An inert marker study for palladium silicide formation: Si moves in polycrystalline Pd_2Si

K. T. Ho, C.-D. Lien, U. Shreter,[a] and M-A. Nicolet
California Institute of Technology, Pasadena, California 91125

(Received 13 June 1984; accepted for publication 1 August 1984)

A novel use of Ti marker is introduced to investigate the moving species during Pd_2Si formation on ⟨111⟩ and ⟨100⟩ Si substrates. Silicide formed from amorphous Si is also studied using a W marker. Although these markers are observed to alter the silicide formation in the initial stage, the moving species can be identified once a normal growth rate is resumed. It is found that Si is the dominant moving species for all three types of Si crystallinity. However, Pd will participate in mass transport when Si motion becomes obstructed.

I. INTRODUCTION

Pd_2Si is one of the most extensively studied metal silicides, both because of its viability as an integrated circuit contact material, due to palladium's dissolving power for surface oxides,[1] and its various unique characteristics. Pd_2Si has a low formation temperature, but is stable up to ~ 750 °C (Ref. 2). Of the many metal silicides which grow epitaxially on crystalline Si substrates, only Pd_2Si occurs as the first phase.[3–5] Reports on properties of Pd_2Si such as the epitaxial quality,[6] electrical properties,[7] formation kinetics and mechanism,[2,6] and impurity effects[8] are abundant in literature.

One uncertainty about Pd_2Si which still remains is the identity of the moving species responsible for the growth. The identity of the dominant moving species is relevant for processing considerations such as lateral silicide growth from contact windows,[9,10] smoothness of silicide silicon interface, and generic trends in silicide oxidation rates that are associated with the moving species.[11] Two earlier works by Chu *et al.*[12] and Pretorius *et al.*[13] reported that both Pd and Si move during Pd_2Si formation from a Pd film on single-crystalline Si. However, it was recently pointed out by Scott and Nicolet that a reinterpretation of the experimental data from the above two references is possible and that an agreement can be reached with their new result that Si is actually the dominant moving species.[8] Other works have contained information on the moving species. Föll and Ho[14] concluded that both elements move based on the incorporation of interfacial oxides within the final silicide layer. However, Scott *et al.*[1] proposed that Pd motion is involved only during the initial oxide reducing process. The dissolved oxide layer is then incorporated in the silicide during the subsequent Si motion, which gives a final appearance of two species moving simultaneously. Cheung *et al.*[6] suggested that the interfacial voids observed at the Pd/silicide interface may be due to a predominant motion of Pd. They further suggested that moving species may differ for silicides formed from ⟨111⟩, ⟨100⟩ Si substrates, and amorphous Si. More recently, Lien *et al.*[15] using an epitaxial structure concluded that Pd is the moving species. The same authors, in another study,[16] repeated the interfacial oxide marker experiment, and found that both species move in the unirradiated sample, but only Si moves after breaking up the interfacial oxide by Si irradiation. These previous results along with the results to be explained from this study in the following text are summarized in Table I. The structure of the Pd_2Si layer grown on ⟨111⟩ Si is reported to be polycrystalline or to be poorly epitaxial in every case here, which is different from the case reported in Lien *et al.*[15] work. This fact will be important for the discussions at the end of the paper. The variation in opinions from previous studies is evident and motivated the present marker investigation using substrates of different orientations and amorphous Si.

The concept of an inert marker has been demonstrated by Chu *et al.*[12] using the implanted noble gases Xe and Ar. van Gurp *et al.*[17] introduced an evaporated discontinuous W film as a marker which eliminates implantation damage to the sample lattice. We studied silicide formation from amorphous Si with the latter marker type. The sample configuration consisted of a W marker placed between the Pd film, which is evaporated on an oxidized Si substrate, and the top amorphous Si layer. This configuration is advantageous for analysis by backscattering spectrometry, because the backscattering signal of the heavier W will not interfere with the signal of the lighter Pd. However, to form a silicide from a single crystalline Si, Pd must be evaporated on top of the Si substrate and the marker, which produces an interference between the signals of the Pd film and the W marker. A lighter element Ti is therefore used in place of the W. Since Ti has a smaller backscattering cross section, a thicker layer is desirable which, however, goes against the criterion that a marker should not interfere with the silicide formation.

II. EXPERIMENTAL PROCEDURES

Samples were *e*-gun evaporated in an oil-free high-vacuum system pumped to a pressure of 3×10^{-6} Torr. For silicide formation on ⟨111⟩ and ⟨100⟩ Si substrates, Pd films were deposited simultaneously by loading half wafers of each orientation side by side. The cleaning procedures for oxidized Si substrates consisted of ultrasonic cleaning in trichloroethylene, acetone, and methanol. The ⟨111⟩ and ⟨100⟩ Si wafers had, in addition to the above, an etch in 20% HF, followed by an RCA solution etch (H_2O_2 : NH_4OH : H_2O in the ratio 1 : 1 : 5), and finally another etch in 6% HF. A sequence of evaporations in the order $\sim$20-Å Pd, $\sim$10-Å Ti, $\sim$20-Å Si, and finally 1550-Å Pd was then carried out with a background pressure of 4×10^{-7} Torr during evaporation. The Pd evaporation rate was $\sim$20 Å/s. The purpose of the sandwich layers next to the marker is to

[a] Present address: Yokneam 20600, Israel.

 0021-8979/85/020227-05$02.40 © 1985 American Institute of Physics

Downloaded 22 Dec 2005 to 131.215.225.9. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

TABLE I. Results of previous studies.

Authors	Ref. No.	Marker	Initial location of marker	Year	Si type	Identification
W. K. Chu *et al.*	12	Argon	in Si	1975		Both
R. Pretorius *et al.*	13	^{31}Si	Top layer of Si	1978	⟨100⟩	Both
N. Cheung *et al.*	6	Kirkendall voids	at Pd/Pd_2Si and Pd_2Si/Si interfaces	1979	⟨111⟩ ⟨100⟩ *a*-Si[a]	Both Pd Pd
H. Föll *et al.*	14	Interfacial oxide	at Pd/Si interface	1981	⟨111⟩	Both
D. M. Scott *et al.*	8	oxygen	in Pd	1983	⟨100⟩	Si
C.-D. Lien *et al.*	15	Epitaxial structure	Pd_2Si	1984	⟨111⟩	Pd[a]
C.-D. Lien *et al.*	16	Interfacial oxide	at Pd_2Si interface	1984	⟨111⟩	no. i.i.[b] Both with i.i.[c] Si
K. T. Ho *et al.*	This work	W, Ti	in Pd_2Si	1984 ⟨100⟩	⟨111⟩ *a*-Si[a]	Si(Pd)

[a] Epitaxial Pd_2Si structure.
[b] No ion irradiation.
[c] With ion irradiation.

cause it to be incorporated into the silicide layer during the initial stage of annealing and thereby minimizing the possibility of interfacial dragging. The sample with amorphous Si was evaporated in the reverse order on an oxidized Si wafer. Amorphous Si of 970-Å thickness was evaporated on top of sandwich layers containing ~20-Å Pd, ~6-Å W and ~20-Å Si, which were evaporated on 1900-Å Pd. Annealing was carried out in a vacuum of 5×10^{-7} Torr. The annealing temperatures used were 250, 300, and 350 °C for samples with a W, a thin Ti, and a thick Ti marker, respectively. Silicide thicknesses were measured by 2-MeV $^4He^+$ backscattering spectrometry, with the detector set at an angle of 170° against the incident beam. No x-ray diffraction was performed to verify the silicide phase formed, since the formation of Pd_2Si has been extensively reported in the literature.[2,3,6] The ratio of the Pd and Si backscattering peak heights does confirm a stoichiometry consistent with that of Pd_2Si.

Silicide growth requires the mass flow of one or both elements across the marker, leaving a different amount of material in front of it. This is equivalent to having a cover layer of changing energy loss, and therefore produces a shift in the position of the marker signal in the backscattering spectrum.

III. RESULTS AND DISCUSSION

The spectra of the Pd/⟨111⟩ Si sample before and after annealing at 300 °C for 7 min are shown in Fig. 1(a). Some spreading of the marker signal occurred during the silicide growth. The spreading is not strictly consistent with the notion of an inert marker. However, if the spread is symmetrical and small, the peak of the distribution still fulfills the function of an inert marker. The marker shift ΔE is taken to be the amount by which the center of the marker peak has moved. Since two sample configurations are studied, we must adopt a sign convention for ΔE that is consistently used, irrespective of the sample configuration being referred to. In the following discussion, a ΔE value which designates dominant Si motion will be taken as positive. By this conven-

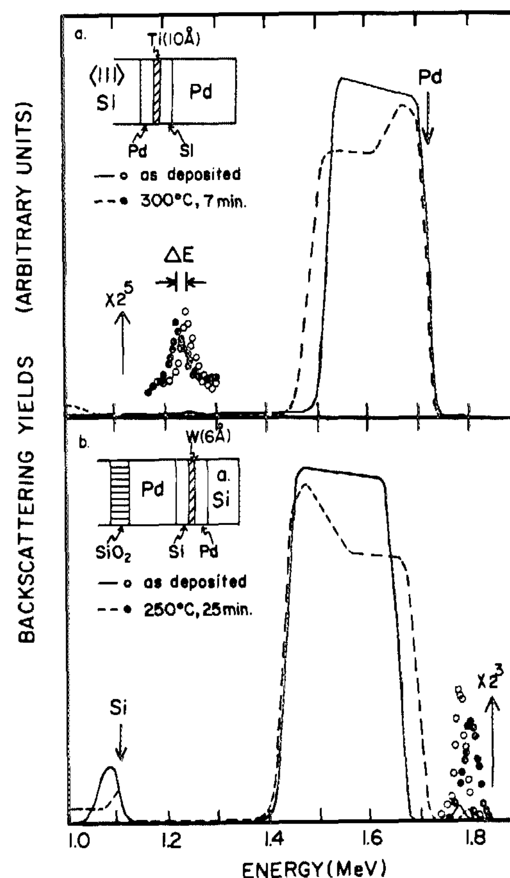


FIG. 1. (a) Pd_2Si formation from a ⟨111⟩ Si substrate, with ~10-Å Ti marker embedded in sandwiched layers of ~20-Å Pd and ~20-Å Si. A marker shift can be measured from the relocation of the Ti peak before and after annealing at 300 °C for 7 min. (b) Pd_2Si formation from amorphous Si is studied with a ~6-Å W marker. RBS spectra show a broadening of the W signal as well as a shift in its peak position, after annealing at 250 °C for 25 min.

Downloaded 22 Dec 2005 to 131.215.225.9. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

tion, the Pd/⟨111⟩ Si sample shows a marker shift of + 9.4 keV after forming 1580 Å of Pd_2Si. The Pd/⟨100⟩ Si sample, whose spectra are not shown, has a Pd_2Si layer of 1440-Å thickness and a marker shift of + 11.3 keV after the same heat treatment. Figure 1(b) shows the spectra for the Pd/amorphous Si sample, which has a W marker, before and after annealing at 250 °C min. A ΔE value of + 22.5 keV is measured for a silicide thickness of 1830 Å.

In Figure 2(a), marker shifts for the three sample configurations are plotted as a function of the corresponding silicide thicknesses. The top and bottom solid lines are the calculated values for the two extreme cases of Si or Pd moving only, respectively. It is found that the data points can be

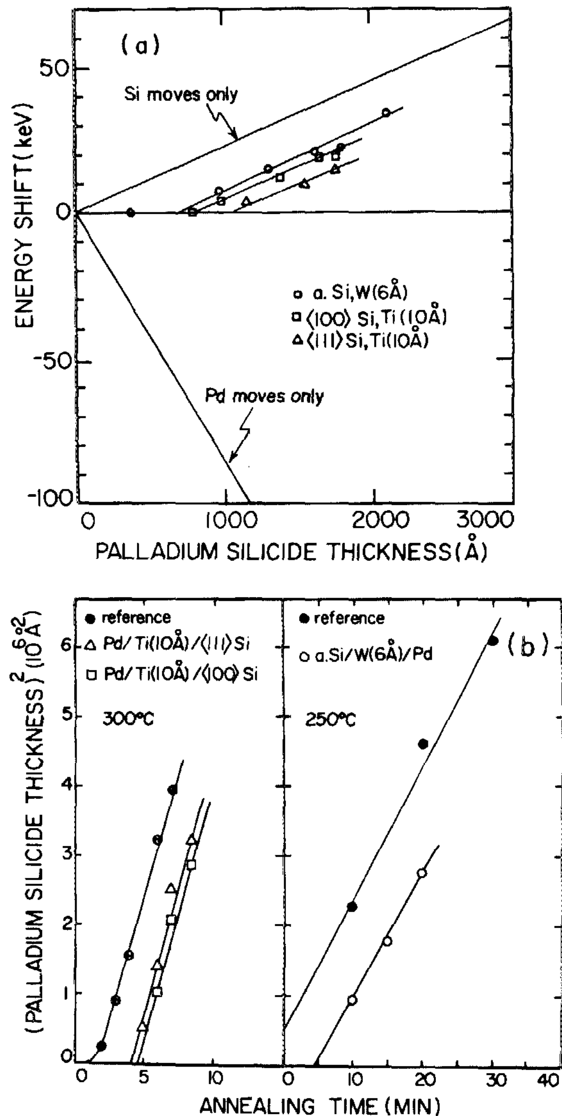


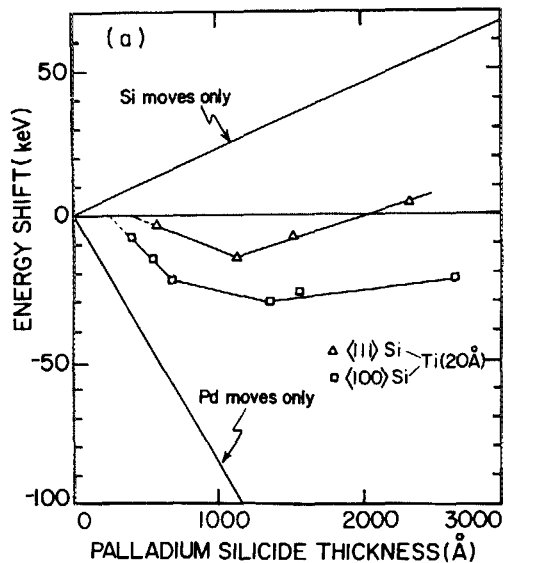
FIG. 2. (a) Energy shift of Ti and W markers plotted as a function of the silicide thicknesses in the respective samples. The top and bottom solid lines are determined from energy stopping calculations for the two extreme cases of only one species moving. By allowing for initial stages of zero marker motion, lines that correspond to the case where only Si moves can be fitted to the data points for all three types of Si crystallinity. The ⟨111⟩ and ⟨100⟩ samples have a Ti marker ~ 10 Å thick. The sample with amorphous Si has a W marker ~6 Å thick. (b) A comparison of Pd_2Si growth kinetics of samples with (open symbols) and without (full dots) markers shows that the growth rates are the same, but after an incubation period for samples with a marker. The initial suppression of interdiffusion and reaction is due to a barrier action associated with the marker.

fitted very well to lines which have the same slopes as the calculated solid line that assumes that only Si moves. However, these three lines do not have zero intercepts as observed in previous marker experiments.[12,16] For the Pd/⟨111⟩ sample, up to 1060 Å of silicide forms without producing a marker shift. To investigate this anomalous initial behavior, we plotted the growth kinetics of these samples and compared them to a reference sample which had no marker [see Fig. 2(b)]. In all cases the growth rates are the same, however, an incubation time is seen for samples with a marker layer, as has been reported by van Gurp *et al.*[17] This delayed reaction of Pd with Si was also reported by Bower and Mayer for Si with a thin surface oxide layer.[18] These facts suggest that a different growth mechanism prevails during the initial annealing period when a barrier action, apparently associated with the marker, must first be overcome. From a similar experiment involving a thin interfacial oxide, Scott *et al.*[1] proposed that Pd acts as the moving species during the penetration of the oxide barrier; Si assumes its natural role as the dominant moving species only after a uniform dissolution of the obstructive oxide by the growing silicide layer has occurred. Alternatively, when the oxide layer is first broken up by Si irradiation, as was carried out by Lien *et al.*[16] Si is identified as the moving species. We propose that, in our case, the presence of the marker layer only partially obstructs Si flow, such that both Pd and Si contribute to the mass transport, giving a negligible marker shift in the initial stage of silicide formation. Once a smooth transport of Si becomes possible, as indicated by the unhindered silicide growth rate, Si then becomes the dominant moving species.

To check this assumption, a second set of samples was prepared using a thicker marker of ~20-Å Ti. The annealing temperature was raised to 350 °C to facilitate breaking down of this thicker barrier. The marker shifts as a function of silicide thickness and the growth kinetics of the silicide for this set of samples are plotted in Figs. 3(a) and 3(b). An apparent dominance of Pd motion is indeed observed at the start of annealing; the corresponding growth kinetics are irregular and slow. With increasing silicide thickness, the growth rates accelerate toward that of the reference sample. Simultaneously, the marker shifts indicate a rising contribution of Si to the total mass transport. These results strongly support a dual moving species model for Pd_2Si growth. Silicon serves as the dominant moving species whenever its diffusion in the silicide layer is free of obstructing barriers (e.g., impurities and epitaxial structure). When a free Si diffusion becomes hindered, Pd participation in the mass transport will be activated. This dual moving species process can be recognized by an accompanying reduction in the silicide growth rate as compared to a sample in which Si diffusion is unobstructed. Qualitatively, the greater the participation of Pd motion, the greater will be the reduction in the silicide growth rate.

The capricious nature of Pd to participate in diffusion when Si traffic is impeded may explain much of the confusion which has clouded the past studies. In particular, a comparison should be made to the structural marker study of Lien *et al.*[15] in which it is found that Pd diffuses through an epitaxial Pd_2Si layer and supports the epitaxial growth of

Downloaded 22 Dec 2005 to 131.215.225.9. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp



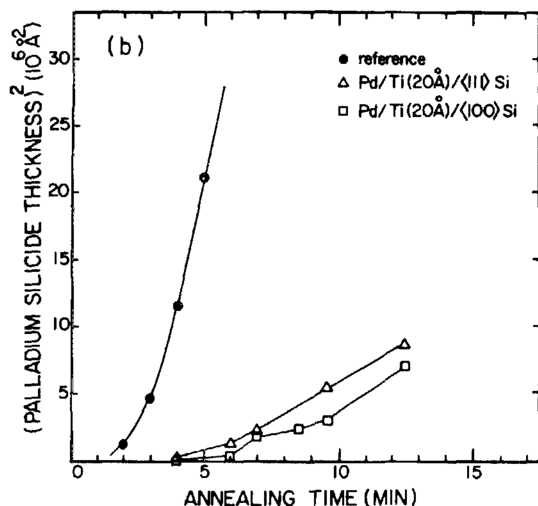


FIG. 3. (a) With a Ti marker ~20 Å thick, a complex diffusion behavior is observed. The initial silicide grows by an apparent dominance of Pd motion, which subsequently subsides in favor of a predominant Si motion, after a substantial Pd_2Si thickness is attained. (b) The time dependence of the Pd_2Si growth of samples with thick Ti markers demonstrate varying degree of retardation. The growth rates slowly approach that of the reference sample without a marker as the silicide layers thicken.

Pd_2Si on an ⟨111⟩ Si substrate. The dominance of Pd motion in that case can be justified by assuming that lattice diffusivity of Si in good quality epitaxial Pd_2Si is low and, therefore, Pd diffusion dominates. A good epitaxial quality of the Pd_2Si layer is verified by channeling. The silicide formed on our ⟨111⟩ substrates is expected to have poorer epitaxial quality than that formed (at 400 °C) by Lien *et al.*[15] because of the incorporation of impurities (Ti) and our lower annealing temperature (300 °C). Indeed, TEM studies have shown that our silicide film on the ⟨111⟩ substrate is composed of preferentially oriented polycrystallites with grain sizes ranging from 300 to 900 Å. The grain boundaries should serve very well as open channels for Si diffusion. Further verification of a poor epitaxial quality comes from channeling measurements. The channeled RBS signal of Pd in Pd_2Si showed no more than 2% decrease in yield, compared to the more than 15% decrease in the channeling yield of Lien *et al.*[15] Therefore, for our ⟨111⟩ samples, Si diffusion is not impeded and Si is the dominant moving species.

It is instructive to review the results listed in Table I in the light of the dual-moving-species model proposed here. Chu *et al.*[12] implanted $1\times10^{16}/cm^2$ Ar into Si as a marker. Although Ar surely behaves differently than those chemically active impurities (e.g., nitrogen) in bulk Si, it is possible, but not certain, that Ar can form a barrier to Si diffusion the way nitrogen does.[19] The result of the experiment then will indicate that both species move as was, in fact, reported. The actual initial position of the Ar marker, however, seems to be in doubt in that experiment.[8] Pretorius *et al.*[13] also concluded that Pd and Si both move, based on experiments with a radioactive ^{31}Si tracer. The annealings in their experiment were carried out at 400 °C, which is substantially higher than most other experiments and may not be a negligible factor. The substrate cleaning procedure is not reported in that paper and it is possible that an initial Pd motion was activated by impurities. Föll and Ho's interfacial oxide does not qualify as an inert marker according to the present view, and as was already pointed out by Scott *et al.*[1] The invalidity of the interfacial oxide as a marker is further confirmed by the results of Lien *et al.*[16], who found that the outcome differs with or without ion irradiation. The oxygen marker studies of Scott and Nicolet,[8] as well as the structure marker study of Lien *et al.*[15] support the dual-moving-species model explicitly. All these experimental studies are thus compatible with the notion of dual moving species. Only the result of Cheung *et al.* is difficult to reconcile with the present model. Their conclusion is based on the observation of interfacial voids in cross-sectional TEM micrographs that are interpreted as Kirkendall voids.[6] It would be very desirable to repeat some of these experiments with special attention given to the details of sample preparation, the Si configuration, and the annealing temperature that the dual-moving-species model dictates. In particular, that model predicts that the growth rate of epitaxial Pd_2Si on ⟨111⟩ Si should be significantly less than that of polycrystalline Pd_2Si on Si of a different structure. The results of Cheung *et al.* are in qualitative agreement with that prediction. The present investigation should also be repeated with other marker species, since the inert nature of any particular marker can never be firmly established.

When the dual-moving-species model is applied to a study of Pd_2Si formation in the presence of nitrogen implanted into Si, further confirmations are found. The N profiles before and after silicide formation are shown in Fig. 4. The horizontal axes are labeled in energy to aid the visualization of the relocation of the energy stopping medium. The signal heights are the normalized nuclear reaction yields; however, the vertical axes are also labeled in atomic percent of nitrogen in its respective matrices. Nitrogen becomes completely incorporated into Pd_2Si after a thermal treatment of 580 min at 230 °C and 10 h at 350 °C. The peak concentration increases over the original value and the profile width becomes correspondingly narrower. Another significant feature is the shift of the entire peak toward lower energy (deeper into the sample). The alteration of the profile shape can only come about by a greater loss of Si than the gain of Pd in the nitrogen-concentrated region (comparison is made with the quantity of each element weighted by its stopping cross-section factor). The peaking of the N profile suppresses the diffusion

Downloaded 22 Dec 2005 to 131.215.225.9. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

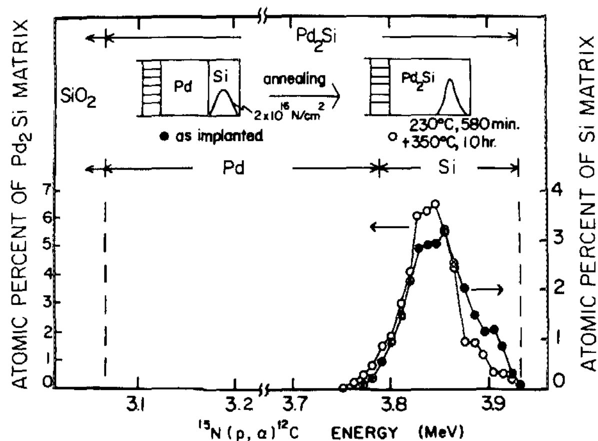


FIG. 4. The narrowing and shifting of the N peak implanted in Si can only be explained by a two-mode diffusion process. First, a predominant Si motion leads to narrowing of the N profile while maintaining its closeness to the sample surface. As the N concentration increases, the Si diffusion is inhibited. A second mode involving Pd diffusion is then activated which shifts the entire N profile deeper into the sample bulk.

of Si and initiates that of Pd, leading to a medium of greater stopping power in front of the N peak and thus the observed shift along the energy axis.

IV. CONCLUSION

We have shown that Si is the dominant moving species during the formation of Pd_2Si under a normal condition. The criterion for a normal condition is that the silicide layer is polycrystalline and the growth rate is the same as that of a reference sample without a marker. Pd diffusion participates in the mass transport when Si motion becomes obstructed (i.e., by an oxide or impurity layer, or an epitaxial silicide structure).

ACKNOWLEDGMENTS

The authors would like to acknowledge Ali Ghaffari for technical assistance. The implanter part of this study was financially supported by the U. S. Department of Energy through an agreement with the National Aeronautics and Space Administration and monitored by the Jet Propulsion Laboratory, California Institute of Technology (D. Burger).

[1]D. M. Scott, S. S. Lau, R. L. Pfeffer, R. A. Lux, J. Mikkelson, L. Wieluński, and M-A. Nicolet, *Thin Solid Films* **104**, 227 (1983).
[2]K. N. Tu and J. W. Mayer in *Thin Films—Interdiffusion and Reactions*, edited by J. M. Poate, K. N. Tu, and J. W. Mayer (Wiley, New York, 1978), p. 359.
[3]M-A. Nicolet and S. S. Lau in, *VLSI Electronics*, edited by N. G. Einspruch and G. B. Larrabee (Academic, New York, 1983), Vol. 6, Chap. 6, p. 329.
[4]R. T. Tung, J. M. Poate, J. C. Bean, J. M. Gibson, and D. C. Jacobson in *Proceedings of the Symposium on Thin Films and Interfaces*, edited by P. S. Ho and K. N. Tu (North-Holland, New York, 1982), p. 79.
[5]H. Ishiwara in *Proceedings of the Symposium on Thin Film Interfaces and Interactions*, Vol. 80-2, edited by J. E. E. Baglin and J. M. Poate (Electrochem. Soc., Princeton, New Jersey, 1980), p. 159.
[6]N. Cheung, S. S. Lau, M-A. Nicolet, and J. W. Mayer in *Proceedings of the Symposium on Thin Film Interfaces and Interactions*, Vol. 80-2, edited by J. E. E. Baglin and J. M. Poate (Electrochem. Soc., Princeton, 1980), p. 494.
[7]M. Wittmer, P. L. Smith, P. W. Lew, and M-A. Nicolet, Solid-State Electron. **21**, 573 (1978).
[8]D. M. Scott and M-A. Nicolet, Nucl. Instrum. Methods **209/210**, 297 (1983).
[9]S. P. Murarka, J. Vac. Sci. Technol. **17**, 775 (1980).
[10]L. R. Zheng, L. S. Hung, J. W. Mayer, G. Majni, and G. Ottaviani, Appl. Phys. Lett. **41**, 646 (1982).
[11]M. Bartur, Thin Solid Films **107**, 55 (1983).
[12]W. K. Chu, S. S. Lau, J. W. Mayer, H. Müller, and K. N. Tu, Thin Solid Films **25**, 393 (1975).
[13]R. Pretorius, C. L. Ramiller, and M-A. Nicolet, Nucl. Instrum. Methods **149**, 629 (1978).
[14]H. Föll and P. S. Ho, J. Appl. Phys. **52**, 5510 (1981).
[15]C.-D. Lien, M-A. Nicolet, and C. S. Pai J. Appl. Phys. **57**, 224 (1985).
[16]C.-D. Lien, M-A. Nicolet, and P. Williams (unpublished).
[17]V. J. van Gurp, D. Sigurd, and W. F. van der Weg, Appl. Phys. Lett. **29**, 159 (1976).
[18]R. W. Bower and J. W. Mayer, Appl. Phys. Lett. **20**, 359 (1972).
[19]K. T. Ho, C.-D. Lien, and M-A. Nicolet J. Appl. Phys. **57**, 232 (1985).

Downloaded 22 Dec 2005 to 131.215.225.9. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp