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Reactive Diffusion in Ni-Si Bulk Diffusion Couples

S. Oukassi and F. Hodaj

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Reactive diffusion in the Ni-Si system has been studied using bulk polycrystalline Ni/Si wafer diffusion couples in the temperature range from 450 to 700 °C and with annealing times of up to 32 h. For all diffusion couples, three phases were detected Ni_2Si, Ni_3Si_2, and NiSi. The thickness e of the reaction product is not homogeneous; its global growth kinetics satisfies the parabolic law and the total growth coefficient k^2 ($e^2 = k^2t$) is found to be expressed by: $k^2 = 2.5\times10^{-4}$ exp (-160 kJ/RT), in m^2/s. The Ni_2Si layer is homogeneous in thickness, and the value of its growth coefficient obtained by extrapolation at lower temperatures is more than two orders of magnitude smaller than the values obtained in thin-film experiments.

Keywords binary diffusion, diffusion couples, experimental kinetics

1. Introduction

Transition metal silicides play an active role in silicon semiconductor device technology, and thin-film metal/bulk silicon reactions have been studied extensively. The remarkable finding was that silicides can form at much lower temperatures in thin-film metal bulk/silicon couples than in bulk/bulk couples.[1] Moreover, it has been well known for several decades that reactive diffusion in thin-film metal/silicon bulk couples usually demonstrates "one-by-one" (sequential) phase formation,[2,3] whereas in bulk/bulk diffusion couples, intermediate phases were found simultaneously.

The reaction of Ni and Si for possible use in microelectronics manufacturing has been extensively studied, starting in the mid-1970s.[2,4] Recently, interest in the low resistivity NiSi compound increased significantly because of its foreseeable use as a contact for the source, drains and gates of complementary metal-oxide-semiconductor (CMOS) devices.

In the literature, the growth kinetics of intermediate phases in Ni-Si bulk diffusion couples is studied in the temperature range from 550 to 900 °C, and $Ni_{31}Si_{12}$ (also referred to as Ni_5Si_2), Ni_2Si, Ni_3Si_2, and NiSi phases were found simultaneously.[1,5-8]

On the contrary, in Ni thin-film/bulk Si couples the growth kinetics of some intermediate phases is studied only in lower temperature ranges. For example, the growth kinetics of the Ni_2Si phase has been studied only for temperatures below about 330 °C (see, for example, Ref 9) because, at higher temperature, the Ni_2Si phase disappears in favor of other phases (sequential phase formation). In studies of thin-film interdiffusion couples, it has been recognized that the kinetic process is usually determined by grain-boundary diffusion in a fine-grained thin film, and, consequently, interdiffusion can occur faster than in bulk samples at lower temperatures.

Although the differences between thin-film and bulk interdiffusion have been known for a long time, there are only a few systems in which both bulk and thin-film diffusion couples have been studied.

The aim of this paper is to study the growth kinetics of intermediate phases in Ni-Si bulk diffusion couples and to provide experimental data for temperatures as low as 450 °C.

2. Experimental Procedure

Annealed samples measuring $5\times5\times0.125$ mm of 99.98% purity Ni (Goodfellow, Lille, France) and monocrystalline Si (001) substrates (0.6 mm in thickness) are chemically etched just before performing the thermal annealing. The agents used for chemical etching of Si and Ni are H_2O(50) + HF(1) and H_2O(50) + HCl(50) mixtures, respectively.

To establish good contact during annealing, a special device was used for diffusion couple experiments with the samples being placed under a pressure ranging from 1 to 5 MPa. Thermal annealing was performed between 450 and 700 °C with annealing times ranging from 30 min to 32 h. The experiments were performed in an alumina chamber furnace under secondary vacuum (10^{-4} Pa). Table 1 summarizes the experimental conditions for all diffusion couple experiments. After the experiments, specimens were sectioned, embedded in resin, and polished for optical and scanning electron microscopy (SEM) observation of the cross section and electron probe microanalysis (EPMA).

3. Results and Discussion

For all diffusion couple experiments performed at $T \geq 450$ °C the interfacial reactivity between Ni and Si

S. Oukassi and **F. Hodaj**, SIMAP—UMR CNRS 5266, Grenoble INP—UJF, BP 75 38402 St. M d'Hères Cedex, France. Contact e-mail: fhodaj@simap.grenoble-inp.fr.

leads to the formation of a reaction product at the Ni/Si interface. Only the diffusion couple experiment performed at $T = 400$ °C did not show any interfacial reactivity despite the fact that the Ni and Si samples were chemically etched just before introducing the couple inside the alumina chamber. In this last case, any thin native oxide layer on the silicon surface constitutes a barrier to diffusion, thus leading to a nonreactive system at low temperature.

Figure 1 displays a typical longitudinal section of a diffusion couple annealed at 700 °C for 1 h, as observed by SEM. The intermediate zone between Ni and Si is composed of intermetallic silicides formed during the reaction. The overall microstructure is made up of elongated needles oriented perpendicular to the reaction front. The needles appear to be homogeneously distributed over the entire cross section.

In almost all samples, a crack was observed running through the Si matrix parallel to the Ni/Si interface and situated about 200 to 300 μm from this interface. This crack suggests that significant thermal contraction effects come into play during cooling of the sample from experimental temperature to room temperature. Indeed, the great difference between the thermal expansion coefficient of Ni (13.3×10^{-6}/K)[10] and Si (3×10^{-6}/K)[11] can lead to very high stresses in the assembly during cooling.

Figure 2 shows a micrograph of a typical reaction zone of a Ni/Si couple annealed at 600 °C for 2 h. A needle microstructure growing from nickel toward silicon perpendicular to the Ni/Si interface can be clearly seen in this figure.

From the phase diagram of the Ni-Si binary system, six equilibrium low-temperature intermetallic phases are expected.[12] From the Ni-rich to the Si-rich side of the diagram they are Ni_3Si, $Ni_{31}Si_{12}$, Ni_2Si, Ni_3Si_2, NiSi, and $NiSi_2$ phases. Two of them present a finite composition range (Ni_3Si, Ni_3Si_2), whereas the other silicides are almost stoichiometric compounds.

In our experiments, only three intermediate phases are observed by SEM; see Fig. 2. The EPMA of these phases shows that these silicides are Ni_2Si (thin layer adjacent to nickel), Ni_3Si_2 (the thickest layer), and NiSi (thin layer forming a coat on the Ni_3Si_2 layer) from the Ni side of the diffusion couple. Note that in Ref 5 to 8, for bulk diffusion couple experiments, four phases were observed: $Ni_{31}Si_{12}$ (also referred to as Ni_5Si_2), Ni_2Si, Ni_3Si_2, and NiSi. However, the thickness of the $Ni_{31}Si_{12}$ layer observed in Ref 6 at 750 °C and in Ref 1 at 850 °C is much smaller than that of the Ni_2Si layer. Conversely, in Ref 5 the thickness of $Ni_{31}Si_{12}$ is reported to be at least twice the thickness of the Ni_2Si phase. This scattering of experimental results shows the complexity of the reactions in the Ni/Si system.

In our experiments, no layer could be detected between the Ni and Ni_2Si layers from optical and scanning electronic microscopy observations. Moreover, from the EMPA it was difficult to confirm the existence of any phase other than Ni_2Si inside this reaction layer or close to the Ni/Ni_2Si interface. However, the scattering of EPMA measurements

Table 1 Experimental conditions for different diffusion Ni/Si bulk couples

T, °C	400	450		500					600				700
t, h	4	4	8	0.5	2	4	8	32	0.5	2	4	8	1

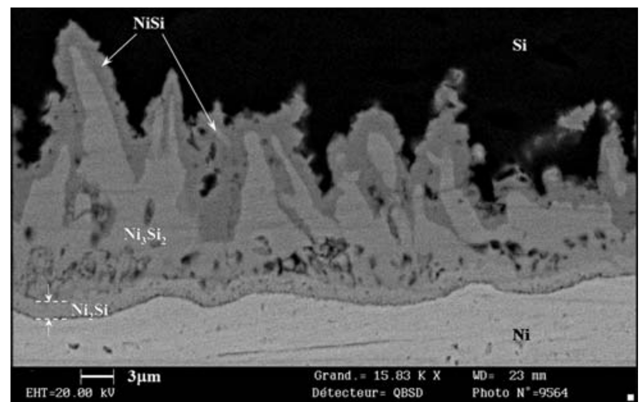

Fig. 2 Scanning electron micrograph of a typical reaction zone at the Ni/Si interface. Experiment performed at $T = 600$ °C for 2 h

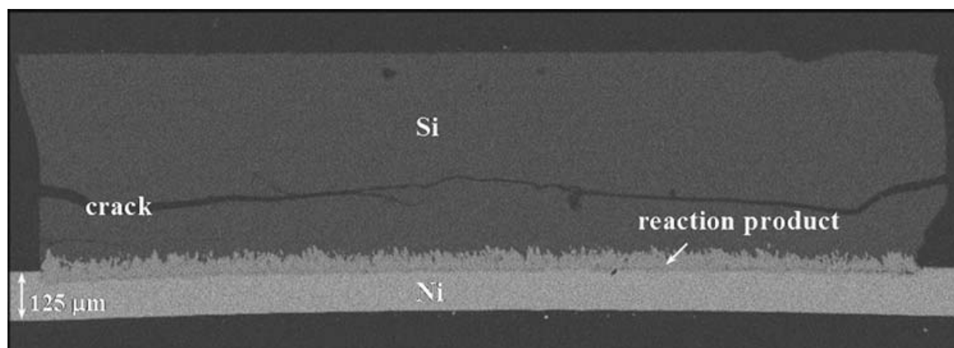

Fig. 1 Backscattered electron imaging of the entire Ni/Si diffusion couple showing the reaction zone formed at the interface. Experiment performed at $T = 700$ °C for 1 h

for this thin layer (giving from about 65 to 68 at.% Ni) do not exclude the existence of $Ni_{31}Si_{12}$ phase inside this layer. For this reason, in this article, the reaction layer near the Ni substrate (see Fig. 2) is considered to consist of a single-phase Ni_2Si.

While Ni_2Si shows a layered morphology, Ni_3Si_2 phase grows in a very irregular fashion as been observed in earlier work.[1,5-8] This point was widely discussed by Borivent et al.,[8] who proposed that this peculiar morphology originates from the highly anisotropic diffusion whereby one crystallographic direction of the Ni_3Si_2 crystals provides a very fast diffusion path along the *c*-axis, while the diffusion properties in planes perpendicular to this direction remain of the same order of magnitude as those observed in other nickel silicides.

The average total thickness (e) of the interaction zone determined from Ni/Si diffusion couple experiments at T from 450 to 700 °C (see Table 1) is plotted against the square root of time in Fig. 3. The linear correlation observed for T = 500 and 600 °C suggests that a diffusion process is valid for assessing the reaction zone growth and that the driving force for diffusion remains almost constant. The value of the total growth coefficient k^2 (defined in this study by $e^2 = k^2 t$) is determined by a linear regression analysis of e versus $t^{1/2}$.

The apparent activation energy (Q) of the interaction zone growth was calculated using the Arrhenius relationship for the diffusion-dominant process for T ranging from 450 to 700 °C (see Fig. 4): $k^2(T) = k_0^2 \exp(-Q/RT)$, where k_0^2 is the interaction zone growth constant (m^2/s). Q is evaluated from the slope of the $\ln(e^2/t)$ versus $1/T$ plot using a linear regression analysis giving $Q = 160 \pm 10$ kJ/mol and $k_0^2 = 2.5 \times 10^{-4} \mathrm{m}^2/\mathrm{s}$, that is:

$$k^2 = 2.5 \times 10^{-4} \exp(-160\,\mathrm{kJ}/RT), \text{ in m}^2/\mathrm{s}.$$

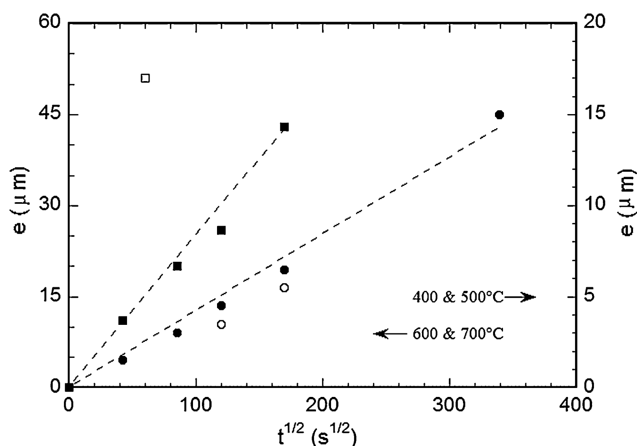

Fig. 3 Average total thickness (e) of the reaction product versus the square root of aging time ($e = kt^{1/2}$) for different diffusion couple experiments performed at temperatures between 450 and 700 °C (see Table 1). Arrows indicate the corresponding e-coordinate values: for experiments performed at 600 and 700 °C (on the left side) and at 450 and 500 °C (on the right side)

Note that this is a rough evaluation of the apparent activation energy of the interaction zone growth which, in our experiments, consists mainly of Ni_3Si_2 and Ni_2Si phases (see Fig. 2). The detailed analysis and calculation of activation energy of Ni_3Si_2 phase growth are given in Ref 8 in the 600 to 800 °C range. In this study, the activation energy of Ni_3Si_2 growth in the direction perpendicular to the Ni/Si interface is found to be about Q_h = 89.9 kJ/mol, whereas for the direction growth parallel to this interface Q_w = 103.5 kJ/mol.

A plot of the thickness of the Ni_2Si layer versus the square root of time at 450 to 700 °C (see Table 1) is shown in Fig. 5. The value of the growth coefficient of the Ni_2Si

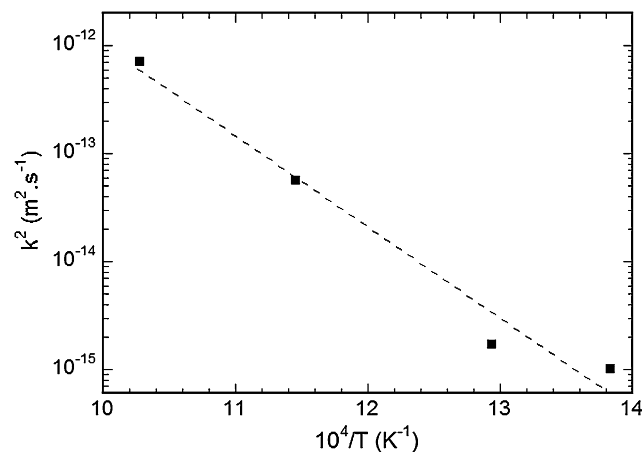

Fig. 4 Arrhenius plot of reaction product growth in Ni/Si diffusion couples $\ln k^2 = f(1/T)$ or $\ln(e^2/t) = f(1/T)$. k^2 is the growth constant (in m^2/s) and e the total thickness of the reaction product (in m)

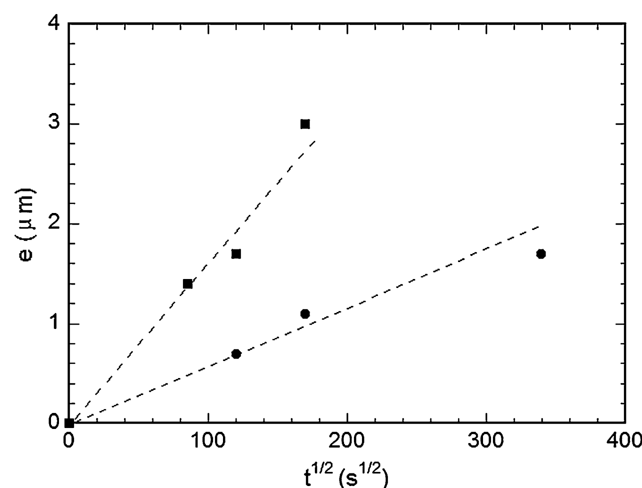

Fig. 5 Relationship between thickness of the Ni_2Si layer and square root of heating time at T = 500 °C (●) and 600 °C (■), see Table 1

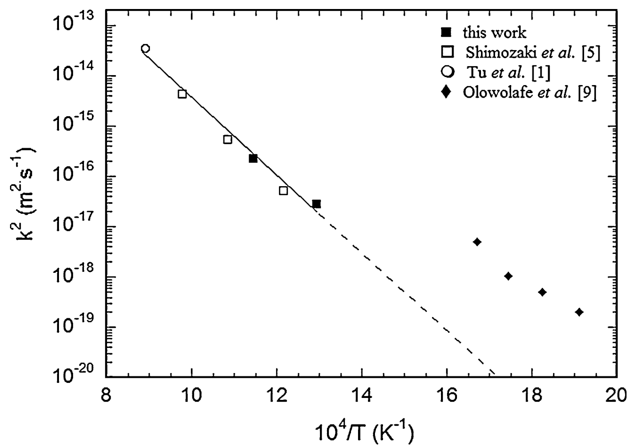

Fig. 6 Temperature dependence of the growth constant of Ni_2Si ($k^2_{Ni_2Si}$) formed in the Ni/Si bulk samples and in the thin film samples

layer $\left(k^2_{Ni_2Si}\right)$ is determined by a linear regression analysis of Ni_2Si thickness (e_{Ni_2Si}) versus $t^{1/2}$.

Figure 6 presents the temperature dependence of $k^2_{Ni_2Si}$ formed in the Ni/Si bulk diffusion couples by reporting the $k^2_{Ni_2Si}$ values obtained in this study, those obtained by Shimozaki et al.[5] for T = 550, 650, and 750 °C as well as values evaluated from the work of Tu et al.[1] This figure also gives values of phase growth rate of Ni_2Si in the case of Ni thin-film/Si wafer interactions evaluated from the experimental results of Olowolafe's work.[9] Figure 6 shows that the values of $k^2_{Ni_2Si}$ for bulk diffusion couples obtained by extrapolation at lower temperatures from 230 to 330 °C are more than two orders of magnitude smaller than values of $k^2_{Ni_2Si}$ obtained in thin-film experiments in the same temperature range. Note that, as emphasized by Shimozaki et al.,[5] the great difference in growth kinetics of the Ni_2Si phase between Ni/Si bulk diffusion couples and Ni thin-film/Si wafer couples is not inevitably due to the fact that, in thin film experiments, at lower temperatures (230-330 °C), boundary grain diffusion dominates the phase-growth process. Indeed, the driving force of the diffusion process during growth of the Ni_2Si phase in thin film experiments is not the same as in the case of bulk diffusion couple samples. The reason is that, in bulk diffusion couples, the Ni_2Si layer grows between $Ni_{31}Si_{12}$ and Ni_3Si_2 layers (or between Ni and Ni_3Si layers), whereas the growth of Ni_2Si in Ni thin-film/Si wafer experiments generally occurs between Ni and Si (Ni_2Si is the first phase to grow), see for example Ref 2, 13-17.

4. Conclusions

In this work, the interfacial reactivity between Ni-Si has been studied using bulk polycrystalline Ni/Si wafer diffusion couples under high vacuum (10^{-4} Pa) in the temperature range from 450 to 700 °C and with annealing times of up to 32 h. Reactivity occurs for temperatures as low as 450 °C, but at lower temperatures (400 °C) no reactivity is observed at the interface despite the fact that the samples are chemically etched just before performing the thermal annealing and a pressure of up to 10 MPa was used to establish good contact between Ni and Si. At temperatures below 400 °C, the native oxide layer on the Si surface constitutes a reaction barrier.

For all diffusion couples, three phases were detected: Ni_2Si, Ni_3Si_2, and NiSi. The overall thickness e of the reaction product is not homogeneous; its overall growth kinetics satisfies the parabolic law and the total growth coefficient k^2 ($e^2 = k^2 t$) is found to be expressed by: $k^2 = 2.5 \times 10^{-4} \exp(-160 \text{ kJ}/RT)$, in m^2/s. The Ni_2Si layer is homogeneous in thickness, and its growth coefficient can be given by $k^2_{Ni_2Si} = 10^{-6} \exp(-160 \text{ kJ}/RT)$, in m^2/s, and the values of $k^2_{Ni_2Si}$ obtained by extrapolation at lower temperatures, from 230 to 330 °C, are more than two orders of magnitude smaller than values obtained in the thin-film experiments in the same temperature range.

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