Reactive Diffusion in a Ni-Si Bulk Diffusion Couple

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Reactive diffusion of the Ni–Si system has been studied by using bulk Ni/bulk Si single crystal diffusion couples in
the temperature range from 823 to 1023 K. The results were compared with the previous experimental results obtained by
using Ni thin film/bulk Si diffusion couples.

In the bulk diffusion couples annealed more than 3.6 ks, Ni₅Si₂, Ni₃Si, Ni₅Si₂ and NiSi were found. The silicides
formed in the bulk diffusion couple grew satisfying the parabolic law and square of growth rate, k², of Ni₅Si could be
expressed by the following equation:

$$k^2 = 3.21 \times 10^{-7} \exp \left(\frac{154 \ \text{kJ}}{RT}\right) \text{ (m}^2/\text{s).}$$

The value k² obtained by extrapolating the above equation to the lower temperatures ranging from 523 to 603 K is
1/10⁷ – 1/10⁸ times smaller than the values for Ni₅Si formed in the thin diffusion couples in the temperature range.
However, the values of interdiffusion coefficients for the thin couples and bulk couples agree well with each other. The
reason for the difference in k² between the thin and bulk samples can be attributed to the difference of phase layers which
are adjacent to the Ni₅Si phase and not to the fast diffusion such as grain boundary diffusion in the thin film diffusion
couples.

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interdiffusion coefficient

I. Introduction

Because transition metal silicides play an active role in
the modern silicon semiconductor device technology, a
great deal of knowledge about the formation of silicides in
thin film metal/bulk silicon diffusion couples has been
accumulated(1-4). The remarkable finding was that sili-
cides can be formed at much lower temperatures in thin
film metal/bulk silicon couples than in bulk/bulk couples.
The stable silicides tend to form sequentially(5,6);
i.e., they appear one by one in thin film/bulk diffusion
couples, instead of several or all of them growing
together as in bulk cases(7,8).

In the studies of the thin film interdiffusion, it has been
recognized that the kinetic process is usually dominated
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 differ-
ences between thin film interdiffusion and bulk one has
been thus pointed out for a long time, there are only a
few systems, e.g., the Ni–Si(3-4) and Pt–Si(9-10) systems,
of which both bulk and thin film diffusion couples have
been studied. Interdiffusion in thin film Ni/bulk Si dif-

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sion couples has been studied by Olowolafe et al.(5) and
Tu et al.(8) They have determined the temperature depen-
dence of phase growth rate of Ni₅Si in the temperature
range from 523 to 602 K. Interdiffusion in a bulk Ni/
bulk Si diffusion couple has also been studied at 1073 and
1023K by Tu et al.(9) Phase growth rates of Ni silicides,
however, have not been reported. Thus, interdiffusion in
bulk couples has not been extensively studied in compar-
ison with that in thin film couples.

Silicides have excellent oxidation resistance, a high
melting point, reasonable strength and density and good
thermal conductivity, as promising structural material at
high temperatures. For such applications, data on dif-
fusion in bulk samples are indispensable. In the present
work, interdiffusion in bulk Ni/Si diffusion couples has
been studied.

II. Experimental Procedure

A <100> oriented, 12.4 mm diameter, 0.6 mm thick-
ness silicon wafer was cut to specimens about 10
mm × 10 mm in size. A 99.99% purity Ni rod was rolled
into a thickness of 1 mm and was cut to the same size as
the Si specimens. The contact surfaces of Si and Ni spec-
imens were ground on abrasive paper and polished metal-
lographically on a buff with fine alumina powder just
before they were tightened together by a stainless-steel
clamp. The diffusion couples thus made were heated in
an evacuated furnace with 10⁻² Pa at 823, 923 and 1023
K for various periods of heating time. After heating they
were mounted in resin. The cross section of the interdiffusion zone was polished metallographically and analyzed by an electron microprobe analyzer (EPMA).

III. Results

A compositional image micrograph of the cross section of a Ni/Si diffusion couple annealed at 923 K for 32.4 ks is shown in Fig. 1(a) and the enlargements of the Ni side as well as the Si side are shown in Fig. 1(b) and (c). Between Ni and Si, 4 kinds of silicides are found and their morphologies are very similar to those at 1123 K reported by Tu et al.\(^7\) According to them, these silicides have been temporally named Ni\(_3\)Si\(_2\), Ni\(_2\)Si, Ni\(_3\)Si, and NiSi from the Ni side, respectively\(^7\), on the basis of electron microprobe analysis.

As shown in Fig. 1, the thicknesses of Ni\(_3\)Si and NiSi layers are too thin to detect distinctly their X-ray intensity by EPMA, so that a thin Ni plate (50 \(\mu\)m in thickness)/bulk Si diffusion couple was annealed at 1023 K for 259 ks. In this couiple a thick layer of NiSi could be obtained. In Table 1, the experimental values of the relative intensity of NiK\(\alpha\) of NiSi thus obtained and of Ni\(_3\)Si\(_2\) and Ni\(_2\)Si\(_2\) are shown. The relative X-ray intensity of Ni\(_3\)Si was not obtained in this work. Although Ni\(_3\)Si\(_2\) has been represented as a line compound in the Ni–Si phase diagram\(^{12}\), a composition range was detected by electron microprobe line analysis. The maximum and the minimum values of relative X-ray intensity for Ni\(_3\)Si\(_2\) are shown in the table. The values of relative intensity were converted into mole fraction with the aid of the ZAF method\(^{12}\). These values are also listed in Table 1 together with those at stoichiometry. From these results, it has been confirmed that the three kinds of silicide correspond to Ni\(_3\)Si\(_2\), Ni\(_2\)Si\(_2\) and NiSi, respectively. The phase between Ni\(_3\)Si\(_2\) and Ni\(_2\)Si\(_2\) is, therefore, concluded to be Ni\(_2\)Si.

The sequential formation of silicides in a Ni thin film/bulk Si diffusion couple reported by Tu et al. could not be confirmed in this experiment. Of course, there is a possibility of occurrence of the sequential formation before the shortest annealing time examined in this experiment.

It has been experimentally found that intermetallic compounds formed in a diffusion couple usually grow satisfying the parabolic law; i.e., \(n\) in the following equation equals \(1/2\),

\[
W = kt^n.
\]

where \(W\) is the thickness of a phase layer, \(k\) is a constant, and \(t\) is the diffusion time.

In this experiment, the thicknesses of the silicides were read from the compositional image micrographs. Although Ni\(_3\)Si\(_2\) and Ni\(_2\)Si show a layered morphology, Ni\(_3\)Si shows a very irregular growth and its measured

\(^7\) In the Ni–Si phase diagram, Ni\(_3\)Si and NiSi\(_2\) are also represented as a line compound. According to Tu et al.,\(^7\) the formation of NiSi\(_2\) has been observed in the diffusion couples annealed at 1023 K for 432 ks but NiSi has not been observed.

\(^{12}\) Table 1 Values of relative X-ray intensity of NiK\(\alpha\) and calculated concentrations of silicides.

<table>
<thead>
<tr>
<th>(I/I_0)</th>
<th>Ni mol fraction (measured)</th>
<th>Phase</th>
<th>Ni mol fraction (stoichiometry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6580</td>
<td>0.502</td>
<td>NiSi</td>
<td>0.50</td>
</tr>
<tr>
<td>0.7168 min</td>
<td>0.576</td>
<td>Ni(_3)Si(_2)</td>
<td>0.60</td>
</tr>
<tr>
<td>0.7357 max</td>
<td>0.600</td>
<td>Ni(_2)Si(_2)</td>
<td>0.7143</td>
</tr>
<tr>
<td>0.8216</td>
<td>0.713</td>
<td>Ni(_3)Si</td>
<td></td>
</tr>
</tbody>
</table>
thickness is the averaged one. A plot of the thicknesses $W$ of silicides, $\text{Ni}_3\text{Si}_2$, $\text{Ni}_5\text{Si}$, $\text{Ni}_7\text{Si}_2$ and $\text{NiSi}$ versus the square root of heating time at 1023 K is shown in Fig. 2. These silicides grow satisfying the parabolic law.

A plot of the thickness of $\text{Ni}_2\text{Si}$ versus the square root of heating time at 923, 973 and 1023 K is shown in Fig. 3. The phase growth rates $k$ at various temperatures were determined by least square fitting from these linear lines and the relationship between the values of $k^2$ and $1/T$ is shown in Fig. 4. Tu et al.\(^{(16)}\) have reported the thickness of $\text{Ni}_2\text{Si}$ formed in the bulk diffusion couple annealed at 1123 K for 28.8 ks to be 55 $\mu$m. The value of $k^2$ was evaluated by using this value and is shown in Fig. 4 by symbol $\triangle$. The linear line can be expressed by the following equation:

$$k^2 = 3.21 \times 10^{-7} \exp(154 \, \text{kJ/RT}),$$

where $R$ is a gas constant, 8.3145 J·mol$^{-1}$·K$^{-1}$.

It has been reported that Ni silicides formed in the thin film couples grow satisfying the parabolic law. Phase growth rates $k^2$ of $\text{Ni}_2\text{Si}$ were determined from the figure in Olowolafe’s paper\(^{(9)}\) and are shown in Fig. 4. Symbols ■ and ♦ correspond to the values for the Ni thin film/⟨111⟩ oriented Si wafer and the Ni thin film/⟨100⟩ wafer or poly Si diffusion couples. The values $k^2$ for the thin samples are far larger than those for bulk samples obtained by extrapolating eq. (2) to lower temperatures and then a rapid phase growth in thin sample is suggested.

However, it should be noted here that $\text{Ni}_2\text{Si}$ formed in the thin sample is directly adjacent to pure Ni and Si\(^{(9)}\), and $\text{Ni}_2\text{Si}$ formed in the bulk sample to $\text{Ni}_3\text{Si}_2$ and $\text{Ni}_5\text{Si}_2$. Because the phase growth rate $k$ depends on the adjacent phases even at the same temperature, we cannot compare these two values of $k^2$ directly. So interdiffusivities of $\text{Ni}_2\text{Si}$ in both thin and bulk samples have been determined by Heumann’s equation\(^{(13)}\) on the assumption of a concentration independent interdiffusivity and linear concentration gradient in the respective phase.

$$\bar{D}_j = \frac{f_j \Delta W_j}{2f_j \Delta C_j x_0} X \, dC_j.$$  \hspace{1cm} (3)

Here, $\bar{D}_j$ is an interdiffusivity, $\Delta W_j$ is a layer thickness, $\Delta C_j$ is a concentration difference, $C_j^{x_0}$ is an average concentration, and $X$ is the distance from the Matano interface. The suffix $j$ means an intermediate phase of $j$’th. In
this experiment $\Delta C_f$ of Ni$_2$Si could not be detected by EPMA analysis. According to the equilibrium phase diagram of the Ni–Si system$^{11}$, Ni$_2$Si is represented as a line compound, i.e., $\Delta C_p=0$, so that $\tilde{D}_j\Delta C_f$ instead of $\tilde{D}$ is determined. Although the interdiffusivity should be determined by taking the volume change effect$^{19}$ into account, it was neglected here because the thickness measurement of Ni$_2$Si$_x$ was not accurate enough and the concentration dependence of $\tilde{D}$ is neglected. The values of $\tilde{D}_j\Delta C_f$ are plotted against $1/T$ in Fig. 5, which reveals the following relationship:

$$\tilde{D}_j\Delta C_f = 4.69 \times 10^{-8} \exp (127 \text{ kJ} / RT).$$

There is no obvious difference between the values $\tilde{D}_j\Delta C_f$ for the thin samples and the extrapolated values for the bulk samples.

IV. Discussion

Because the temperature dependence of $\Delta C_f$ of Ni$_2$Si is not known, the magnitudes of interdiffusivity in the thin and bulk samples are discussed qualitatively. However, from the present experimental results it has been suggested that the grain boundary diffusion does not necessarily dominate the phase growth process in the thin diffusion couples.

Although the contribution of grain boundary diffusion on the growth process of diffusion layer has not been well understood, several investigators have suggested that the values of $n$ in eq. (1) may not be 1/2 when grain boundary diffusion dominates the phase growth process. For examples, Bastin et al.$^{15}$ have shown from their experimental results of interdiffusion in a Ti–TiNi bulk diffusion couple that $n$ for Ti$_2$Ni in the initial stage of diffusion is larger than 1/2 and it may be influenced by grain bound-

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ary diffusion. On the basis of Whipple’s grain boundary diffusion model$^{16}$, Farrell et al.$^{17}$ have shown that in the phase growth process $n$ may be 0.35 when grain boundary diffusion participates. On the other hand, the experimental values of $n$ for silicides such as Ni$_2$Si$^{20}$ formed in a thin sample has usually been determined to be 1/2.

Of course, there is a possibility that $n$ becomes 1/2 no matter how boundary diffusion dominates the phase growth process in the thin sample as well as in the bulk sample. So, it is not clear whether or not the boundary diffusion affects the values of $n$. It may be true that thin films contain fine grains. One possible explanation of the existence of the parabolic law even in such fine grained thin samples is that the grains of silicides formed by the reaction between silicon and metals are sufficiently large in comparison with the thickness of the deposited thin metal film or silicides formed in the diffusion couples. It follows that grain boundary diffusion does not necessarily dominate the growth process of silicides. Some investigators$^{20}$ have measured the grain sizes of silicides formed in thin samples by use of a transmission electron microscope and found them to be about 0.1–0.5 μm. For example, Olowolafe et al. have reported that the grain size of Ni$_2$Si formed in the Ni thin film/bulk Si diffusion couple annealed at 598 K for 34.8 ks is about 0.13–0.14 μm$^{20}$. This value is very small in a case of bulk diffusion but is sufficiently large compared with the thickness of the Ni thin film, 0.16 μm, or Ni$_2$Si formed in the thin film couple.

In order to confirm the absence of the obvious difference in interdiffusivities in the thin and bulk samples, the reactive diffusion of the Pt–Si system is now being investigated. According to the preliminary study, no obvious difference in interdiffusivity of the Pt–Si system has been suggested.

V. Summary

Reactive diffusion of the Ni–Si system has been studied by using bulk diffusion couples consisting of pure Ni and pure Si wafer in the temperature range from 823 to 1023 K. The experimental results were compared with the previous results obtained by using Ni thin film/bulk Si diffusion couples. The results obtained in this work are summarized as follows:

1. In the bulk Ni/Si diffusion couple, Ni$_5$Si$_3$, Ni$_3$Si$_2$, Ni$_2$Si and NiSi are formed.

2. The extrapolated values of the phase growth rate $k^2$ for Ni$_2$Si formed in bulk diffusion couples are about $10^{-3}$–$10^{-4}$ times smaller than $k^2$ for Ni$_2$Si formed in thin diffusion couples in the temperature range from 523 to 623 K.

3. There is no obvious difference between the interdiffusion coefficient for Ni$_2$Si formed in the thin diffusion couples and the extrapolated values of the coefficient in the bulk diffusion couples.

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