The Role of Iron in Ti on the Growth of Ti Silicides in Bulk Ti/Si Diffusion Couples

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Reaction diffusion in the Ti-Si system has been studied to clarify the role of iron in Ti on the growth of TiSi_2 by using sandwich type diffusion couples consisting of 99.5%(2N)Ti, 99.9999%(6N) Ti and $\langle 111 \rangle$ oriented Si wafer in the temperature range between 1164 and 1323 K. The growth of TiSi_2 formed in 2N-Ti/Si diffusion couples at the lowest temperature in this experiment, 1164 K, was slower than that in a 6N-Ti/Si couples. The difference between the growth rate of 2N-Ti/Si and that in 6N-Ti/Si diffusion couples becomes to be small and to have the same value at 1213 K. These results could be expected from our previous experimental results that the higher the purity of Ti the faster the growth rate and that the lower the purity of Ti the larger the activation energy in the temperature range between 973 and 1123 K. However, the Arrhenius plot of the growth rate, k^2 , for 2N-Ti/Si couple bends at 1213 K and have the same value as the 6N-Ti/Si diffusion couples above 1213 K.

As a possible explanation for this behavior of the growth of TiSi_2 in the 2N-Ti/Si couple it has been considered that in the high temperature range impurity iron atoms which segregate at grain boundaries of TiSi_2 and slow down the movement of titanium and silicon atoms diffusing through the grain boundaries in the lower temperature range will redistribute into matrix and the effects become negligible small at high temperature.

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I. Introduction

In the field of device technology, titanium silicides have attracted attention because of their low and metal-like resistivity and their high temperature stability. So the interaction between thin film titanium and silicon wafer has been studied in the past⁽¹⁾⁻⁽⁵⁾. However, very little is known about the formation and growth kinetics of titanium silicides. The authors have previously⁽⁶⁾⁽⁷⁾ studied the reactive diffusion in the Ti-Si binary system by using bulk diffusion couples consisting of 99.5%Ti (2N-Ti), 99.99%Ti (4N-Ti) and 99.9999%Ti (6N-Ti) and a silicon wafer having $\langle 111 \rangle$ orientation. The results have been summarized in Fig. 1 (see Fig. 5 in Ref. (7)) where the Arrhenius plots of growth rates k^2 of TiSi_2 formed in various kinds of diffusion couples are shown. Figure 1 shows that the growth of TiSi_2 is faster the higher the purity of Ti. To identify the element which slows down the growth rate of TiSi_2 in bulk Ti/Si diffusion couples, the effect of iron, nitrogen, oxygen and carbon was studied by depositing iron or carbon on 6N-Ti plates in an evacuated chamber at room temperature and absorbing oxygen or nitrogen gas into the 6N-Ti plates in a quartz capsule at 1073 K. Ti specimens thus made were called as Ti(Fe) or Ti(O) and so on. Sandwich-type

diffusion couples, consisting of these Ti specimens and silicon wafer, for example, Ti(Fe)/Si/6N-Ti, were made. As shown in Fig. 1, the growth rate of TiSi_2 formed in Ti(Fe)/Si diffusion couples is controlled while those in Ti(N)/Si and Ti(O)/Si are not. Since it has also been clarified that iron atoms segregate at the grain boundary of TiSi_2 in the lower temperature range⁽⁷⁾, the authors concluded that iron atoms which segregate at the boundary slow down the diffusion of Ti and Si which pass through the boundary. Consequently, grain boundary diffusion has been suggested as a dominant process for the growth of the TiSi_2 in the Ti/Si diffusion couples.

From the Fig. 1, it is expected that the growth of TiSi_2 for 2N-Ti/Si diffusion couples becomes faster than that for 6N-Ti/Si couples in the high temperature range because the activation energy for 2N-Ti/Si diffusion couples is larger than that for 6N-Ti/Si couples. However, according to our previous results⁽⁷⁾ it has been suggested that the growth rate of TiSi_2 in a 2N-Ti/Si couple cannot be faster than that in 6N-Ti/Si couple because iron in a 2N-Ti slows down the growth of TiSi_2 in the 2N-Ti/Si couple⁽⁷⁾.

This experiment has been performed to check this point of view. By this experimental results the role of iron is expected to be clear. Ti transforms from the hcp to the bcc structure at 1156 K, so the effect of change in crystal

Fig. 1 Temperature dependence of the growth rates k^2 of TiSi_2 for various kinds of diffusion couples.

structure on the growth behavior of titanium silicides is also studied.

Silicides combine excellent oxidation resistance, a high melting point and reasonable strength and density, making them a promising material for structural applications at high temperature. For such applications, data on diffusion in bulk samples are indispensable.

II. Experimental Procedure

A 6N titanium disk (Sumitomo SiTiX Co. LTD) and a 2N titanium sheet used here are the same one as those in the previous paper⁽⁶⁾⁽⁷⁾. The concentration of Fe was 200 ppm for 2N-Ti and less than 0.1 ppm for 6N-Ti, respectively. They were rolled and cut to the specimens about 10 mm × 10 mm × 0.5 ~ 1.5 mm in size. The thick specimens were used for the experiment at high temperature for a long period of anneal. Ti specimens thus made were not recrystallized to avoid the contamination during the anneal. As it has been shown⁽⁶⁾, any differences between the growth of silicides formed in a recrystallized Ti/Si couple and a non-recrystallized Ti/Si diffusion couple have not been found. A $\langle 111 \rangle$ oriented, 12.4 mm diameter, 0.6 mm thickness silicon wafer was cut to the same size of Ti specimen. The contact surfaces of Si and Ti specimens were ground on abrasive papers and polished metallographically on a buff with fine alumina powder. The surface of Ti is chemically polished in a solution consisting of 30% HF and 70% fuming HNO_3 .

The Ti specimen thus prepared was tightened together with a Si specimen by a stainless steel clamp. To perform the experiment under the same conditions, 6N-

Ti/Si/2N-Ti sandwich-type diffusion couples were assembled. The couple was heated in an evacuated furnace at a pressure of about 10^{-5} Pa at 1164, 1213, 1266, 1292 and 1323 K for various periods of heating time. After the heating they were removed and mounted in a resin. The cross section of the diffusion zone was polished metallographically and analyzed by an electron probe micro analyzer (EPMA: JEOL JCA 733).

III. Results

1. Ti silicides formed in 2N-Ti/Si and 6N-Ti/Si diffusion couples

In the Ti-Si binary phase diagram⁽⁸⁾, five kinds of silicides, i.e., Ti_3Si , Ti_5Si_3 , Ti_5Si_4 , TiSi and TiSi_2 , are represented. Four kinds of the silicides have already been detected in both Ti/Si diffusion couples⁽⁶⁾⁽⁷⁾. Two of them from Si side are TiSi_2 and TiSi respectively. The rest two layers were too narrow to be identified. At the highest temperature in this experiment, 5 kinds of silicides could be found by the EPMA component image. The concentrations of these silicides determined by the ZAF method are shown in Table 1. That for the third layer from Si side corresponds to Ti_5Si_4 . The rest two layers can be supposed to be Ti_5Si_3 and Ti_3Si , respectively.

2. Growth behavior of titanium silicides

The relationships between the widths, W , of TiSi_2 and TiSi formed in 6N-Ti/Si and 2N-Ti/Si diffusion couples and the square root of annealing time, t , at 1164, 1266, 1292 and 1323 K are shown in Fig. 2 through Fig. 5. At 1164 K, both TiSi_2 and TiSi grow satisfying the parabolic law. The widths of TiSi_2 and TiSi formed in 6N-Ti/Si diffusion couple are obviously thicker than that in 2N-Ti/Si couples. On the other hand, the total width and the width of TiSi formed in these diffusion couples at 1266, 1292 and 1323 K are almost the same. It should be noted, here, that the growth of TiSi in 2N-Ti/Si diffusion couple at 1266 K satisfy the parabolic law, while the growth of TiSi_2 does not. Similar growth of TiSi and TiSi_2 was also found at 1292 K at shown in Fig. 4. At these temperature the growth of TiSi_2 at the early stage of the anneal is rapid and the width in 2N-Ti/Si couple is thicker than the 6N-Ti/Si couple though it becomes slow and the width is reversed. So at 1266 and 1292 K, two values of k^2 for TiSi_2 have been determined. One is determined by the

Table 1 Concentrations of silicides determined by the ZAF method.

Layer number from Si side	Ti (at%)		Phase
	ZAF	Stoichiometry	
1	33.4	33.33	TiSi_2
2	50.1	50.0	TiSi
3	55.1	55.56	Ti_5Si_4
4	60.9	62.5	$\text{Ti}_5\text{Si}_3?$
5	—	—	$\text{Ti}_3\text{Si}?$

Fig. 2 Relationship between thickness, W , of TiSi_2 and TiSi layers formed in the 2N-Ti/Si and 6N-Ti/Si diffusion couples and square root of annealing time at 1164 K.

Fig. 4 Relationship between thickness, W , of TiSi_2 and TiSi layers formed in the 2N-Ti/Si and 6N-Ti/Si diffusion couples and square root of annealing time at 1292 K.

Fig. 3 Relationship between thickness, W , of TiSi_2 and TiSi layers formed in the 2N-Ti/Si and 6N-Ti/Si diffusion couples and square root of annealing time at 1266 K.

Fig. 5 Relationship between thickness, W , of TiSi_2 and TiSi layers formed in the 2N-Ti/Si and 6N-Ti/Si diffusion couples and square root of annealing time at 1323 K.

least square fitting under an intentional condition that the line start from the origin, $W=0$ at $t=0$. The other is determined by using only the data for the early stage of anneal. At 1323 K, both TiSi_2 and TiSi grow satisfying the parabolic law again as shown in Fig. 5.

The Arrhenius plots of growth rate, k^2 , of TiSi_2 for both diffusion couples thus determined are shown in Fig. 6 together with our previous data⁽⁷⁾. The symbol, $\bullet$, for 2N-Ti/Si couple at 973 K means that TiSi_2 formed in this temperature has irregular morphology as has been

Fig. 6 Temperature dependence of the layer growth rate constant k^2 and $\Delta N \cdot \bar{D}$ of TiSi_2 for various types of diffusion couples.

reported previously⁽⁶⁾. The data at 1164 and 1213 K for 2N-Ti/Si diffusion couple locate just on the extension of the linear broken line. The line is represented by

$$k^2 = 1.8 \times 10^{-5} \exp(-251.5 \text{ kJ} \cdot \text{mol}^{-1} / RT).$$

Although the data at 1266, 1292 and 1323 K represented by symbol $\bullet$ deviate from the linear broken line, the Arrhenius plot is not affected by the transformation of Ti from the hcp to the bcc at 1156 K. The data represented by symbol $\odot$ were those obtained by using only the data at the early stage of the anneal.

On the other hand, the Arrhenius plot of k^2 for 6N-Ti/Si can be drawn by a linear line from 1023 to 1323 K while the datum at 973 K represented by symbol Δ deviates from the line. The linear line is approximated by

$$k^2 = 7.9 \times 10^{-13} \exp(-39.4 \text{ kJ} \cdot \text{mol}^{-1} / RT).$$

The activation energy, $39.4 \text{ kJ} \cdot \text{mol}^{-1}$, is very small in comparison with the values, $251.5 \text{ kJ} \cdot \text{mol}^{-1}$ for the 2N-Ti/Si diffusion couple and $132 \text{ kJ} \cdot \text{mol}^{-1}$ reported in the previous paper⁽⁷⁾. In order to confirm the deviation of the symbol Δ from the line, a diffusion couple, 6N-Ti/Si/2N-Ti, was annealed at 990 K. The datum for the 6N-Ti/Si diffusion couple is shown in Fig. 6 by the symbol, Δ . It also deviates from the linear line, namely, a high activation energy is required in the lower temperature range. The symbol, $\odot$, for 2N-Ti/Si couple means that irregular morphology was observed in the 2N-Ti/Si couple as was so at 973 K⁽⁶⁾. The authors have previously obtained such low activation energy in a high temperature range and high activation energy in a low temperature range in the reaction diffusion of Ti-Al system⁽⁹⁾. The activation energy for growth of TiAl_3 in the

4N-Ti/Al diffusion couple was $33.8 \text{ kJ} \cdot \text{mol}^{-1}$ and that in the 2N-Ti/Al diffusion couple in the higher temperature range was $61.4 \text{ kJ} \cdot \text{mol}^{-1}$, while that in the lower temperature range was more than $250 \text{ kJ} \cdot \text{mol}^{-1}$. This phenomenon has been explained by correlating with the effects of diffusion barrier in the lower temperature range, i.e., diffusion of Al is controlled by the diffusion of Al in the diffusion barrier such as oxide film. The large activation energy in the low temperature range in the Ti-Si system can also be attributed to this diffusion barrier effect. The bend of the Arrhenius plot of k^2 of TiSi_2 for the 2N-Ti/Si diffusion couple above 1266 K will be explained by the effect of iron in the following.

3. Temperature dependence of diffusion coefficients

In general, Arrhenius plot of the value k^2 of a phase, α , is not necessarily represented by a linear line because the value k is influenced by the kind of adjacent phases, a drastic change of diffusion coefficient, for example, due to the phase transformation of the adjacent phase and the temperature dependence of solubility of the α phase or concentration gaps between the α phase and the adjacent phases⁽¹⁰⁾⁻⁽¹²⁾, while the plot of the interdiffusion coefficient, $\bar{D}$, is represented by a linear line. Therefore, determination of interdiffusion coefficient has been tried. However, it is difficult because titanium silicides have very small solubility. So, here, $\Delta N \cdot \bar{D}$ instead of $\bar{D}$ has been determined with the aid of the Heumann's method⁽¹³⁾ taking the effect due to the change in volume during diffusion anneal into account. Temperature dependence of $\Delta N \cdot \bar{D}$ thus determined is shown in the Fig. 6 for TiSi_2 and Fig. 7 for TiSi .

The values of $\Delta N \cdot \bar{D}$ of TiSi_2 are about 1/8 of the values of k^2 , so the plot of $\Delta N \cdot \bar{D}$ is similar to that for k^2 . The effect of the phase transformation of titanium at 1156 K on the value of $\Delta N \cdot \bar{D}$ of TiSi_2 is not observed on the Arrhenius plot. In this experiment, the diffusion layer of β Ti phase could not be detected by EPMA analysis. So, the diffusion in the β Ti phase seems to be very slow in comparison with that in TiSi_2 . Because the diffusion in the α Ti phase is also very slow, the transition from α to β may affect nothing the growth of TiSi_2 , in other words, the diffusion layers of both α and β phases are too narrow to influence the growth of TiSi_2 .

The pre-exponent factor and the activation energy are $6.8 \times 10^{-13} (\text{m}^2 \cdot \text{s}^{-1})$ and $56.8 (\text{kJ} \cdot \text{mol}^{-1})$ for TiSi_2 in 6N-Ti/Si diffusion couples in the temperature range from 1023 to 1323 K and $5.3 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$ and $260.3 \text{ kJ} \cdot \text{mol}^{-1}$ for 2N-Ti/Si couples in the temperature range from 1023 to 1213 K, respectively. The activation energy, $56.8 \text{ kJ} \cdot \text{mol}^{-1}$ for TiSi_2 in 6N-Ti/Si diffusion couples is very small.

The Arrhenius plots of $\Delta N \cdot \bar{D}$ of TiSi for both type diffusion couples also show a deviation from the linear line at 1213 K. Although the temperature dependence of ΔN can be considered as one of the possible reasons, there is no information about the temperature dependence of ΔN .

The pre-exponent factor and the activation energy are

Fig. 7 Temperature dependence of the $\Delta N \cdot \bar{D}$ of TiSi.

$3.4 \times 10^{-7} \text{ (m}^2 \cdot \text{s}^{-1})$ and $196.2 \text{ (kJ} \cdot \text{mol}^{-1})$ for TiSi_2 in 6N-Ti/Si diffusion couples in the temperature range between 973 and 1213 K and $3.3 \times 10^{-2} \text{ m}^2 \cdot \text{s}^{-1}$ and $314.4 \text{ (kJ} \cdot \text{mol}^{-1})$ for 2N-Ti/Si couples in the temperature range between 1023 and 1213 K. The values, $\Delta N \cdot \bar{D}$, of TiSi formed in the 6N-Ti/Si and 2N-Ti/Si diffusion couples also become to have the same values in the high temperature range.

IV. Discussion

The most interesting result obtained in this experiment is that the thicknesses of TiSi_2 and TiSi formed in both 2N-Ti/Si and 6N-Ti/Si diffusion couples in the high temperature range become to have the same value. As reported previously, iron atoms segregate at grain boundaries in 2N-Ti/Si diffusion couples (see Figs. 1(c), (d) in Ref. (6)) and they control the movement of almost of silicon and titanium atoms which pass through the boundaries. In addition, the TiSi_2 layer has needle like columnar grains less than $1 \mu\text{m}$ in diameter even in the diffusion couple annealed at the highest temperature in the previous experiment (e.g., see Fig. 2 in Ref. (6)). On the basis of these experimental results the grain boundary diffusion model has been proposed as a dominant diffusion process in Ti-Si system. This boundary diffusion model is also useful to explain the low activation energy in the 6N-Ti/Si diffusion couples.

The present experimental result that the thickness of TiSi_2 and TiSi formed in both 2N-Ti/Si and 6N-Ti/Si diffusion couples in the high temperature range become to have the same value can be explained by using this boundary diffusion model as follows. The iron atoms

which segregate at grain boundary in the low temperature range redistribute into the matrix, i.e., TiSi and TiSi_2 in the high temperature range then the effect of iron atoms vanishes.

In this experiment, TiSi_2 layer has needle like columnar grains less than $3 \mu\text{m}$ in diameter even at the highest temperature. This size is enough small so that we can consider the grain boundary diffusion model in this temperature range.

The authors have proposed some questions in the previous paper that “Does the boundary diffusion dominate the diffusion process in such higher temperature range?” and “Can the phase growth follow the parabolic law under the condition that the boundary diffusion dominate the diffusion process while Bird⁽¹⁴⁾ and Lidiard *et al.*⁽¹⁵⁾ have pointed out a possibility of parabolic growth of diffusion layer in the reaction diffusion couple even though in a limited condition”. This experimental result supports the boundary diffusion model in such higher temperature range and the parabolic growth of diffusion layers even under the boundary diffusion dominated condition.

In this experiment, a non $t^{1/2}$ dependence has been observed for the growth of TiSi_2 in 2N-Ti/Si couple at 1266 and 1292 K. Corcoran *et al.*⁽⁵⁾ have reported that the TiSi_2 growth has a non $t^{1/2}$ dependence and is much better described by a grain boundary diffusion limited model. They studied the growth kinetics between deposited thin film Ti and $\langle 100 \rangle$ or $\langle 111 \rangle$ oriented Si wafers at 1023 K and the experiment was limited only for short times ranging from 5 to 45 s in a nitrogen ambient. In such early stage of annealing, the non $t^{1/2}$ dependence may be possible even though in the later stage of anneal, the growth becomes to satisfy the parabolic law.

Since, it has been suggested from our experimental results that the boundary diffusion dominates the diffusion process in the Ti/Si system although the phase growth in Ti/Si diffusion couples follows the parabolic law, so we should try to explain this non $t^{1/2}$ time dependence by another way excepting the grain boundary limited growth model. As causes of a non $t^{1/2}$ time dependence growth of diffusion phase layer, some reasons can be considered. One is that due to the non-simultaneous formation of diffusion phase layer as it has been well known in the reaction diffusion between silicon and metals as well as the Fe-Zn binary system⁽¹⁶⁾. According to the previous study it has been shown⁽¹⁷⁾ that when a new phase is formed in a diffusion couple the growth of the new phase and the existing phase do not follow the parabolic law temporarily. One is a breakdown of the experimental condition of semi-infinite solid during a long period isothermal anneal.

At least, both the non simultaneous formation of the diffusion phase layer and breakdown of the experimental condition of the semi-infinite solid for pure titanium and silicon could not be found at these temperatures. So, at present, the reason for the non $t^{1/2}$ time dependence growth of TiSi_2 is not clear. One candidacy is a change of limiting process during the isothermal anneal which

controls the growth of TiSi_2 or TiSi . In the lower temperature range, width of the TiSi layer is very narrow, so Fe atoms can easily pass through TiSi and reach TiSi_2 . On the other hand, in the higher temperature range, the width of TiSi is relatively thick than that in the lower temperature range. So it needs a long time until Fe atoms reach TiSi_2 layer. Until Fe atoms reach TiSi_2 layer, the effect of Fe could not be detected. However, there are some questions. Why the width of TiSi_2 at the early stage of anneal in the 2N-Ti/Si couple can be thicker than that in the 6N-Ti/Si couple at 1266 and 1292 K. Are there some elements which enhance the diffusion in TiSi_2 ? Further, why the activation energy for interdiffusion in TiSi_2 formed in the 6N-Ti/Si diffusion couple is so small?. To answer these questions, further experiment are required.

V. Summary

Reaction diffusion in the Ti-Si binary system has been studied by using sandwich-type bulk diffusion couples consisted of 99.5%Ti, 99.9999%Ti plates and $a\langle 111 \rangle$ oriented Si wafer in the temperature range from 1164 to 1323 K. The experimental results have been compared with our previous data obtained in the temperature range from 973 to 1123 K. The results are summarized as follows.

(1) The growth rate of TiSi_2 formed in 6N-Ti/Si diffusion couples is faster than that in 2N-Ti/Si couples at 1164 K. However, they become to have the same values in the high temperature range. This means that the effect of iron on the growth of TiSi_2 vanishes in the high temperature range.

(2) As one possible explanation for the result (1) it has been considered that in the higher temperature range, iron atoms which segregate at grain boundaries in the lower temperature range redistribute into the matrix, so

the effect of iron at grain boundaries vanishes.

(3) The Arrhenius plots of the growth rate constant k^2 for TiSi_2 and TiSi are not affected by the transition of Ti from α to β .

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REFERENCES

- (1) H. Kato and Y. Nakamura: *Thin Solid Films*, **34** (1976), 135.
- (2) R. W. Bower and J. W. Mayer: *Appl. Phys. Lett.*, **29** (1972), 359.
- (3) W. K. Chu, S. S. Lau, J. W. Mayer and H. Muller and K. N. Tu: *Thin Solid Films*, **25** (1975), 393.
- (4) S. P. Murarka and D. B. Fraser: *J. Appl. Phys.*, **51** (1980), 342.
- (5) Y. L. Corcoran, A. H. King, N. Laneroll and B. Kim: *J. Elect. Mater.*, **19** (1990), 1177.
- (6) T. Shimozaki, K. Chikumaru, Y. Wakamatsu and M. Onishi: *J. Japan Inst. Metals*, **60** (1996), 29.
- (7) T. Shimozaki, T. Okino, M. Yamane, Y. Wakamatsu and M. Onishi: *Trans. JIM*, **38** (1997), 865.
- (8) P. Nash and A. Nash: *Binary Alloy Phase Diagrams*, Vol. 2, ed. by T. B. Massalski *et al.*, American Society for Metals, Metals Park, Ohio, (1986), p. 2056.
- (9) T. Shimozaki, T. Okino, M. Yamane, Y. Wakamatsu and M. Onishi: *Defect and Diffusion Forum*, **143-147** (1997), 591.
- (10) W. Seitz: *Diffusion in Metallen*, Springer Verlag, Berlin, (1955), 158.
- (11) G. V. Kidson: *J. Nucl. Mater.*, **3** (1961), 21.
- (12) S. Tuji: *J. Japan Inst. Metals*, **41** (1977), 678.
- (13) Th. Heumann: *Z. Phys. Chem.*, **201** (1952), 168.
- (14) J. D. Baird: *J. Nucl. Energy, Part A*, **11** (1960), 81.
- (15) A. B. Lidiard and K. Tharmalingam: *Disc. Faraday Soc.*, **28** (1959), 64.
- (16) M. Onishi, Y. Wakamatsu and H. Miura: *Trans. JIM.*, **15** (1974), 331.
- (17) T. Shimozaki, Y. Wakamatsu and M. Onishi: *J. Japan Inst. Metals*, **57** (1993), 1376.