Reactive Diffusion in Bulk Pt/Si Diffusion Couple

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Reactive diffusion of the Pt-Si system has been studied by using bulk Pt/bulk Si single crystal diffusion couples in the temperature range from 673 to 923 K in an evacuated atmosphere of $10^{-3}$ Pa. To study the effect of the atmosphere on the growth rate of the diffusion layers, some diffusion couples have been annealed at 673, 873 and 923 K at a pressure $10^{-3}$ Pa. The experimental results were compared with the previous results obtained by using Pt thin film/bulk Si diffusion couples.

In the bulk Pt/Si diffusion couples annealed at 673 K for 3.6 ks or more, Pt$_3$Si and PtSi have been found. The silicides, Pt$_3$Si, Pt$_5$Si$_3$, and Pt$_7$P$_4$ were formed above 723 K. All of them grew satisfying the parabolic law.

The interdiffusion coefficients of PtSi and Pt$_3$Si in bulk samples almost coincide with the minimum values for thin film diffusion couples, respectively, in spite of a general recognition that interdiffusion in thin film diffusion couples can occur faster than in bulk sample at low temperature.

This result partly supports our previous result of reactive diffusion in the Ni-Si system that any apparent difference between the diffusion phenomenon in bulk and thin film diffusion couples could not be found.

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I. Introduction

Because transition metal silicides play an active role in modern silicon semiconductor device technology, a great deal of knowledge about formation of silicides in thin film metal/bulk silicon diffusion couples has been accumulated$^{(1)-(8)}$. The remarkable finding in the knowledge was that reaction between bulk silicon and thin film metal formation of silicides can be observed at a much lower temperature than in bulk couples. The stable silicides tend to form sequentially$^{(9)-(32)}$, 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$^{(33)}$.

In the studies of the thin film interdiffusion, it has been recognized that in a fine grained thin film, the kinetic process is generally dominated by grain boundary diffusion, so that interdiffusion can occur faster than in the bulk sample at low temperature$^{(3)}$.

However, in our previous study$^{(34)}$ on reactive diffusion of the Ni-Si system by use of bulk diffusion couples it has been found that although the growth rate $k$ ($= W^2 / t$ where $W$ is the thickness of a silicide layer and $t$ is the annealing time) of Ni$_3$Si in the thin film sample is more than $10^2 \sim 10^4$ times larger than the extrapolated value of $k$ of Ni$_3$Si in the bulk sample as has been recognized, any apparent difference between these two interdiffusion coefficients could not be found. Therefore the authors have maintained that the reason for the rapid growth rate of the silicide in the thin sample can be attributed to the difference of the diffusion phase layers which are adjacent to the Ni$_3$Si layer, i.e., pure Ni and pure Si are to Ni$_3$Si in the thin sample while Ni$_3$Si$_3$ and Ni$_3$Si$_2$ are in the bulk sample.

This work was performed to support our previous results on reactive diffusion of the Ni–Si system. The Pt–Si system was chosen because there are many studies on the formation and growth kinetics in thin film Pt/bulk Si diffusion couples$^{(7)-(14)}$ but only few studies$^{(15)}$ on bulk diffusion of this system to our knowledge.

II. Experimental Procedure

A $\langle 111 \rangle$ oriented, 12.4 mm diameter, 0.6 mm thickness silicon wafer was cut to specimens about 10 mm $\times$ 10 mm in size. A 99.99% purity Pt plate 1 mm in thickness was rolled and cut to the same size as Si specimens. They were annealed at 1273 K in an evacuated furnace for 86.4 ks to yield crystal grain growth. The contact surfaces of Si and Pt specimens were metallographically polished on a buff with fine alumina powder just before they were tightened together by a stainless-steel clamp. The majority of measurements were made for diffusion couples consisting of $\langle 111 \rangle$ Si and pure Pt at 673, 723, 773, 873 and 923 K in the furnace evacuated to $10^{-2}$ Pa for various periods of diffusion time. Some of
these diffusion couples were also used to study the Kirkendall effect by inserting aluminum particles of 1 μm diameter between the Pt and Si interface. After heating they were removed from the clamp and mounted in resin. The cross section was polished metallographically and analyzed by electron microprobe (EPMA). The width of the diffusion layer was determined by measuring the width on photomicrographs of the EPMA component image.

III. Results

1. Silicides formed in diffusion couples

Photomicrographs of the compositional image of the cross section of Pt/⟨111⟩ orienting Si wafer couples annealed at 673, 723, 773, 923 K for 360, 291.6, 90 and 3.6 ks, respectively, are shown in Figs. 1(a)–(d). In these figures, two (Fig. 1(a)), three (Fig. 1(b)), four (Fig. 1(c)) and five (Fig. 1(d)) layered silicides are found between Si and Pt.

Identification of these phase layers was done with the aid of EPMA analysis using a calibration curve, i.e., a relationship between relative intensity of PtL₂ and Pt concentration. Here, the calibration curve was obtained by the ZAF method. In the equilibrium phase diagram of Pt–Si system, five silicides have been represented as a line compound. It was confirmed that the silicides in Figs. 1(a)–(d) correspond to these stable silicides in the phase diagram, i.e., PtSi, Pt₂Si, Pt₃Si, Pt₄Si and Pt₅Si from the Si side, respectively.

The two phase layers in Fig. 1(a) are Pt₂Si and PtSi.

It has been known that Pt₂Si is the first phase to grow in thin film Pt/Si diffusion couples below 673 K, and PtSi sequentially starts to grow between Si/Pt₂Si interface. The beginning time t₀ of formation of PtSi has been reported to be about 2.4–4.8 ks at 588 K and 0.6 ks at 649 K for example. Because t₀ becomes faster the higher the temperature, it is easily supposed that formation of PtSi at 673 K occurs far before 3.6 ks, i.e., the shortest anneal time in this experiment. The third phase to grow is Pt₅Si. As shown in Fig. 1(b) this phase appears between Pt₂Si and PtSi. The fourth phase, Pt₃Si, is formed between Pt and Pt₂Si, (see Fig. 1(c)). Because it is difficult to distinct thin layer of Pt₃Si from pure Pt, there is a possibility that Pt₃Si phase might have been formed before formation of Pt₅Si. Finally, fifth phase, Pt₄Si₁, is formed between Pt₃Si and Pt₅Si, (see Fig. 1(d)).

2. Kirkendall effect

In Fig. 1(d) the Kirkendall interface, represented by K, can be seen in the Pt₂Si phase layer. The ratio, Dₚt/Dₚ₁, of intrinsic diffusion coefficients at the Kirkendall marker is roughly estimated to be 10, i.e., Pt atoms move 10 times faster than Si atoms in Pt₂Si. From this result a preferential diffusion of Pt atoms in the Pt₂Si phase has been indicated.

The preferential diffusion of Pt atoms in Pt₂Si phase has also been reported by Wittmer et al. By use of transmission electron microscopy they found the Kirkendall void network at Pt/Pt₂Si interface in the sputter deposited thin film/Si substrate diffusion couples annealed at

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Fig. 1 Photomicrographs of compositional image of the cross section of pure Pt/Si wafer diffusion couples annealed at 673 K for 360 ks (a), 723 K for 291.6 ks (b), 773 K for 90 ks (c), 923 K for 3.6 ks (d).

Nava et al. reported that the beginning time t₀ of formation of PtSi varies depending on the oxygen content in a deposited thin film Pt.
573 K\(^{9}\) and stated that the location of the voids is a clear indication that the dominant diffusion mechanism in Pt silicides is vacancy-assisted diffusion of the Pt atom.

In this experiment, however, it was very difficult to study the Kirkendall effect at temperatures lower than 773 K because insertion of markers such as aluminum powder prevents the diffusion at the welded interface. Nevertheless, a suggestion of the preferential diffusion of Pt atoms in Pt\(_2\)Si is given from Figs. 1(a), (b) and (c) in which an array of inclusions can be seen as black spots at the Pt/\(\text{Pt}_2\)Si interface in Figs. 1(a) and (b) and the Pt\(_2\)Si/\(\text{Pt}_2\)Si interface in Fig. 1(c).

3. Growth rate and interdiffusivity of Pt\(_2\)Si and PtSi phases

Relationships between the width of diffusion layers formed in Pt/\(\{111\}\) oriented Si couples and the square root of diffusion time are shown in Fig. 2 for 673 K and in Fig. 3 for 723 K. In this experimental temperature range, all diffusion layers grew satisfying the parabolic law. For example, the relationships between the widths of Pt\(_2\)Si and PtSi at various temperatures and \(\sqrt{t}\) are shown in Fig. 4 for Pt\(_2\)Si and in Fig. 5 for PtSi. The
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Fig. 6 A comparison of the growth rates $k(=W^2/t)$ for Pt$_2$Si formed in bulk diffusion couples with those reported previously by use of thin film diffusion couples.

Fig. 7 A comparison of the growth rates $k(=W^2/t)$ for PtSi formed in bulk diffusion couples with those reported previously by use of thin film diffusion couples.

growth rates $k(=W^2/t)$ for Pt$_2$Si and PtSi were determined and the Arrhenius plots are shown in Figs. 6 and 7 together with those determined previously by use of thin film Pt/bulk silicon diffusion couples. Although various different types of Si diffusion halves have been used by the previous investigators, for example, sputtered polycrystalline silicon(7), amorphous silicon(12), (100) or (111) oriented single crystal(9), it has been known that the growth rate of Pt$_2$Si does not depend or depend a little on the type of silicon but depend largely on the oxygen partial pressure during evaporation of Pt(10) as well as on the oxygen content in deposited Pt(9). Both maximum values of $k$ for Pt$_2$Si and PtSi have been obtained by Crider et al.(15) who performed the evaporation of Pt under a higher ultra high vacuum atmosphere over $10^{-7}$ Pa than less than $10^{-13}$ Pa by the other workers.

The present value of $k$ for Pt$_2$Si is smaller than those for thin film diffusion couples and the Arrhenius plot tends to curve down in a high temperature range while that for PtSi almost coincides with the minimum value of $k$ for thin film diffusion couples. The reason for the curved Arrhenius plot for Pt$_2$Si can be attributed to the change in the number of the diffusion phases and the kind of diffusion phases which are adjacent to the Pt$_2$Si layer. For example, at 673 K only two-phase layers were formed and pure Pt and PtSi are adjacent to Pt$_2$Si while 5 layers were formed and Pt$_2$Si$_1$ and Pt$_2$Si$_2$ are adjacent to Pt$_2$Si at 873 and 923 K.

Thus, the value $k$ usually depends on the kind of adjacent phases. So, here, a comparison of the interdiffusion coefficients, $D_i$, between the bulk diffusion couples and the thin film ones has been tried. As most of the silicides in the binary systems are represented in their phase diagrams as a line compound, the concentration difference, $\Delta C$, in Pt$_2$Si and PtSi was also too small to be detected in this experiment. Division by $\Delta C$ is indispensable for calculating the interdiffusion coefficient, so $D$ could not be calculated. Therefore, $\Delta C \cdot D$ instead of $D$ has been determined with the aid of the Heunemann's equation(19). Using previous data on the phase growth rates, $k$, of Pt$_2$Si and PtSi formed in the thin samples, $\Delta C \cdot D$ for Pt$_2$Si has also been determined by assuming that only Pt$_2$Si is formed between pure Pt and pure Si in the thin film couples. The temperature dependence of $\Delta C \cdot D$ for the bulk and thin film samples thus determined are shown in Fig. 8. The present values of $\Delta C \cdot D$ are represented by a linear line and agree well with the minimum values of $\Delta C \cdot D$ for the thin film diffusion couples.

It has been often reported(7)-(9),(11)-(13) that the formation of PtSi starts after the consumption of all pure Pt during the heating and the condition of a semi-infinite solid diffusion couple does not valid. However it has also been well known that even after the consumption of pure Pt, PtSi grows satisfying the parabolic law(8)-(9),(11)-(13). From the result it is suggested that the Pt/Si diffusion couple can be regarded as Pt$_2$Si/Si diffusion couples after the consumption of pure Pt. On this assumption of Pt$_2$Si/Si diffusion couple, $\Delta C \cdot D$ of PtSi in thin film diffusion couple was calculated.

The temperature dependence of $\Delta C \cdot D$ of PtSi for the bulk and thin film diffusion couples is shown in Fig. 9. $\Delta C \cdot D$ for the bulk sample coincides well with the minimum values of those for the thin samples contrary to those reported by Crider et al.(15)

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7 It should be noted that $D$ used here differ, in general, from the so-called diffusivity in the previous papers, for example, Ref. (7). In which the growth rate $k$ in m$^2$/s has been used as the interdiffusion coefficient.

Although $k$ depends on the kind of diffusion couples, interdiffusion coefficient does not depend on it, in general.
IV. Discussion

As shown in Figs. 8 and 9, the extrapolated values of $\Delta C \cdot \bar{D}$ of Pt$_2$Si as well as PtSi formed in the bulk diffusion couples almost coincide with the minimum values of those for the thin film diffusion couples but smaller than those obtained by Crider et al. Because the maximum values of $k$ for Pt$_2$Si and PtSi were obtained at a higher ultra high vacuum atmosphere over more than $10^{-7}$ Pa by Crider et al. than less than $10^{-5}$ Pa by the other workers, in other words, the present data agree well with the values obtained at a less evacuated atmosphere but disagree with those at a highly evacuated atmosphere.

According to the previous studies of thin film Pt/bulk Si diffusion couples the presence of oxygen slows down the growth rates of Pt$_2$Si and PtSi and the effect of oxygen has been considered as follows\cite{79McGill, 82McGill}. During the silicide formation, oxygen originally contained in the Pt thin film segregates at the Pt$_2$Si/Pt interface. This accumulation acts as a barrier for the transport of Pt\cite{80Cory}. Because the anneal in this experiment was carried out at a pressure about $1 \times 10^{-3}$ Pa while the thin film diffusion experiments were done at a pressure more than $10^{-5}$ Pa, there is a possibility that the oxygen in the atmosphere diffuses into a welded interface at the initial stage of diffusion anneal or into bulk specimen during the anneal and slows down the growth rates of Pt$_2$Si and PtSi.

To study the effects of annealing atmosphere as well as oxygen on the value of $\Delta C \cdot \bar{D}$, some diffusion couples which were made in the same manner as described previously were annealed in an evacuated furnace equipped with a turbo-molecular pump (Osaka Vacuum: ST160VA-1A) at a pressure of about $10^{-5}$ Pa at 673, 873, 923 K. For example, the relationship between width of diffusion layers and square root of anneal time at 873 K is shown in Fig. 10 in comparison with that for the couples annealed at $10^{-3}$ Pa. As shown in Fig. 10, any obvious difference in width between PtSi and Pt$_2$Si for the couples annealed in the two different atmospheres could not be found. Similar results were also obtained at 673 and 923 K. So, we cannot attribute the difference between the values of $\Delta C \cdot \bar{D}$ of Pt silicides formed in the bulk and thin samples to the presence of oxygen or the difference of the annealing atmosphere. However, the effects of oxygen should be further examined because the degree of order of the pressure of this experiment is less than $10^{-7}$ Pa and because in the pure Pt bulk specimen some extent

Fig. 8 Temperature dependence of $\Delta C \cdot \bar{D}$ for Pt$_2$Si formed in bulk and thin film diffusion couples.

Fig. 9 Temperature dependence of $\Delta C \cdot \bar{D}$ for PtSi formed in bulk and thin film diffusion couples.

Fig. 10 A comparison of the widths of silicide layers formed in diffusion couples annealed at 873 K at a pressure $10^{-5}$ Pa with those at a pressure $10^{-2}$ Pa.
of oxygen may be contained and slow down the growth rate.

Although any clear evidence for the existence of the effect due to oxygen on the growth rate of Pt silicides in the bulk diffusion couple could not be found in this experiment, the fact that the values of $\Delta C \cdot \hat{D}$ for the bulk diffusion couple agree well with the values of $\Delta C \cdot \hat{D}$ for the thin film diffusion couple annealed in the less evacuated atmosphere supports partially our previous result on reactive diffusion of the Ni–Si system that any apparent difference between the diffusion phenomena in the bulk and thin film diffusion couples could not be found.

V. Summary

Reactive diffusion of the Pt–Si system has been studied by using bulk Pt/bulk Si single crystal diffusion couples in the temperature range from 673 to 923 K at an evacuated atmosphere of $10^{-2}$ Pa. To study the influence of the atmosphere on the growth rate of the diffusion layers, some diffusion couples have been annealed at 673, 873 and 923 K at a pressure $10^{-5}$ Pa. The experimental results were compared with the previous results obtained by using Pt thin film/bulk Si diffusion couples. The results of this work are summarized as follows,

1. In the bulk Pt/Si couples annealed at 673 K for more than 3.6 ks, Pt5Si and PtSi are found. The silicides Pt2Si, Pt3Si and Pt5Si are formed above 723 K. All of them grow satisfying the parabolic law.

2. The Arrhenius type plot of phase growth rate $k$ for the Pt5Si phase layer shows a bending. This can be attributed to a difference of the phases which adjacent to the Pt5Si phase.

3. The phase growth rate $k$ obtained by this experiment does not depend on the atmosphere in a pressure range $10^{-3}$ to $10^{-2}$ Pa.

4. The Arrhenius plots of $\Delta C \cdot \hat{D}$ for Pt5Si and PtSi formed in the bulk diffusion couples are represented by a linear line, respectively, and the extrapolated values of $\Delta C \cdot \hat{D}$ agree well with the minimum values for those of Pt5Si and PtSi phases formed in thin film diffusion couples which were annealed in a less evacuated atmosphere.

The agreement between the values of $\Delta C \cdot \hat{D}$ for bulk diffusion couple and the minimum values for the thin film diffusion couple supports our previous result on reactive diffusion in the Ni–Si system that any apparent difference between the diffusion phenomena in the bulk and thin film diffusion couples could not be found.

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