

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 42, NO. 2, 1972

PHYSICO-CHEMICAL STUDIES OF PLATINUM-SILICON INTERFACES*

BY DAIZABURO SHINODA

Identifications of microscopic compositions in alloyed layers of heat-treated Pt-Si contacts and analysis of chemical kinetics of solid-solid reactions between Pt and Si have been carried out. The layer structure of the Pt-Si contact sequentially changes, through Pt-Pt₂Si-Si, Pt-Pt₂Si-PtSi-Si and Pt₂Si-PtSi-Si, into PtSi-Si during heat treatment at temperatures ranging from 200°C to 700°C. The grown PtSi layer has the preferred crystallographic orientation in the [001] direction. The rate-determining process of the solid-solid reaction in the Pt-Si contact is the diffusion process of Si into Pt and/or platinum silicides. The rate constants are well represented by the following Arrhenius relationships: $k_{\text{Pt}_2\text{Si}} = 1.5 \times 10^{-3} \exp(-24100/RT) \text{ cm}^2/\text{sec}$ and $k_{\text{PtSi}} = 2.5 \times 10^{-1} \exp(-33900/RT) \text{ cm}^2/\text{sec}$.

Introduction

The electrical properties of Pt-Si contacts have been extensively investigated because of their usefulness in device applications to ohmic and Schottky barrier contacts¹⁻³). Therefore, interest in the crystallography and kinetics of compound formation between Pt films and bulk Si has been greatly stimulated.

The constitution and structure of Pt-Si binary alloys prepared by melting and sintering have been studied in detail by Gohle and Schubert⁴). It was shown that there were at least five compounds in the Pt-Si system, e.g., Pt₃Si, Pt₇Si₃, Pt₂Si, Pt₆Si₅ and PtSi. It has been first reported by Lepselter¹) that Pt films deposited onto Si react with Si at temperatures considerably below their eutectic points and platinum silicides are formed. Details of the crystallographic properties of the interfacial alloyed layer in sputtered Pt-Si contacts have been studied by Kawamura *et al.*⁵). They have found that Pt films sputtered onto Si wafers react with Si at temperatures above 600°C to form Pt₂Si and PtSi and that the interfacial PtSi layer has the preferred orientation characteristic of the temperature of heat treatment. Recently, the low temperature migration of Si into sputtered Pt films and the formation of a Pt₂Si-like compound at 350°C has been confirmed, using the backscattering method, by Hiraki *et al.*⁶). Electron

(Received November 17, 1972)

* A part of this paper was published in *J. Appl. Phys.*, **43**, 2913 (1972)

1) M. P. Lepselter, *Bell System Tech. J.*, **45**, 233 (1966)

2) D. Kahng and M. P. Lepselter, *ibid.*, **44**, 1525 (1965)

3) M. P. Lepselter and J. M. Andrews, "Ohmic Contacts to Semiconductors", p. 159, ed. by B. Schwartz, The Electrochemical Society, New York (1969)

4) R. Gohle and K. Schubert, *Z. Metallk.*, **55**, 503 (1964)

5) T. Kawamura, D. Shinoda and H. Muta, *Appl. Phys. Letters*, **11**, 101 (1967)

6) A. Hiraki, M. A. Nicolet and J. W. Mayer, *ibid.*, **18**, 178 (1971)

transmission observations in evaporated Pt-Si systems have been carried out to identify phases formed during heat treatment by Drobek *et al.*⁷⁾ They showed that the Pt₃Si compound formed initially, followed by the formation of Pt₂Si and PtSi. However, little work on reaction kinetics of Pt-Si contacts has been reported.

The purpose of the present investigation is to identify the compound phases formed by heat treatment of Pt-Si contacts, to determine the layer structure of the alloyed phase and to elucidate kinetics of solid-solid reactions in Pt-Si systems.

Experimental

Sample preparation

Pt-Si contacts were prepared as follows. Pt films, ranging from 800 to 10,000 Å in thickness, were vacuum deposited onto the (111), (110) and (100) surfaces of Si wafers through an oxide window by electron beam evaporation under a pressure less than 2×10^{-7} torr. The Si wafers used were *n*-type having a resistivity of 0.5 Ω·cm. Immediately before loading into the vacuum system for deposition, the Si wafers were cleaned in boiling HNO₃, etched in a diluted HF solution for 20 sec, rinsed in flowing deionized water and blown dry. The substrates were not intentionally heated during evaporation. The Pt-Si contacts were subjected to heat treatment over the temperature range from 200°C to 700°C in a hydrogen atmosphere. The duration of heat treatment was varied from 20 sec to 2 hr. The heat treatment process is as follows. A sample holder made of quartz was first placed at a high temperature zone in a furnace. After the holder was heated up, it was pulled out to the end of the furnace. When the temperature of the holder cooled down to a predetermined temperature, the sample was immediately placed on it with the Pt side down and was inserted into the high temperature zone so that the sample was heated up as early as possible. After heat treatment, the sample was quenched to room temperature.

X-ray diffraction and microscopic analysis

X-ray diffraction analysis was made as follows. Each of the heat-treated samples was mounted on a rotating sample holder or a flat plate sample holder of an X-ray diffractometer. The sample was irradiated with Ni-filtered CuK_α radiation from the side of Pt. The scanning region was chosen from 20° to 90° in 2θ . X-ray precession photographs were taken of the sample heat-treated at 400°C for 30 min. In this case, the sample was thinned to less than 20 μm in thickness by etching from the Si substrate side and then irradiated with unfiltered MoK radiation with a precession angle of $\mu=20^\circ$. The precession axes are parallel to and perpendicular to the surface of the Si substrate. Microscopic analysis of the alloyed layer was carried out using an electron probe microanalyser. In this case, the sample was beveled at an angle of about 1°. The about 1.0 μm diameter electron beam was irradiated at an angle of about 30° with the surface. The direction of the electron beam was held parallel to the interfacial alloyed layer.

7) J. Drobek, R. C. Sun and T. C. Tisone, *Phys. Stat. Sol. (a)*, **8**, 243 (1971)

Measurement of reaction rate

The samples for the measurements of the growth rate of the alloyed layer were also beveled at an angle of 1°, as shown in Fig. 1. Films of Cr and Au were used to protect the edge of the beveled plane. In order to clarify the phase boundary of the alloyed layer, the beveled samples were dipped in a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{HF} + \text{H}_2\text{O}$ solution⁸⁾ for copper decoration. The thickness of the alloyed layer was measured within an accuracy of $\pm 5\%$ by comparison with the thickness of the SiO_2 film which was previously measured by the interferometric method.

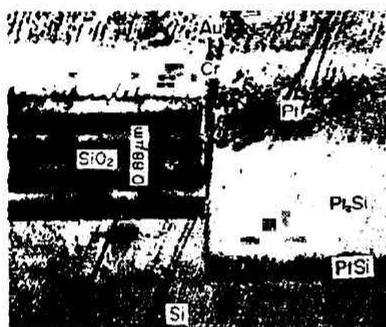


Fig. 1 Beveled plane of a Pt-Si contact heat-treated at 300°C for 2 hr

Results

Identification of the alloyed layer

A typical example of X-ray diffraction patterns for Pt-Si contacts heat-treated at 350°C are shown in Fig. 2, except for the diffraction lines of the (111) Si substrate. As-deposited samples show only Pt

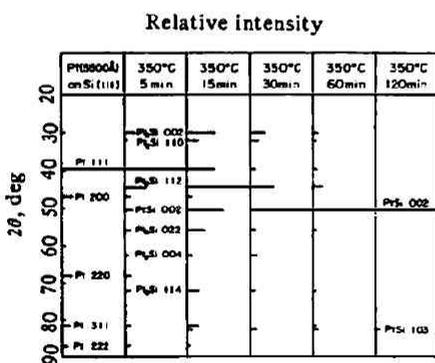


Fig. 2 X-ray diffraction spectra for Pt-Si contacts heat-treated at 350°C. All the intensities of the spectra are expressed relative to the maximum intensity of each sample

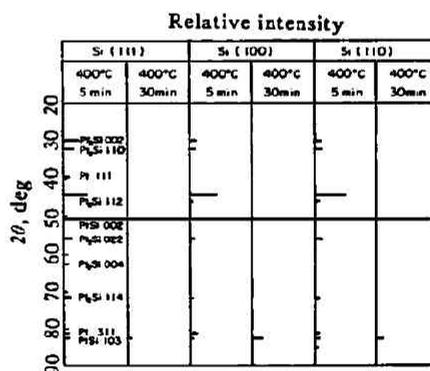


Fig. 3 X-ray diffraction spectra for Pt-Si contacts with various crystallographic orientations of Si substrates. Heat treatment was made at 400°C for 5 and 30 min

8) D. R. Turner, *J. Electrochem. Soc.*, **106**, 701 (1959)

diffraction lines. In the sample heat-treated for 5 min, the diffraction lines corresponding to Pt_2Si and PtSi are observed in addition to those of Pt. No diffraction lines corresponding to Pt_3Si are observed. It is worth noting that the observed intensities of the diffraction lines of Pt_2Si are nearly in proportion to calculated values, except for the overlapping diffraction lines with PtSi , while the intensity distribution of PtSi is very different from the calculated values⁹⁾. In the samples heat-treated for 2 hr or more, both the diffraction lines of Pt and Pt_2Si disappear and only diffraction lines corresponding to 002 and 103 lines of PtSi remain. Variation of X-ray diffraction spectra with temperature of isochronal heat treatment for 5 min of Pt-Si contacts was also observed. The results are similar to those in the case of isothermal heat treatment at 350°C. Weak diffraction lines of Pt_2Si begin to be observed at 200°C. After heat treatment at a higher temperature, additional PtSi diffraction lines appear. The grown PtSi layer has the preferred crystallographic orientation. The characteristic orientation is the [001] direction, which is identical with that observed on the sputtered Pt-Si contacts heat-treated at 800°C for 30 min⁵⁾.

Fig. 3 shows the X-ray diffraction spectra of Pt-Si contacts having the different substrate orientations. Si wafers with (111), (110) and (100) surface orientations were used. As seen in Fig. 3, the diffraction spectra and the observed intensities of the diffraction lines are the same. This means that the preferred oriented growth of the interfacial PtSi layer does not depend on the substrate orientation.

Figs. 4 (a) and (b) show X-ray precession photographs taken of the Pt-Si contact heat-treated at 400°C for 30 min to confirm the distribution of the orientation growth. In this case, the (110) Si substrate was used. The weak fiber-like pattern in Fig. 4 (a) and the weak circular pattern in Fig. 4 (b) for PtSi were observed along with the strong reciprocal lattice pattern for the (110) Si substrate. Judging from Figs. 4 (a) and (b), PtSi crystallites do not have preferred orientation in the plane parallel to the (110) Si substrate, though the preferred oriented growth is marked in the direction perpendicular to the (110) Si substrate.

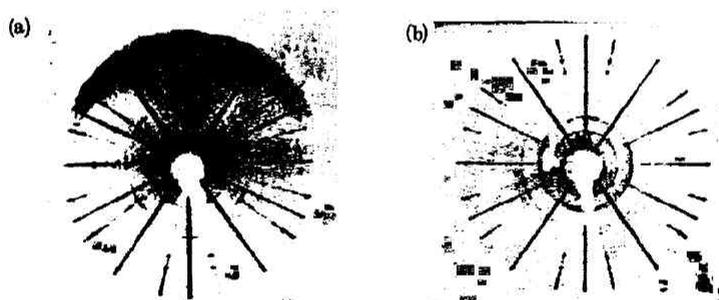


Fig. 4 Zero level X-ray precession photographs of PtSi treated at 400°C for 30 min, set with the precession axes (a) parallel to and (b) perpendicular to the (110) Si substrate

Figs. 5 (a) and (b) show the characteristic X-ray spectra obtained by an electron probe micro-analyser. Relative intensity of the characteristic X-ray peaks of Pt and Si for the alloyed layers were

9) H. Pfisterer and K. Schubert, *Z. Metallk.* **41**, 353 (1950)

compared with those for bulk Pt_2Si and $PtSi$, prepared by melting the constituent elements in a hydrogen atmosphere. This result reveals that the intermetallic compound grown near Pt is Pt_2Si and that grown near Si is $PtSi$.

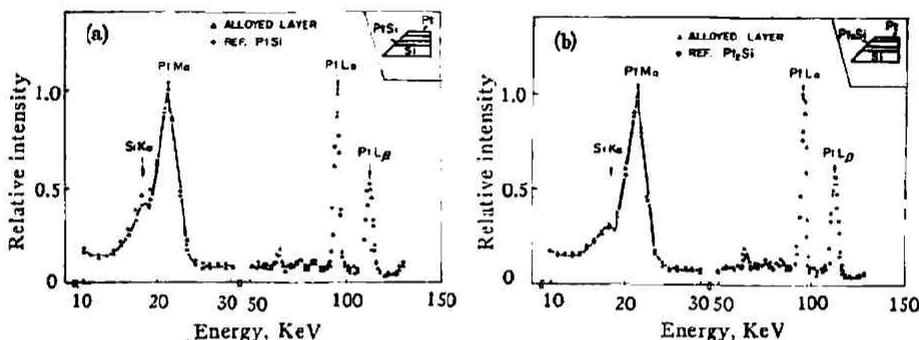


Fig. 5 Characteristic X-ray spectra obtained by an electron probe microanalyser for (a) the alloyed layer near the Si substrats and (b) that near the surface

X-ray diffraction analysis and microscopic observation lead to the following results. (1) Platinum silicides are formed by solid-solid reactions at temperatures far below their eutectic points. (2) The Pt_2Si phase is first grown at the interface between Pt and Si and then the $PtSi$ phase is grown after heat treatment for a longer period and/or at a higher temperature. (3) The grown $PtSi$ layer has the preferred crystallographic orientation. (4) It is probable that the Pt-Si contact changes sequentially through Pt- Pt_2Si -Si and Pt- Pt_2Si - $PtSi$ -Si to Pt_2Si - $PtSi$ -Si, and finally the $PtSi$ -Si contact is formed by heat treatment. (5) The crystallographic properties of the alloyed layers do not depend on the surface orientation of the Si substrate.

Growth kinetics

Figs. 6 (a) and (b) are the plots of the thickness of the alloyed layer as a function of the square root of the alloying time for different temperature ranging from 200°C to 550°C. The growth rates of the platinum silicide layers closely follow the parabolic rate law. This means that the growth rate is controlled by interdiffusion of Pt and Si, obeying the following equation:

$$X^2 = kt, \quad (1)$$

where X is the layer thickness, t is the time for heat treatment and k is the rate constant. The slopes of these curves yield the rate constants k as given in Eq. (1). In Fig. 7, the logarithmic values of the rate constants are plotted against the reciprocals of absolute temperatures of heat treatment. The rate constant are adequately fitted by Arrhenius relationships, as follows:

$$k_{Pt_2Si} = 1.5 \times 10^{-3} \exp(-24000/RT) \text{ cm}^2/\text{sec}, \quad (2)$$

$$k_{PtSi} = 2.5 \times 10^{-1} \exp(-33900/RT) \text{ cm}^2/\text{sec}. \quad (3)$$

These relationships are valid over the temperature range from 200°C to 700°C, when the supply of Pt is sufficient.

Fig. 8 is a plot of the thickness of the alloyed layer as a function of the initial thickness of the Pt film. This result reveals that, when Pt is depleted after heat treatment, the thickness of the alloyed layer approaches a constant value at a high temperature where only the 002 diffraction line of PtSi is observed. The saturated value of the layer thickness is linearly proportional to the initial thickness of the Pt film, as shown in Fig. 9. The proportional constant is about 1.97, which is in agreement with

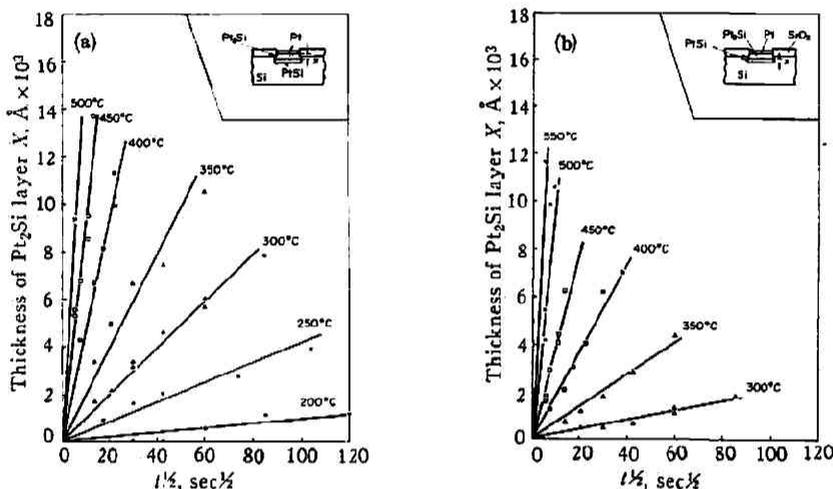


Fig. 6 Thickness of the intermetallic layer X as a function of the square root of alloying time at different temperatures. (a) is for Pt_2Si and (b) is for $PtSi$

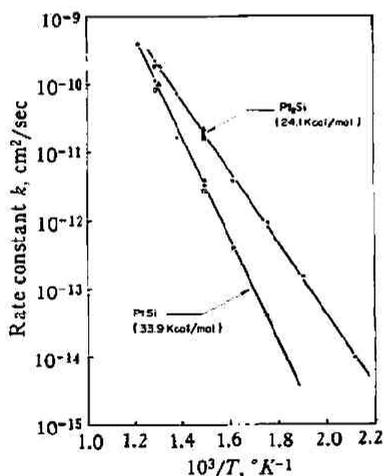


Fig. 7 Arrhenius plot for the rate constant k for Pt_2Si and $PtSi$

- : Si(111)
- △▲: Si(110)
- : Si(100)

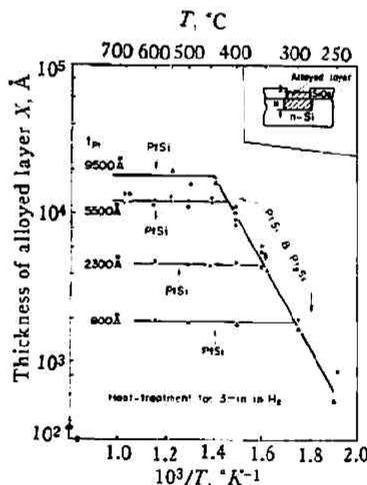


Fig. 8 Variation of the thickness of the alloyed layer with the temperature of isochronal heat treatment for Pt-Si contacts having various Pt film thicknesses

the value deduced from the lattice constant of PtSi⁹⁾, assuming the preferential growth oriented in the [001] direction.

The effect of the crystallographic orientation of the Si substrate on the growth kinetics of the interfacial platinum silicide layer was also studied. The rate constants are plotted in Fig. 7. No substantial difference in the rate constant of the solid-solid reaction is observed on the Pt-Si contacts having three different substrate orientation.

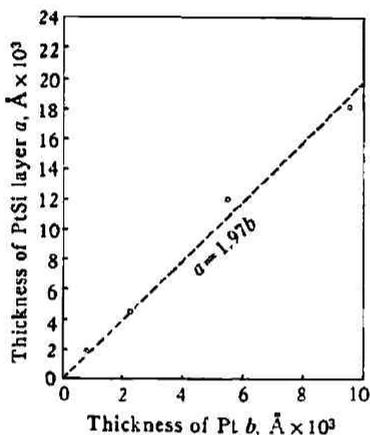


Fig. 9 Final thickness of the PtSi layer as a function of the initial thickness of the Pt film

Experimental results show that (1) growth kinetics observed in the formation of interfacial Pt₂Si and PtSi layers obey a parabolic rate law, (2) the rate-determining step of the solid-solid reaction may be the interdiffusion process of Pt and Si, (3) the rate constants are well represented by the Arrhenius relationship and (4) no dependence of the growth kinetics on the substrate orientation are observed.

Discussion

Existence of a compound phase in solid-solid reactions

There are at least five compounds in the Pt-Si system¹⁰⁾, as shown in Fig. 10. However, only two compounds are identified in this work *e.g.* Pt₂Si and PtSi. As shown by Kidson¹⁰⁾, the existence of a compound phase in the equilibrium phase diagram of two pure elements is a necessary but not sufficient condition for the formation of a compound in a diffusion couple of the pure components. The kinetics of the diffusion process may be such that not all compounds may form. Generally, the existence of a compound is related in a complex way to the diffusion coefficient, concentrations of components as well as the solubility range and the miscibility gaps. Therefore, it is very difficult to deduce the existing phases in the heat-treated Pt-Si contact because the related diffusion data are not available. Other workers⁷⁾ have reported the presence of Pt₃Si in *as-deposited* samples on *n*-type (100) Si. In this work,

10) G. V. Kidson, *J. Nucl. Mater.*, **3**, 21 (1961)

11) F. A. Shunk, "Constitution of Binary Alloys, Second supplement", p. 624, McGraw-Hill Co., New York (1966)

the Pt_3Si phase cannot be detected. It may probably be that, if the Pt_3Si phase is grown at the first stage of heat treatment, its layer is very thin so that it cannot be detected by X-ray diffraction analysis.

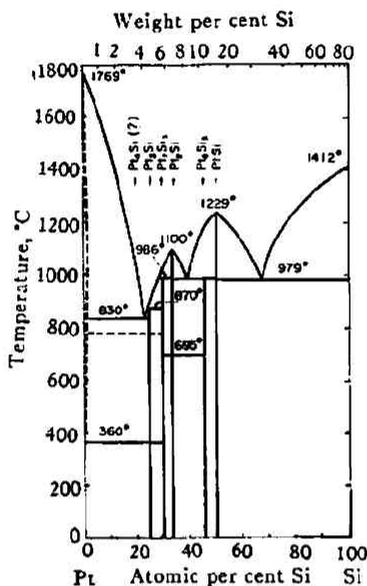


Fig. 10. Equilibrium phase diagram of the Pt-Si system

On growth kinetics

The general factors governing the kinetic laws for solid-solid reactions are (1) the rates of diffusion of reactants, (2) chemical reactions at phase boundaries and (3) the rates of nucleation and recrystallization. The form of the over-all kinetic law will depend on the relative rates of these processes. However, one process will be frequently rate-controlling. As described previously, the growth kinetics of solid-solid reactions in Pt-Si system obey a parabolic rate law. This means that the rate-controlling process of the formation of Pt_2Si and PtSi phases is an interdiffusion process. Recently, growth kinetics of metal silicides formed from thin films of Pd, Ti, Cr and Mo evaporated onto Si wafers have been investigated using the backscattering method by Bower and Mayer¹²⁾. They have found that the thickness of the silicide phase increases with the square root of time for Pd_2Si and TiSi_2 and linearly with time for CrSi_2 and MoSi_2 . The time dependence of the growth rate is accounted for as follows. In the case of Pd-Si and Ti-Si systems, the growth rate is governed by the diffusion process of components and conversely, linear growth of the CrSi_2 and MoSi_2 is associated with a reaction rate limitation. It is reasonable that solid-solid reactions in Pt-Si and Pd-Si systems show similar behaviors because equilibrium phase diagrams of both systems^{11,13)} are the same type and reactivity of these metals against Si is equal grade. Hiraki and Lugujo¹⁴⁾ have found that the low temperature migration of Si atoms into Pt and other metals is limited by the Si dislodgment at the Si-metal interface and that cry-

12) R. W. Bower and J. W. Mayer, *Appl. Phys. Letters*, **20**, 359 (1972)

13) R. P. Elliott, "Constitution of Binary Alloys, First supplement", p. 731, McGraw-Hill Co., New York (1965)

14) A. Hiraki and E. Lugujo, "Proc. of 5th International Vacuum Congress at Boston", Oct. 1971

stallographic orientation of Si substrate has an obvious influence upon the migration of Si atoms. In this work, no effect of the Si substrate orientation on the growth rate of the Pt₂Si and PtSi phases was observed. This means the rate-limiting process for the formation of Pt₂Si and PtSi is the volume diffusion process and not the dislodgment of Si atoms.

Oriented growth of the PtSi layer

It is interesting that the grown PtSi layer has the preferred crystallographic orientation in the [001] direction. Similar oriented growth was observed in the Pt-Si contacts prepared by low energy sputtering⁶⁾. In the case of the sputtered Pt-Si contact with the (111) Si substrate, the characteristic orientation varies from [101] at 600°C and 700°C, through [121] at 750°C, to [001] at 800°C. However, in this experiment, variation of the growth orientation of PtSi layer with annealing temperature was not observed. Recently, Sinha *et al.*¹⁵⁾ have found that the preferred orientation of the PtSi layer depends on thickness of Pt, surface orientation of Si substrate, as well as thermal history of the sample. However, no effect of substrate orientation is observed in this work, as shown in Fig. 3. The reason for this difference is not clear, but the difference of surface contaminants and/or intervening layer of oxide may be responsible for the wide variation in the type of the preferred orientation of PtSi.

Acknowledgment

The author wishes to express his sincere thanks to Prof. J. Osugi for valuable guidance. The author is indebted to Dr. S. Asanabe for his encouragement and to Dr. T. Kawamura and H. Muta for their helpful discussion and experimental work.

*Central Research Laboratories
Nippon Electric Company Ltd.
Kawasaki, Japan*

15) A. K. Sinha, R. B. Marcus, T. T. Sheng and S. E. Haszko, *J. Appl. Phys.*, **43**, 3637 (1972)