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Further insights in the growth mechanism of the non-stoichiometric θ -Ni₂Si phase

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Abstract:

The solid state reaction of 50nm Ni with Si(100) substrate was investigated using in situ X-ray diffraction (XRD). The sequence is simultaneous; it begins by δ -Ni₂Si phase then the metastable θ -Ni₂Si phase is formed. Both phases grow simultaneously. The growth mechanism of the non-stoichiometric θ -Ni₂Si phase is discussed on the basis of the evolution of its XRD peak during annealing. The results show that, during its growth, the non-stoichiometric θ -Ni₂Si phase is split into two regions of different concentrations. This “original” behavior is justified by the discontinuous variation with composition of both the diffusion coefficient and the d-lattice spacing through the θ -Ni₂Si phase.

Key words: diffusion coefficient, non-stoichiometric phases, lattice spacing.

I. Introduction

Owing to the beneficial properties of NiSi silicide (low contact and sheet resistance, low formation thermal budget), it is so far the promising candidate for application in microelectronic devices.

The formation of NiSi phase, via solid state reaction between Ni film ($e_c > 4,8\text{nm}$) and Si(100), is preceded by a simultaneous formation of Ni-rich phases [1]. Recent studies have shown that the sequence of Ni-rich phases and their characteristics (texture, resistivity and interface quality) is altered by the substrate orientation [2], film thickness [1,3,4], the presence of dopants [5] and alloy elements [1,6,7]. The formation of Ni-rich phases is albeit evidenced for all preparation conditions. Their identification has been the subject of several investigations [8,9,10]. Nevertheless, it is complicated by the fact that most Ni-rich phases have relatively low symmetry (except cubic Ni₃Si) which results in a multitude of possible XRD peak position, many of which are common to different phases. It was reported that the formation of Ni₃Si₂ from Ni₂Si and NiSi, was attributed to the destabilization of δ -Ni₂Si by the surface energy when

it becomes too thin. The formation of $\text{Ni}_{31}\text{Si}_{12}$ is observed during faster ramp annealing of thick Ni film ($e = 500\text{nm}$) deposited on c-Si [9].

Using sophisticated probes as X-ray pole figure measurements, scrutiny has led to significant knowledge [9]. In particular, the metastable $\theta\text{-Ni}_2\text{Si}$ has been shown to form at low temperature at the $\delta\text{-Ni}_2\text{Si}/\text{Si}$ interface. Its formation at low temperature has been attributed to a lower nucleation barrier resulting from a combination of the texture inheritance and/or epitaxy and the ability of the non-stoichiometric θ phase to nucleate in the strong composition gradient present at the interface [9]. The $\theta\text{-Ni}_2\text{Si}$ phase is normally stable above 825°C of hexagonal structure, the lattice parameters decrease with the enrichment in Si of ($a = 3.836\text{\AA}$ and $c = 4.948\text{\AA}$) for 37.5at.% Si to ($a = 3.802\text{\AA}$ and $c = 4.863\text{\AA}$) for 43at.% Si [11]. This composition range is restricted at low temperature to 38, 5- 43at.% Si [9]. Few data about the $\theta\text{-Ni}_2\text{Si}$ growth kinetic are available in literature. The growth of $\theta\text{-Ni}_2\text{Si}$ is of interface control; the growth rate is of $10 \exp(-0,85\text{eV}/kT) \text{ cm/sec}$ [10]. However, diffusion may play a role on its growth mechanism. Indeed, it was observed that $\theta\text{-Ni}_2\text{Si}$ forms during isothermal annealing at lower temperature (180°C) [4, 5] than that reported, in several investigations during isochronal annealing (280°C) for different preparation conditions [1, 2,6] .

In this article, the growth mechanism of the non-stoichiometric $\theta\text{-Ni}_2\text{Si}$ phase was investigated. Thanks to the in situ-XRD measurements one can assess, as a first approximation, the variation of both the XRD intensity and the lattice parameter of the $\theta\text{-Ni}_2\text{Si}$ phase versus Ni concentration.

II. Experimental procedure:

Ni films of 50nm thick were deposited by magnetron sputtering on Si substrates with (100) orientation. Prior to deposition, the substrates were cleaned in a dilute 5% HF solution to remove the native oxide. The deposition was performed in a sputtering chamber with a base pressure of 10^{-8}Torr using 99,999% pure Ar gas flow and a 99,99% pure Ni target. The wafer was rotating during deposition to improve the homogeneity of the layer. In situ-XRD measurements were performed during annealing which was performed in vacuum ambient of about 10^{-5}mbarr. (. In situ analyses were performed after ramping from room temperature to 200°C with a rate of $35^\circ\text{C}/\text{min}$. The temperature was then increased by step of 5K until 920°C and the temperature was kept constant during the XRD measurements that lasted typically two

minutes. The 2θ interval was selected from (30° to 50°) since it contains the characteristic x-ray diffraction peaks for the important phases in Ni-Si system.

III. Results

Figure 1 shows the result of XRD (three dimensional views) measurements during the reaction of 50 nm Ni film with Si(100) from 200 to 920°C .

XRD spectra show that the reaction initiates, around 200°C , with the formation of the $\delta\text{-Ni}_2\text{Si}$ (211) and (020) phase. An additional peak appears around 47° attributed to $\theta\text{-Ni}_2\text{Si}$ (110) peak. In agreement with previous investigations, only one XRD peak is attributed to this phase [2,9]. We observe that the $\theta\text{-Ni}_2\text{Si}$ exists over a sharply temperature window ($280\text{-}350^\circ\text{C}$). Around 320°C , the Ni film is fully consumed; a shift towards high angles is mentioned, on both θ and $\delta\text{-Ni}_2\text{Si}$ peaks due to stress relaxation. At this temperature, NiSi phase appears with multiple XRD peaks. Further heating leads to an increase in NiSi intensity peaks and a disappearance of the $\delta\text{-Ni}_2\text{Si}$ phase. As the temperature increases further, a weak XRD peak emerges around 47° (the beginning of this peak is not clear) and this could be attributed to the NiSi_2 phase. .

A zoom-in on the $\theta\text{-Ni}_2\text{Si}$ XRD peak is presented in figure 2. This peak has a striking behavior. During heating, several shifts of $\theta\text{-Ni}_2\text{Si}$ peak are observed: the first one towards high angles, and then an important shift towards low angle is observed with increasing temperature. When the Ni film is fully consumed the stress is relaxed and the $\theta\text{-Ni}_2\text{Si}$ peak shifts again towards high angles.

The first and the second shifts were already observed and attributed to the variation in composition due to different equilibrium at different interfaces during the reaction [10, 5]. A close look on the θ - XRD peak (Figure2) reveals that it is not a simple shift, however the peak is also split into two peaks labelled $\theta_1\text{-Ni}_2\text{Si}$ and $\theta_2\text{-Ni}_2\text{Si}$.

This behavior is clearly depicted in 2D (right): the peaks are presented in order from low (peak1) to high annealing temperature (peak11), in particular pic 9 (red). The division of the $\theta\text{-Ni}_2\text{Si}$ XRD peak into two close peaks in two different Bragg positions is never reported in literature. Thus a deep analysis is required to identify the mechanisms behind the observed behavior. Isothermal annealing at low temperature (180°C) are of interest, this type of annealing permits to slow-down the reactions hence to get more details on the evolution of the $\theta\text{-Ni}_2\text{Si}$ XRD peak.

Figure 3(left) shows the evolution of the θ -Ni₂Si(110) XRD peak intensity during isothermal annealing at 180°C. (The in situ XRD measurements performed from (30 to 50°) are presented in references 4 and 5). The figure3(left) shows clearly that the XRD peak follows the same behavior mentioned during isochronal annealing: i.e. the θ -Ni₂Si(110) peak is split into two very close peaks in two Bragg positions

We present in figure 3(right) the variation of the lattice spacing of the (110) planes of the θ -Ni₂Si phase during isothermal annealing at 180°C. For such isothermal annealing, the variation of d-spacing should be originating from variation of composition through the θ -Ni₂Si phase. ().

The d-spacing is deduced from the Bragg's law: $d = \frac{\lambda}{2\sin\theta}$.

Figure 3 (right) shows that the θ -Ni₂Si phase is stable over 1,5h annealing at 180°C. As Ni is the more mobile species, one can expect the same behavior of d-spacing versus Ni composition. The d-spacing of (110) planes of θ -Ni₂Si exhibits a minimum value of 1,917Å after 0,8h annealing and increase to 1,924Å and to 1,928Å on both minimum sides over its time span (see Figure 3right). Such discontinuous variation of the lattice spacing is not without precedent; indeed the same behavior was mentioned during the formation of the non-stoichiometric Ni₂Al₃ phase [12].

IV. Discussion:

The formation of Ni-rich phases via solid phase reaction requires a detailed understanding on the growth kinetics. We focus our attention on the non-stoichiometric θ -Ni₂Si phase; its growth mechanism cannot be investigated without considering the possibility of a varying composition during the reaction and the nature of the defects over the composition range of the θ -Ni₂Si phase. The growth of non-stoichiometric phases was first investigated for the intermetallic compounds [13, 14, 12]. The obtained results are then formalized by d'Herurle and Ghez as a simple model generally valid for all diffusive reactions in the solid state [15].

a) Phase sequence

The in situ XRD measurements (Fig.1) clearly indicate a simultaneous formation of only δ and θ -Ni₂Si phases, the latter grows by consuming δ -Ni₂Si and Si. The θ -Ni₂Si phase is characterized by only the two (110) XRDpeaks centered at 47°. Nor Ni₃Si₂ neither Ni₃Si were detected under these annealing conditions. When Ni is fully consumed, the NiSi phase grows by consuming both δ -Ni₂Si and θ -Ni₂Si phases. The NiSi₂ is the last phase to form at high

temperatures: it grows at the expense of NiSi. The phase sequence mentioned is consistent with previous works on the reaction of different Ni thicknesses ($e > 4,8\text{nm}$ [1]) with Si(100) during isothermal and isochronal annealing [1,2, 5, 9, 10].

b) The kinetic growth of θ -Ni₂Si

As depicted in Figure 2, the XRD peak of θ -Ni₂Si is split into two peaks in two close Bragg positions (θ_1 -Ni₂Si and θ_2 -Ni₂Si). One may wonder about the origin of this behavior. It could be explained by the presence of two separate phases in thermodynamic equilibrium.

However as discussed above, only θ -Ni₂Si and δ -Ni₂Si phases precede the formation of NiSi. No other Ni-rich phase forms. Hence, the two XRD peaks centered at 47° should be attributed to the θ -Ni₂Si phase and could be originating from the growth mechanism of this phase.

Figure 3 shows the variation of (110) d-spacing planes of the two XRD-peaks of the θ -Ni₂Si phase during time annealing. The minimum in d-spacing occurs at some intermediate Ni composition (corresponding to $t=0,8\text{h}$) which is unknown. It was also shown that the evolution of the lattice parameter of Ni₂Al₃ phase versus composition shows a minimum at off-stoichiometry Ni₂Al₃ [12]. On the other hand, the variation of the lattice parameter of the AlNi solid solution vs composition shows a maximum at also off-stoichiometry NiAl [13].

Our first interest is focused on the increase of d-spacing on both sides of the minimum of d-spacing through the θ -Ni₂Si phase. The increase in d-spacing, which occurs after 0,8h annealing, is expected on the Ni rich side of θ -Ni₂Si with an excess of Ni atoms. On the other hand, the increase in d-spacing observed in the Si-rich side ($t < 0,8\text{h}$ annealing) is difficult to understand. This could be however possible when the small Si atoms are accommodated on interstitial sites; in the same way as it was reported in Ni₂Al₃ phase [12]. The discontinuous variation of lattice spacing may thus be due to different type of defects through the θ -Ni₂Si phase. The dependence of the lattice parameters on the defect nature was evidenced for intermetallic compounds NiAl [13] and Ni₂Al₃ [12].

It's important to underline that when the defect nature (vacancies and/or interstitial) are composition sensitive, they could have dramatic effects on the diffusion behavior [14]. This is

indeed what the XRD measurements evidenced. The growth of the θ -Ni₂Si phase with two XRD peaks is certainly due to the split of the θ -Ni₂Si phase into sharply defined regions of different composition. Let us recall that, although the growth of θ -Ni₂Si is not purely controlled by diffusion, one can assume that the intensity of the XRD peaks could be representative, as first approximation, of the volume fraction of the θ -Ni₂Si phase which scales with diffusion coefficient D. It is clear from figure 2, that the θ -Ni₂Si XRD peak shows two intense peaks, separated by an intermediate zone with low intensity. This results from the variation of diffusion coefficient versus composition which goes through a minimum for an intermediate composition (see figure 4) in a similar fashion to AgMg[16], AuCd[17], NiAl [13, 14] and Ni₂Al₃[12, 15] non-stoichiometric phases. The growth of the θ -Ni₂Si phase with two XRD peaks may appear as the growth of two phases but in fact correspond to the θ -Ni₂Si phase that is split into relatively sharply defined regions of different composition. The two regions represent regions of maximum diffusion coefficients. The variation in the diffusion coefficient leads thus to the discontinuous variation of d-spacing versus composition.. Indeed, the regions of maximum diffusion coefficient corresponding to high defect concentration regions. The θ -Ni₂Si phase with minimum of defect concentration should thus not appear since it has a low diffusion coefficient and will be “consumed” by high diffusion θ -Ni₂Si phase. .

We underline that a good agreement is evidenced between the discontinuous variation of lattice spacing and the intensity of the XRD peak of the non-stoichiometric θ -Ni₂Si phase, both of which reinforce the growing phase to appear as separate regions. A more quantitative understanding may be obtained by looking at different XR peaks using reciprocal space mapping techniques. . In addition, the growth mechanism of θ -Ni₂Si discussed could be sensitive to both preparation conditions (substrate orientation, the presence of dopants, thickness of deposited film and the presence of alloying elements...) and annealing conditions, thus further analysis is required to thoroughly characterize the θ -Ni₂Si phase.

V. Conclusion:

The solid state reaction of 50nmNi with Si (100) was followed by in situ XRD during isochronal annealing from 200 to 920 ° C. The evolution of the XRD peaks intensities and lattice spacing of the non-stoichiometric θ -Ni₂Si phase allow us to deduce that θ -Ni₂Si is split into two defined regions of different composition separated by a zone corresponding to the minimum in the diffusion coefficient.

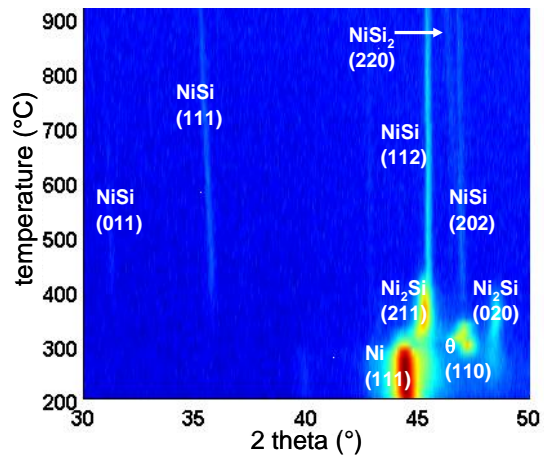


Figure1. In situ XRD measurements on 50nmNi/Si(100) sample during thermal ramp at 35°C/min from 200°C to 920°C .

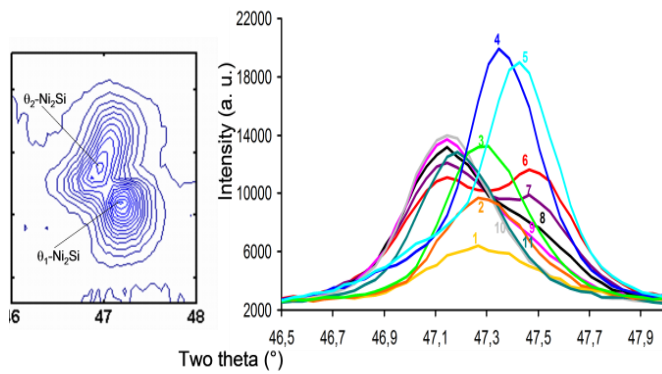


Figure2. (Left) Zoom-in on the XRD peak of the θ -Ni₂Si phase from figure 1. (Right) Evolution of θ -Ni₂Si peaks (2D) during heating: from low temperature (peak1) to high temperature (peak11).

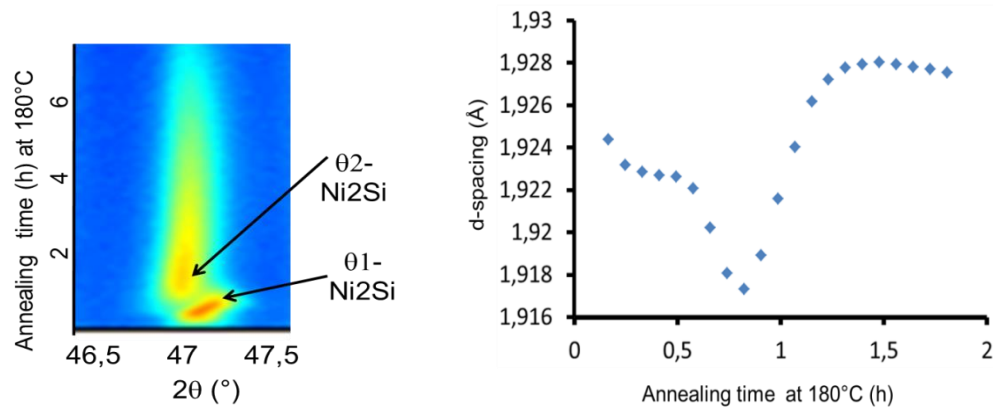


Figure3. (Left) the evolution of the XRD peak of the θ -Ni₂Si phase during isothermal annealing at 180°C. (Right) The variation of θ -Ni₂Si lattice spacing during isothermal annealing at 180°C.

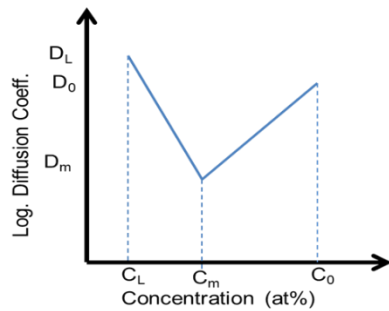


Figure 4. Schematic representation of the variation of the diffusion coefficient as a function of composition in phases such as AlNi [15].

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