Silicide formation with bilayers of Pd-Pt, Pd-Ni, and Pt-Ni[a]

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Evaporated two-layered thin films of Pd-Ni, Pt-Ni, and Pt-Pd on single-crystal Si have been vacuum annealed in the temperature range 200–900°C. The sequence of films as well as substrate orientation have been varied. The silicide formation has been studied by MeV He$^+$ backscattering spectrometry and glancing angle x-ray diffraction. The silicide layers are highly inhomogeneous in the elemental depth distribution for annealing below 600°C. Above 700°C, the distributions become homogeneous. The silicide-substrate interface shows varying sharpness depending upon substrate orientation and evaporation sequence. We suggest the existence of ternary monosilicides of the type $Pt_{1-x}Pd_xSi$, $Pt_{1-x}Ni_xSi$, and $Pd_{1-x}Ni_xSi$. The $Pt_{1-x}Pd_xSi$ ternary silicide is stable up to 900°C; the others are not.

I. INTRODUCTION

Silicide formation with single layers of Ni, Pt, and Pd has been extensively studied.[1] For Ni films on Si, it has been found that Ni_2Si is the first phase to form (200–350 °C). Between 350 and 750 °C, NiSi is obtained. Above 750 °C, $NiSi_2$ is found. This latter compound grows epitaxially on $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ Si in a nonuniform manner. For Pt films on Si, it has been found that Pt_2Si first starts to grow (200 °C) and PtSi is the end phase of the reaction for temperatures above 300 °C. Pd_2Si first starts to grow (110 °C) for the Si/Pd system. Above 700 °C, PdSi is found.

Silicide formation with Ni-Pt double layers on Si has previously been studied by Thomas and Terry[2] and by Finstad.[3] The silicide formation in this system is rather complex, but according to Finstad,[3] a ternary monosilicide of the type $Pt_xNi_{1-x}Si$ might exist at temperatures above 700 °C. The present investigation was undertaken to see whether similar phenomena occur for Pd-Pt and Pd-Ni double layers on Si.

Silicide formation with double layers of metals are of technical importance for multilayered metallization schemes in regard to diffusion barriers and to (controlled) modification of Schottky-barrier heights.

II. EXPERIMENTAL

Single-crystal silicon wafers cut normal to the $\langle 100 \rangle$ or $\langle 111 \rangle$ axis were organically cleaned and given a dip in HF just prior to loading in the evaporation chamber. Ni, Pd, and Pt were electron-gun evaporated at typical rates of 40, 15, and 5 Å/s, respectively. All three combinations of double layers in both possible sequences with respect to the substrate were prepared. The samples were heat treated in a vacuum better than 10^{-6} Torr at temperatures ranging from 200 to 900 °C.

The samples were analyzed by 1.5- and 2-MeV ^{4}He backscattering spectrometry.[4] The scattering angle was 170°,

and the energy resolution was about 20 keV. In the analysis of the spectra, we have used the semiempirical stopping cross sections given by Ziegler and Chu.[5] Some samples were also examined by glancing angle x-ray diffraction. We have used CuKα radiation and a Read Camera.[6] This technique has good sensitivity for thin films, but rather poor accuracy (about 1°) and resolution (about 0.5°).

III. RESULTS
A. Si-Pt-Pd

In Fig. 1(a) is shown a 2-MeV ^{4}He$^+$ backscattering spectrum of a sample with the structure $\langle 100 \rangle$ Si/680 Å Pt/750 Å Pd. The Pt and Pd signals overlap. Their individual contributions were found by backscattering at 1.5 MeV and tilting

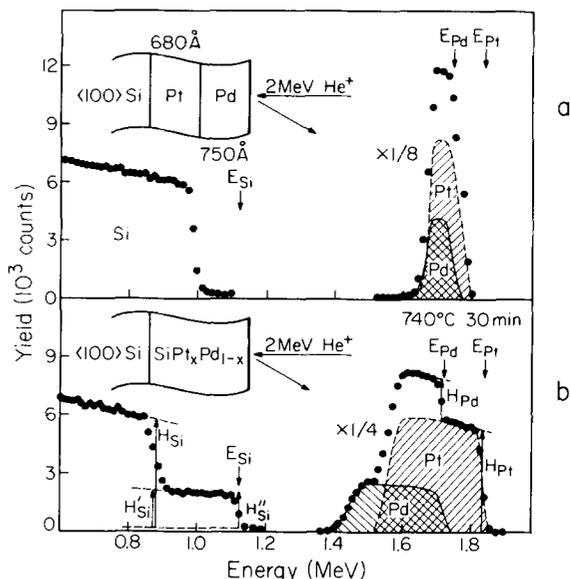FIG. 1. 2-MeV ^{4}He$^+$ backscattering spectra of samples with the structure indicated in the insets. The signal of each element has been shaded differently. The energy for scattering of each element, if located at the surface, is indicated by the arrows labeled E_{Si}, E_{Pd}, and E_{Pt}. (a) The as-deposited sample. (b) The sample after annealing at 740 °C for 30 min in vacuum. The heights of the various signals are indicated in the figure, and the observed ratios between the heights are given in Table I.

TABLE I. Ratios between signal heights as defined by Fig. 1(b). The observed values may be compared with those assuming a ternary monosilicide $Pd_xPt_{1-x}Si$, where x is determined by the initial thickness of the Pd and Pt films and is 0.53 for the sample in Fig. 1(b). There is also a column showing the calculated ratios expected if one assumes a homogeneous mixture of Pd_2Si and PtSi.

Height ratios	Observation	Calculation $Pd_xPt_{1-x}Si$ $x=0.53$	Pd_2Si and PtSi
H'_{Si}/H_{Si}	0.33 ± 0.02	0.34	0.27
H'_{Si}/H_{Pt}	0.075 ± 0.004	0.075	0.056
H'_{Si}/H_{Pd}	0.19 ± 0.02	0.19	0.12
H_{Pd}/H_{Pt}	0.38 ± 0.03	0.40	0.40

the sample 45° with respect to the beam direction. Upon annealing in the range 300–500 °C, silicides form, but the elemental distributions with depth are highly nonhomogeneous, and a description is difficult because of the relatively small separation between the Pd and the Pt signals. After 30 min of annealing at 740 °C, the elemental distributions with depth become quite homogeneous, as shown by Fig. 1(b). In this spectrum, we have compared the ratios of the signal heights of the various elements in the silicide and also the height of the signal of Si in the compound film to the height of the Si in the substrate. The observed ratios are listed in Table I. We compare these ratios with calculations which assume, in one case, that the silicide consists of a mixture of Pd_2Si and PtSi and, in the other case, that a ternary monosilicide of the type $Pd_xPt_{1-z}Si$ is present. The comparison is shown in Table I and details on the calculations are given in the Appendix. The symbols used in Table I are defined in Fig. 1(b). Table I suggests that the elemental composition of the silicide is close to that of a ternary monosilicide of the type $Pd_xPt_{1-x}Si$ where x and $1-x$ correspond to the overall atomic fractions of the two metals. Uncertainties in the stopping cross sections will not change the calculated values considerably. Calculations of yield ratios for other hypothetical combinations of silicides like PdSi and Pt_2Si, or Pd_2Si and Pt_2Si, yield values further away from the observed ratios than the cases considered.

When single layers of Pt on $\langle 100\rangle$ Si are annealed at 740 °C for 30 min, we observe the phase PtSi. When single layers of Pd are reacting with $\langle 100\rangle$ Si, the dominant phase is Pd_2Si as determined by backscattering. We detect some x-ray diffraction lines which could originate from the initial nucleation of PdSi, in agreement with what was observed by Hutchins and Shepela.[7]

In Fig. 2 are shown line diagrams of the x-ray diffraction pattern obtained from the sample of Fig. 1(b) together with patterns derived from the d spacing of PtSi, PdSi, and Pd_2Si given in the ASTM file. The observed pattern shown has been assigned the same zero point as that of an observed pattern of PtSi which was positioned to give the best agreement with the pattern for PtSi derived from the ASTM file. Lines with relative intensity less than 30% have been dropped from the ASTM-derived patterns. Also shown in

Fig. 2 is a pattern calculated for a hypothetical compound $Pd_xPt_{1-x}Si$ assuming an orthorhombic crystal structure and lattice parameters that vary linearly with x between the lattice parameters of PdSi and PtSi. The value of x is 0.53 as determined from the initial composition of the two films revealed in the backscattering spectrum of Fig. 1(a). It is seen that the observed pattern agrees well with this calculated one. It is also seen that the strong (228) and (408) lines are not present in the observed pattern, indicating that the amount of Pd_2Si phase, if any, is small. Two very faint lines in the observed pattern at 26° and 27.5° could not be identified.

We obtain spectra which are indistinguishable within experimental uncertainties whether we anneal directly at 740 °C for 30 min or we anneal the sample at successively higher temperatures ending with an annealing at 740 °C for 30 min. The silicide grows so fast at 740 °C that we were unable to determine whether at this temperature the growth goes through stages with large nonhomogeneity or not. However, we did observe that the surface concentration of Pt increases for annealing times up to 10 min at 740 °C.

For a sample with the reverse sequence of metal films ($\langle 100\rangle$ Si/1000 Å Pd/545 Å Pt), we observe highly inhomogeneous and intermixed silicides for annealing in the range 300–500 °C and spectra corresponding to a ternary monosilicide after annealing at 740 °C for 30 min. The height ratios observed are in excellent agreement with those calculated for a solid solution of monosilicides. The interface toward the substrate is less sharp than for the reverse sequence of films, however. X-ray patterns observed after annealing at 740 °C for 30 min are also in close agreement with those calculated for a hypothetical compound $Pd_xPt_{1-z}Si$, making the same assumptions as previously described.

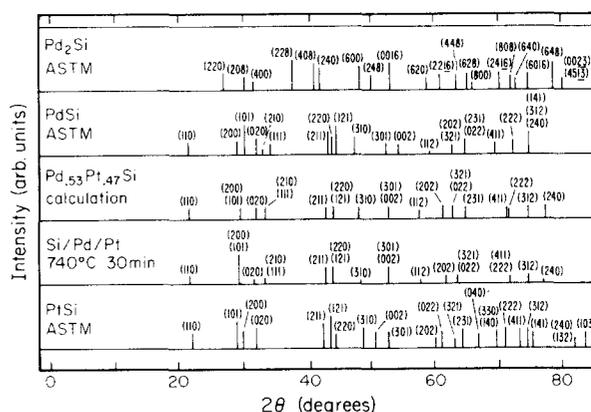The ternary silicide is stable for heat treatments of 20 min up to 900 °C as determined by backscattering spectrom-

FIG. 2. Line diagrams of x-ray diffraction patterns for Cu$K\alpha$ radiation. The patterns are from the top downward as follows: (i) for Pd_2Si, derived from d spacings given by ASTM card No. 19-893, lines with relative intensities less than 30% having been omitted; (ii) for PdSi, derived from ASTM card No. 7-127; (iii) calculated for $Pd_xPt_{1-x}Si$, where x has been derived from the initial amounts of Pt and Pd indicated by the spectrum of Fig. 1(a) and is 0.53; the calculation assumes an orthorhombic crystal structure and lattice parameters that vary linearly in x; (iv) as observed for the sample of Fig. 1(b); (v) for PtSi, derived from ASTM card No. 7-251.
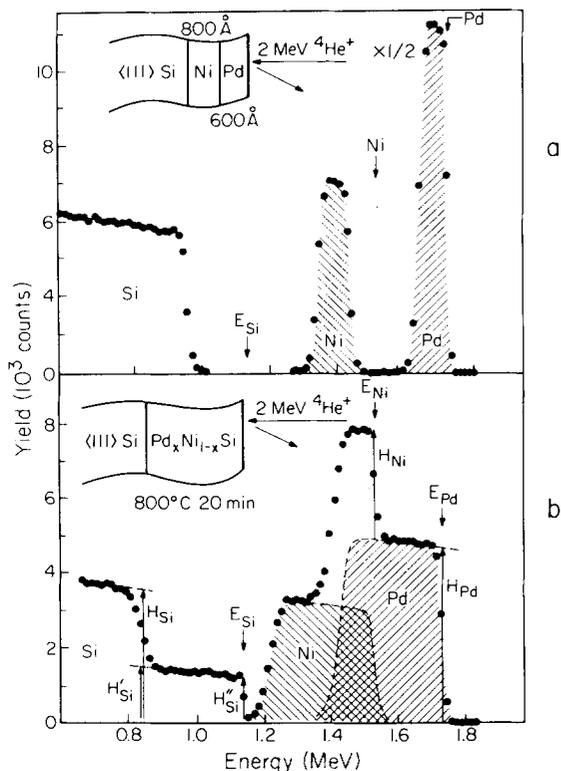
FIG. 3. 2-MeV ⁴He⁺ backscattering spectra of samples with the structure indicated by the insets. (a) The as-deposited sample. (b) The sample annealed at 800 °C for 20 min. Ratios between various heights defined in the figure are tabulated and compared with calculated values in Table II.

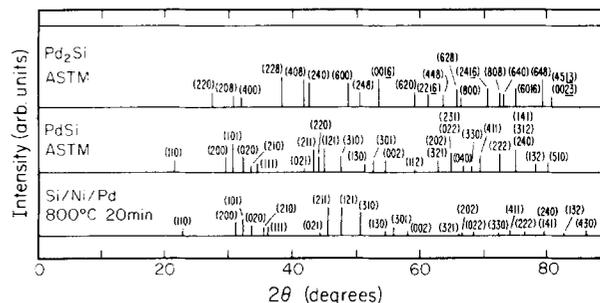FIG. 4. Line diagrams of x-ray diffraction patterns for Cu$K\alpha$ radiation. The patterns are from the top downward as follows: (i) for Pd₂Si, derived from ASTM card No. 19-893; (ii) for PdSi, derived from ASTM card No. 7-127; (iii) as observed for the sample of Fig. 3(b). The indexing has been done in analogy to that of the PdSi pattern.

etry, except for unintentional oxidation of the surface during annealing at high temperatures.

B. Si-Ni-Pd

Figure 3(a) shows the backscattering spectrum of a sample with the structure $\langle 111 \rangle$ Si/800 Å Ni/600 Å Pd. Upon annealing in the temperature range 300–500 °C, silicides with inhomogeneous depth distribution are formed. Annealing at 800 °C for 20 min yields a highly homogeneous compound. The height ratios of the backscattering signals are in agreement with those calculated for a compound of the type $Pd_xNi_{1-x}Si$ with a value of x equal to 0.35 as determined from the spectrum of Fig. 3(a). (See Table II.) Howev-

TABLE II. Signal height ratios as defined by Fig. 3(b). The observed values may be compared with those assuming a ternary monosilicide like $Pd_{1-x}Ni_xSi$, where x is determined from the thickness of the original Pd and Ni film to be 0.35. There are also columns showing calculated ratios for assumed mixtures of Pd₂Si and NiSi or of PdSi and NiSi₂.

Height ratios	Experiment	Calculation $Pd_xNi_{1-x}Si$ $x=0.35$	Pd₂Si and NiSi	Pd₂Si and NiSi₂
H'_{Si}/H_{Si}	0.42±0.03	0.41	0.36	0.50
H''_{Si}/H_{Si}	0.41±0.03	0.41	0.34	0.59
H''_{Si}/H_{Pd}	0.26±0.02	0.28	0.23	0.40
H_{Ni}/H_{Pd}	0.64±0.04	0.68	0.68	0.68

er, the difference between observed height ratios and those calculated assuming a homogeneous mixture of Pd₂Si and NiSi are not large enough to totally exclude the latter configuration based upon the backscattering spectrum alone. Upon annealing single layers of Ni on $\langle 100 \rangle$ Si at around 600 °C for 30 min, we find a uniform layer of NiSi. This compound is not stable for annealing at 740 °C for 30 min as determined by backscattering. The NiSi₂ phase probably starts growing. This compound has been identified by Tu et al.[8] after annealing thin Ni films on Si at 800 °C for 1 h.

In Fig. 4 are shown line diagrams of the x-ray patterns observed for the sample of Fig. 3(b), together with patterns derived from the ASTM values for the d spacings of PdSi and Pd₂Si. The zero point for the observed pattern is the same as that of the observed pattern of Fig. 2. The observed pattern does not agree with that which we calculated for a compound of the type $Pd_xNi_{1-x}Si$ and $x=0.35$ when the lattice constants are allowed to vary linearly with x. However, one can see that there are similarities in the observed pattern and the pattern for PdSi shown in Fig. 4. We indexed the lines in the observed pattern according to that of PdSi. We then can calculate the lattice constants for the unknown compound, assuming that the crystal structure is orthorhombic. The calculation gives $a = 5.79 \pm 0.03$ Å, $b = 5.34 \pm 0.08$ Å, and $c = 3.21 \pm 0.03$ Å. The values for a and b are both between those for NiSi and PdSi, whereas the lattice constant for c is smaller than that for both NiSi and PdSi. Also note from Fig. 3 that Pd₂Si is not detected.

The heat treatment required to homogenize the silicide layer may depend upon the Ni :Pd ratio. When the sample of Fig. 3(a) is heat treated at 750 °C, it is not homogenized for annealing times less than 150 min, whereas samples with the structure $\langle 111 \rangle$ Si/800 Å Ni/200 Å Pd were already homogenized after an annealing at 740 °C for 40 min; so were samples with the structure $\langle 111 \rangle$ Si/200 Å Pd/800 Å Ni. The sharpness of the interface between the Si substrate and the silicide depends upon the crystal orientation of the substrate. The interface is less sharp for $\langle 100 \rangle$ substrates than it is for $\langle 111 \rangle$ substrates for both film sequences.

After annealing to 900 °C for 20 min, the samples become laterally very nonuniform. The film evidently undergoes further reaction at these higher temperatures.
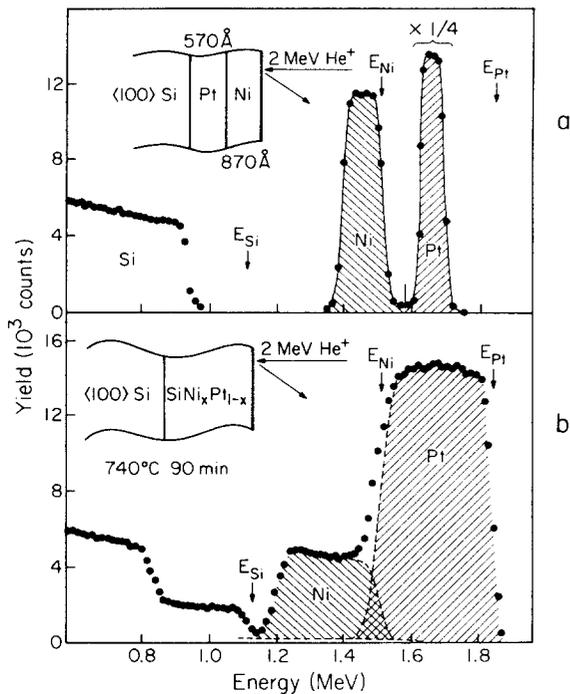
FIG. 5. 2-MeV ⁴He⁺ backscattering spectra of samples with the indicated structure. (a) The as-deposited sample. (b) Annealed at 740 °C for 90 min.

C. Si-Pt-Ni

The annealing behavior of double layers of Ni and Pt on Si has previously been described.[3] In Fig. 5(a), we show backscattering spectra of one sample with the structure $\langle 100 \rangle$ Si/570 Å Pt/870 Å Ni. The evolution of the depth profiles is complicated.[3] After an annealing at 740 °C for 90 min, however, the silicide layer homogenized to within approximately 5% in the elemental distributions as deduced from Fig. 5(b). Finstad has previously investigated x-ray diffraction patterns of samples with different Ni : Pt atomic ratios. These measurements indicate the existence of ternaries of the type $SiNi_{1-x}Pt_x$. Both sequences of films yield compounds with uniform distributions of the elements.

After annealing at 950 °C for 20 min, the samples are highly nonuniform.

IV. DISCUSSION

The monosilicides of Pd, Pt, and Ni all have the same crystal structure,[9] and the lattice parameters are only slightly different, as seen from Table III. In such a case, one would expect every pair of the monosilicides to be mutually soluble in all proportions. For isomorphous systems forming a solid solution, it is often observed that to a first approximation the lattice parameters vary linearly between those for the two constituents.

We have studied silicide formation with different bilayers of Pd, Pt, or Ni on silicon. After thermal annealing (200–500 °C), the elemental distributions are relatively complex. These distributions become uniform after annealing at high temperatures (750–800 °C). The backscattering data

for the silicides are in agreement with those expected for a solid solution of two monosilicides (ternary silicides) after annealing at high temperatures. The same data would, of course, also have been obtained if the silicide layer was a two-phase mixture of monosilicides. Even though the x-ray data are crude and not very accurate, they rule out this possibility. The x-ray patterns observed strongly suggests the existence of ternary monosilicides of the type $Pd_xPt_{1-x}Si$ and $Pd_xNi_{1-x}Si$. We have previously presented evidence for the existence of monosilicides of the type $Pt_xNi_{1-x}Si$. The x-ray data are in agreement with a description where the silicides have an orthorhombic crystal structure and where the lattice parameters vary linearly with the relative fraction of one of the monsilicides, except for $Pd_xNi_{1-x}Si$. When x equals about 0.5 in this compound, the smallest lattice constant is found to be smaller than that of both PdSi and NiSi, assuming that our indexing of the diffraction pattern is correct.

It is not a priori obvious that one can obtain these ternary compounds by a reaction between a bulk silicon crystal and double layers of metals since the monosilicides are not the only silicides in the binary phase diagrams. Complications might also arise in cases where the metals form compounds. For Pd-Ni, Pd-Pt, and Ni-Pt, however, the binary phase diagrams all show solid solutions.[9]

Since PtSi and NiSi probably coexist over a large temperature range, the homogenization of the layers are dependent upon the self-diffusion in the layers. It is somewhat surprising that one has to anneal above 700 °C to flatten out the concentration profiles considering the relatively high self-diffusion of Si in NiSi found by Pretorius et al.[12] at 450 °C.

For the $\langle 100 \rangle$ Si-Pd-Pt, it is interesting to note that we observe solid solutions of PdSi and PtSi at temperatures lower than where one would find PdSi if only Pd is reacting with Si. It would be interesting to know how much Pt has to be added to a Pd_2Si layer to convert it to $Pd_xPt_{1-x}Si$.

For the Si-Pd-Ni system, we observe a ternary monosilicide for annealing at temperatures where $NiSi_2$ is found if Ni alone is reacting with Si. It thus seems that $Pd_xNi_{1-x}Si$ is more stable than NiSi for the x values investigated.

Since $NiSi_2$ and not NiSi is the end phase in the Si-Ni binary reaction, one would expect that a ternary monosilicide with this element is less stable than $Pd_xPt_{1-x}Si$ where

TABLE III. Crystal structures and lattice constants for NiSi, PtSi, and PdSi.

Compound	PdSi (Ref. 10)	NiSi (Ref. 9)	PtSi (Ref. 11)
Crystal structures	Orthorhombic MnP type	Orthorhombic MnP type	Orthorhombic MnP type
Lattice constants			
a	6.133 Å	5.62 Å	5.932 Å
b	5.599 Å	5.18 Å	5.595 Å
c	3.381 Å	3.34 Å	3.603 Å

both binary monosilicides are stable. This agrees with our observations.

These findings could have some interest for applications to Schottky barriers. The formation of ternary silicides may be a way to obtain a controlled variation of the Schottky-barrier height. Attempts to accomplish this have previously been reported for double layers of Ni and Pt, and a dependence of the barrier height on the Ni : Pt ratio was observed.[2] In light of the work of Thomas and Terry[2] and Finstad,[3] the reason for the variation of the barrier height reported in those experiments is probably not due to the formation of an interface between a uniform monosilicide ternary and the substrate.

The silicides formed in the studied systems are quite different from those observed for bilayers of Pd-Cr,[13] Pt-Cr,[14] and Pd-Ti.[15] There the silicides do not homogenize. Rather, distinct silicides grow on top of each other in layers. Those combinations of bilayers have potential as diffusion barriers in metallization schemes. The present investigation clearly shows that combinations of the elements Pd, Pt, and Ni do not behave in such a manner.

ACKNOWLEDGMENTS

APPENDIX

We will show here how we calculate the yield ratios for a sample consisting of a layer of a ternary monosilicide of the type $Pd_xPt_{1-x}Si$ or for a layer consisting of a mixture of Pd_2Si and $PtSi$.

The value of x in the indexing of the ternary is easily calculated from the measured thicknesses of the initial Pd and Pt films.

The ratio between the height H'_{Si} of the silicon signal from the silicide and the signal height H_{Si} of Si in the substrate, both measured at an energy corresponding to the interface, is given by

$$H'_{Si}/H_{Si} = 0.5([\epsilon]_{Si}^{Si}/ [\epsilon]_{Si}^{Pt_1 , Pd , Si}),\qquad (A1)$$

where $[\epsilon]_{Si}^{Pt_1 , Pd , Si}$ is an energy-loss parameter defined by

$$\Delta\rho \times [\epsilon]_{Si}^{Pt_1 , Pd , Si} = \Delta E_{Si}.\qquad (A2)$$

Here $\Delta\rho$ is the total number of atoms in a silicide layer and ΔE_{Si} is the energy width of the Si signal corresponding to the given number of atoms. The energy-loss parameters is given by the stopping cross section of the compound. We have obtained the stopping cross section for a compound from those of the single elements by assuming Bragg's rule. We used tabulated semiempirical stopping cross sections given by Ziegler and Chu[5] in our calculations. The other ratios between the signal heights of a ternary are calculated analogously.

A layer consisting of a uniform mixture of Pd_2Si and PtSi may, for purposes of calculating the height ratios, be modeled as a layer of an imaginary compound $Pd_kPt_lSi_m$, where k, l, and m are the atomic fractions of each element in the compound and are easily calculated from the measured initial thicknesses of the Pd and the Pt films. Then the ratio between the silicon signal height from this layer and the silicon signal height from pure Si is given by

$$H'_{Si}/H_{Si} = m([\epsilon]_{Si}^{Si}/ [\epsilon]_{Si}^{Pd_k Pt_l Si_m}).\qquad (A3)$$

[1] *Thin Film Interdiffusion and Reactions*, edited by J.M. Poate, K.N. Tu, and J.W. Mayer (Wiley, New York, 1978).
[2] S. Thomas and L.E. Terry, J. Appl. Phys. **47**, 301 (1976).
[3] T.G. Finstad, Thin Solid Films (to be published).
[4] W.K. Chu, J.W. Mayer, M-A. Nicolet, T.M. Buck, G. Amsel, and F. Eisen, Thin Solid Films **17**, 1 (1973).
[5] J.F. Ziegler and W.K. Chu, At. Data Nucl. Data Tables **13**, 463 (1974).
[6] S.S. Lau, W.K. Chu, J.W. Mayer, and K.N. Tu, Thin Solid Films **23**, 205 (1974).
[7] G.A. Hutchins and A. Shepala, Thin Solid Films **19**, 343 (1973).
[8] K.N. Tu, E.I. Alessandrini, W.K. Chu, H. Kräutle, and J.W. Mayer, Jpn. J. Appl. Phys. Suppl. 2, 669 (1974).
[9] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).
[10] ASTM card No. 7-127.
[11] ASTM card No. 7-251.
[12] R. Pretorius, C.L. Ramiller, and M-A. Nicolet (unpublished).
[13] J.O. Olowolafe, M-A. Nicolet, and J.W. Mayer, J. Appl. Phys. **47**, 5182 (1976).
[14] R. Pretorius, J.O. Olowolafe, and J.W. Mayer, Philos. Mag. A **37**, 327 (1978).
[15] T.G. Finstad (unpublished).