the thermal expansion or temperature effect during thermal treatment as reported in Section 3.2-2. As the phase evolution during isothermal annealing is slower in comparison with ramping, the lifetime of the Ti_{al} phase is longer and the Ti_5Si_3 phase may develop.

By accounting all TEM and X-ray diffraction data, it is possible to resolve the sequence of coexisting phases in the following terms :

- * Ti + Ti_{al} + amorphous silicide
- * Ti_{al} + amorphous silicide + Ti_5Si_3
- * Ti_{al} + amorphous silicide (fraction) + Ti_5Si_3 + C49 $TiSi_2$
- * Ti_{al} + unidentified transient silicide (fraction) + C49 $TiSi_2$.

To precise the mechanisms of Ti_5Si_3 formation and transformation into C49, the evolution of the square of the 002 Ti_5Si_3 line intensity was plotted as a function of time. This is made because a

linear variation would be the indication of a diffusion-limited mechanism. Similar behavior has been reported in another study³⁰. A linear evolution is indeed obtained at the three temperatures as shown in Fig. 6 and thus confirms that Ti_5Si_3 formation and transformation are diffusion-limited^{31, 32 and references therein}. Under this assumption, the Ti_5Si_3 thickness $h(t)$ can then be described by

$$h^2(t) \propto D \times (t - t_0) \quad (1)$$

where D is an interdiffusion coefficient and t_0 the delay time preceding Ti_5Si_3 formation or transformation. As $h(t)$ and $I(t)$ relate to the mass of the reaction product, they are proportional to each other. To determine diffusion coefficients, it is necessary to know $I(t_{\text{fin}})$ values. This is usually obtained by using Eq (2)

$$\frac{h(t)}{h(t_{\text{fin}})} = \frac{I(t)}{I(t_{\text{fin}})} \quad (2)$$

where t_{fin} stands for a complete transformation. Unfortunately, the $I(t_{\text{fin}})$ values cannot be obtained because Ti_5Si_3 phase is highly transient and thus, only a limited fraction of the Ti film transforms into Ti_5Si_3 . Moreover, a calculation of $I(t_{\text{fin}})$ is highly dubious: very important microstructural parameters such as the degree of grain alignment have to be introduced in the calculation. As, they cannot be simply obtained, $I(t_{\text{fin}})$ has not been determined. We are thus limited to determine pseudo-interdiffusion coefficients $D' = D/\text{constant}$ from the I^2 time dependence (Fig. 6). A semi-log plot of D' versus $1/T$ shows that D' , and therefore D , follows an Arrhenius behavior. The activation energy values for the Ti_5Si_3 growth and transformation are high, 9.4 eV and 6.6 eV respectively, but high activation energies are also found in literature for other silicides: 3.7 eV for Mo_5Si_3 and W_5Si_3 formation³³, 4.4–5.7 eV for the transformation of the metastable C49 TiSi_2 phase into the stable C54 phase³⁴⁻³⁶. We have no further experimental support for these energy values.

As a matter of conclusion of this section, XRD and TEM analyses of temperature and time dependence of the Ti film microstructure evolution allowed us to precise the formation/transformation of several phases:

Ti_5Si_3 : it only grows in isothermal runs performed in a narrow range of annealing temperatures (412-434°C in our study). In temperature runs, there remains some doubt about the C49 TiSi_2 formation: either, it is directly formed and it would be very likely that Ti_5Si_3 locally forms as very fine particles. Ti_5Si_3 would thus not be detected in the diffraction pattern. Or, a transient and unidentified phase containing more silicon forms before C49 nucleates. This demonstrates the crucial role of kinetics factors in the transient phase growth and, more generally, in phase formation sequence. We have shown that Ti_5Si_3 formation and transformation into C49 are diffusion-limited. In their thermodynamic study based on free energy diagrams of the system, Wang and Chen showed Ti_5Si_3 and C49 TiSi_2 have the largest and lowest driving forces (ΔG) at 500°C, respectively²⁰. Accordingly,

and as observed in this study, the sequence of intermediate crystal phases starts with Ti_5Si_3 and come to an end with C49 TiSi_2 . However, we have detected no additional intermediate phase such as Ti_5Si_4 or TiSi in our experimental conditions. In domains of phase coexistence, Ti_{al} , Ti_5Si_3 and C49 TiSi_2 have been simultaneously observed in films annealed at 422°C for 420 mn.

Amorphous interface layer: a series of papers report that the growth process of the amorphous interlayer is diffusion-controlled⁹⁻¹⁰: the amorphous layer grows into the metal layer by diffusion of Si and a composition gradient extends from about 70% Si near the substrate (i.e. close to TiSi_2) to about 30% Si close to the Ti interface⁷. When saturation is locally reached, i. e. the composition at the amorphous layer/Ti interface matches that of a particular compound - Ti_5Si_3 for instance - then, as expected from thermodynamic considerations, crystallization occurs without any composition change. Further, Si feeding is then only used to grow crystal grain and the amorphous layer reaches a critical thickness. This model explains our TEM observations of a thin Ti_5Si_3 crystalline layer at the amorphous layer/ Ti interface.

4. Conclusion

In-situ XRD experiments correlated with TEM observations allowed us to go further in the understanding of the first steps of the Ti/Si solid phase reaction. Prereactional phenomena are assigned to Si diffusion from 360°C: first, it proceeds by Ti grain boundary diffusion which develops a very compressive stress on Ti grains; then, upon further heating up to 450°C, Ti intra-grain diffusion is detected from the observed broadening of the diffraction profiles. Such titanium is thus designed as alloyed titanium.

The XRD and TEM observations at typical stages of the Ti-Si reaction reveal that the formation of reaction products is highly temperature and time dependent. An amorphous silicide layer reaching a maximum 20 nm thickness is first observed before the first crystallized phases start to be detected at temperatures close to 500°C in the case of temperature ramp or at lower temperatures during isothermal runs.

The time evolution of the system at selected temperatures is quite similar to the temperature evolution. However, the phase evolution is slower during isothermal runs and the most important difference is the existence of transient phases before C49 nucleation, such as Ti_5Si_3 in the case of isothermal runs and probably a phase containing more silicon in temperature runs. The Ti_5Si_3 transient phase has been repeatedly observed in a series of samples. It is formed via diffusion-limited mechanisms and exists only if annealing temperature is in the range (412-434°C). The lifetime and the volume fraction of the initial metal layer transformed into Ti_5Si_3 are naturally tightly temperature dependent. Ti_5Si_3 crystals have been localised at the amorphous layer/Ti interface. Isothermal runs

performed during longer periods give evidence of C49 TiSi_2 formation in addition to Ti_5Si_3 ; the simultaneous presence of alloyed Ti, amorphous silicide, Ti_5Si_3 and C49 TiSi_2 in the film has thus been observed. C49 TiSi_2 has been found to crystallize from the Si/amorphous layer interface and to consume the major part of the amorphous layer after 420 mn at $T=422^\circ\text{C}$.

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Figures

Figure 1 : Expansion of the Ti lattice in Ti/Si thin films on annealing. Evolution of d-spacings (a), integrated intensities (b) and FWHM values (c) for both 002 (open symbols) and 101 (full symbols) Ti diffraction lines. Four temperature domains refer to conventional thermal expansion (I), Si diffusion in Ti grain boundaries (II), Si diffusion in Ti grains (III) and formation of the first crystallized silicides (IV). Error bars are important in domains III-IV because the Ti line intensities are very small.

Figure 2 : TEM cross-section images of the Ti film in the as-deposited state (a) and at different stages of the Ti-Si reaction obtained either by thermal annealing (b) ($T=433^{\circ}\text{C}$), or after a kinetic experiment (c) ($T=434^{\circ}\text{C}$ for 45 min) and (d) ($T=422^{\circ}$ for 420 min). Observations were made at room temperature. In (b), the film was progressively heated up to $T=427^{\circ}\text{C}$, stabilized at this temperature for 53 min and then, heated again up to 433°C . The SiO_2/Si interface has been taken as a reference line from (a) to (d).

Figure 3 : Ex-situ X-ray patterns of Ti films observed by TEM. Annealing conditions are given in Fig. 2. Normalized diffracted intensities are given on a Log scale in the inserts for comparison.

Figure 4 : In-situ X-ray patterns recorded during ramping process after temperature stabilization in the various temperature domains referred in Fig. 1: (a) $T=435^{\circ}\text{C}$, (b) $T=444^{\circ}\text{C}$, (c) $T=472^{\circ}\text{C}$, (d) $T=529^{\circ}\text{C}$, (e) $T=547^{\circ}\text{C}$, (f) $T=567^{\circ}\text{C}$. Acquisition times were 800 s.

Figure 5 : In-situ X-ray patterns recorded as a function of time at $T=422^{\circ}\text{C}$: (a) $t=0$, (b) $t=226$ min, (c) $t=258$ min, (d) $t=273$ min, (e) $t=420$ min. Acquisition times were 500 s.

Figure 6 : Time dependence of the square of the 002 Ti_5Si_3 line intensity. t_0 is the delay time preceding Ti_5Si_3 formation or transformation into C49 TiSi_2 . Arrhenius plots of the corresponding pseudo-interdiffusion coefficients $D'=D/\text{constant}$ of Ti_5Si_3 during its growth and decay are given in the insert.

Fig. 1

Fig. 2

Fig. 3
- 18 -

Fig. 4

Fig. 5
- 20 -

Fig. 6