

Chemical bonding and reactions at the Pd/Si interface

G. W. Rubloff, P. S. Ho, J. F. Freeouf, and J. E. Lewis

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 28 August 1980)

The electronic structure of the clean Pd/Si(111) and Pd/Si(100) interfaces has been investigated using angle-integrated and angle-resolved ultraviolet photoemission (UPS) and Auger electron spectroscopies (AES), in conjunction with transmission electron microscopy (TEM), work-function, and low-energy electron diffraction measurements. Since the interface is highly reactive, studies were made by processing the reaction in two ways: (i) sequential annealing steps of thick metal overlayers, and (ii) sequential deposition steps of very thin metal overlayers, considerably less than a monolayer per step. The UPS and AES spectra of the bulk reaction product (Pd₂Si) were first determined in films sufficiently thick for TEM phase analysis ($\geq 5 \text{ \AA}$), taking care to be sure that surface segregation effects (due to thin-film reaction kinetics) in these cases were negligible. On this basis, lower coverage (submonolayer) spectra could then be interpreted. Formation of the Pd₂Si compound is interface driven and extremely rapid at the clean Pd/Si interface. This compound formation dominates the microscopic chemistry and electronic properties of the interface. Chemical shifts observed in the electron spectroscopy measurements can be interpreted in terms of real or effective stoichiometry variations in the Pd₂Si compound (i.e., retaining its lattice structure); these appear as Si-rich Pd₂Si near the interface, with the Si excess decreasing with distance from the interface. Although silicide formation accounts for most aspects of the electronic structure, other effects such as localized interface bonds, defect states, etc., may make additional contributions at low metal coverage.

I. INTRODUCTION

Chemical bonding (i.e., electronic structure coupled with atomic microstructure) determines many of the properties of the metal/semiconductor interface. Because of its significance in semiconductor device applications, the most important electrical property is probably the Schottky barrier height: Ohmic (low barrier) contacts to semiconducting materials are needed simply to make use of active devices, while both high and low barrier contacts may be employed as active devices themselves (Schottky diodes).

Although the Schottky barrier has been the subject of intensive study for many years, a fundamental understanding of the mechanisms underlying Schottky barrier formation is still lacking. Phenomena intrinsic to an abrupt metal/semiconductor interface can in principle determine the Schottky barrier height.¹ Such phenomena include surface² and interface³⁻⁷ states, interface resonances associated with metal wave-function tails extending into the semiconductor,^{8,9} interface dipole layers,^{3,5,9} surface plasmons,¹⁰ gap closure,¹¹ etc. Even though theoretical calculations of interface electronic structure have illustrated some of these effects and experimental studies have been interpreted as evidence for some of these phenomena, recent theoretical^{7,12} and experimental^{3-5,13,14} work has increasingly emphasized the need for a microscopic understanding of the detailed

chemical bonding, and structure, at each specific interface. Nevertheless, characterizing these chemical interactions has proven difficult.

The importance of interfacial chemistry is particularly clear in the case of reactive interfaces. A broad class of metal/Si interfaces (mostly transition metals) is known to be reactive, forming metal-Si compounds (silicides) which grow from the interface.¹⁵ These interfaces have seen increasing application in electronic devices. They represent an attractive subject for Schottky barrier studies as well because: (i) extensive thin-film investigations have revealed much about the film growth kinetics, microstructure, and compound phases of the silicide reaction products, and (ii) metal/semiconductor interface chemistry should be simpler for the elemental semiconductors. Furthermore, the Schottky barrier height of the resulting silicide/Si contact exhibits the importance of the interfacial chemistry in its correlation with silicide heat of formation¹⁶ and eutectic temperature.¹⁷

We have chosen to study the Pd/Si interface because contact reaction at up to $\sim 700^\circ\text{C}$ yields only a single product,¹⁵ Pd₂Si. This choice makes it possible to interpret observations of chemical interactions quite clearly and thus to reveal the initial stages of interface formation. The microscopic chemistry and properties of the Pd/Si interface are dominated by compound formation at the interface, which represents the initial step in the silicide formation

reaction.^{18,19} This compound formation seems to be accompanied by stoichiometry variations (Si excess) in the silicide near the interface and by additional band-gap states specifically associated with the interface.²⁰ These results provide little evidence that phenomena intrinsic to the abrupt interface play an important role in Schottky barrier formation at the Pd/Si interface.

These studies concentrated on the atomically clean Pd/Si(111) and Pd/Si(100) interfaces for very thin ($\leq 0.25 \text{ \AA}$) as well as thicker metal overlayers. Surface electronic structure was measured by angle-resolved and angle-integrated photoemission spectroscopy (ARUPS and AIUPS, respectively) and Auger electron spectroscopy (AES), complemented by transmission electron microscopy (TEM), low-energy electron diffraction (LEED), and work-function measurements. Abbreviated descriptions of these results have been published earlier.^{18,19} A discussion of relevant electronic properties of bulk Pd₂Si, based on experimental results described here and on theoretical calculations, has been published separately.²¹

During editorial processing of this paper, several related studies²² of silicide/Si interfaces have appeared in the literature. These investigations reveal compound formation and give chemical-shift evidence for stoichiometry variations near the interface similar to the behavior which we reported earlier.^{18,19} In this paper we present our results for the Pd/Si interface in full, and we discuss in detail the central issues toward which our previous studies as well as those of other groups have been directed, including the nature of the initial stages of silicide formation, the character of electronic states present at the interface, the relation of spectroscopically observed chemical shifts to stoichiometry variations at the interface or alternatively to interface chemical-environment effects, and the problem of distinguishing between stoichiometry variations in a thin film and the surface segregation and enrichment phenomena which are a consequence of thin-film reaction kinetics.

II. EXPERIMENTAL TECHNIQUES

All depositions and measurements except the TEM studies were carried out in ultrahigh vacuum (UHV, $p \sim 1 \times 10^{-10}$ torr). Samples were cut from 0.010-in.-thick Si(111) and (100) wafers. The surfaces were cleaned by *in situ* ion bombardment. Surface-structure damage was then removed by annealing to $\sim 800\text{--}850^\circ\text{C}$ for 5–30 min using direct resistive heating of the sample through Ta clamps holding the sample; visual inspection of the glowing surface during annealing revealed that the sample temperature was quite uniform ($\leq 50^\circ\text{C}$) over the entire portion of the surface between the clamps, where spectroscopy

measurements were done. The sample temperature was monitored by a Chromel-Alumel thermocouple spot welded to one of the Ta clamps. Temperatures during annealing were also checked by optical pyrometry; this also showed the clamps to be within $\sim 50^\circ\text{C}$ of the sample temperature.

After the sputter cleaning and annealing, ordered surface structures were observed by LEED. For Si(111), studies on both the (7×7) reconstructed surface and a (1×1) surface [probably representing a disordered (7×7)] were carried out and gave essentially the same results. The Si(100) surface exhibited a $c(4 \times 2)$ superstructure, with $c(4 \times 2)$ LEED spots faint but clearly visible in addition to the (2×1) structure. AES showed the surface to be contaminant free to about 1% of a monolayer.

Pd overlayers were evaporated by direct sublimation from a resistively heated 0.010-in.-diam Pd wire. Pd coverages were determined using a quartz crystal microbalance and also by Auger composition analysis; coverages are given in terms of equivalent Pd metal thickness. The Pd source could be maintained at a constant sublimation temperature for a low deposition rate ($\sim 1 \text{ \AA}/\text{min}$); controlled deposition amounts could then be made by removing a shutter from the evaporant path to the sample for a fixed length of time. In this way relative coverages were accurate to $\sim 10\text{--}20\%$ for sequential deposition studies.

UPS measurements were made using a differentially pumped He resonance lamp (He I, He II, and Ne I lines at incident photon energies $h\nu = 21.2, 40.8$ and 16.8 eV, respectively). For the angle-resolved UPS studies a VG ADES 400 spectrometer was used, while a PH1 15-255G cylindrical mirror analyzer was employed for angle-integrated UPS and AES measurements. Electron counting techniques were used for UPS. The work function ϕ of the surface was obtained from the width of the UPS distribution (secondary electron cutoff to Fermi energy cutoff), which is simply $(h\nu - \phi)$. Both AES derivative and integrated spectra [dN/dE and $N(E)$, respectively] were measured in analog detection mode with a 5-kV primary beam of $\sim 1 \mu\text{A}$ defocused to ~ 1 mm diam; beam chopping was employed for the $N(E)$ measurements. AIUPS and AES spectra were acquired into a computer using a device coupler²³; this facilitated the calculation of difference spectra as well as graphics analysis.

TEM studies were carried out after the Pd/Si samples were removed from the UHV system to investigate the compound phases formed, their lattice constants, degree of epitaxy, and interfacial microstructure. Related TEM and AES results on the Pd/Si(111) interface have been published previously.^{18,24}

The surface spectroscopy studies of the interfacial reaction were carried out in two ways. First, progress

of the reaction was monitored for relatively thick Pd overlayer films ($\sim 100\text{--}300 \text{ \AA}$) as a function of sequential annealing cycles. Second, the character of the film surface was studied as a function of distance from the interface by observing the spectra after successive depositions of very thin Pd layers ($\sim 0.25 \text{ \AA}$). These very-thin-film-deposition results reveal in a rather direct fashion the microscopic chemical properties during the initial stages of interface formation. The spectroscopy measurements are sensitive to the interface for metal coverages of order the electron escape depth ($\sim 5\text{--}25 \text{ \AA}$); if further metal deposition does not alter the properties of the underlying interface, then these measurements give information characteristic of the buried contact. Furthermore, we note that the interface properties measured here under clean UHV conditions may also be relevant to "real" ("dirty") interfaces: for many cases of silicide formation (including that of Pd_2Si) on contaminated, oxide-covered surfaces, the reaction front moves into the Si substrate to yield a relatively clean silicide/Si interface.¹⁵

III. RESULTS

A. Sequential annealing of thick films

UPS results for successive annealing cycles to react a thick Pd overlayer film illustrate the progress of the reaction and reveal the basic electronic structure of the reaction product, Pd_2Si , as shown in Fig. 1. First a clean, ordered Si(111) surface was produced and measured, in this case by angle-resolved UPS; the

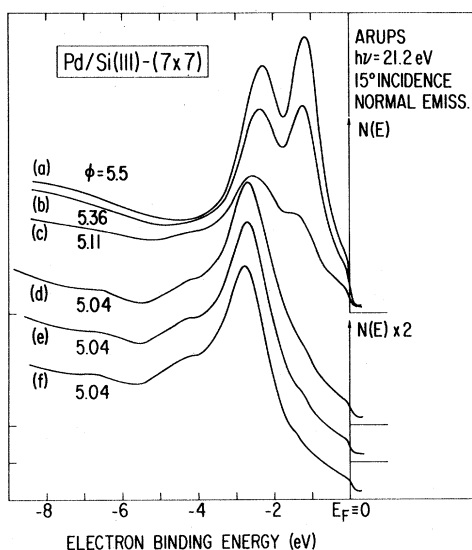


FIG. 1. (a) ARUPS spectrum for $\sim 300 \text{ \AA}$ Pd deposited on Si(111) at 25°C ; (b)–(f) subsequent spectra taken after stepwise annealing cycles of 30 sec at 150°C .

ARUPS properties of this surface were in agreement with those reported previously.²⁵ A relatively thick Pd film ($\sim 300 \text{ \AA}$) was then evaporated onto the Si substrate which was held at 25°C . The ARUPS spectrum of this overlayer for 15° angle of incidence of the He I light and normal emission is shown in Fig. 1(a). The Pd(4*d*) bands of Pd metal produce the strong doublet structure seen between -3 eV and -0.5 eV , while a distinct metallic cutoff is observed at the Fermi energy E_F . The work function of this surface, obtained from the width of the UPS spectrum, is $\phi = 5.5 \text{ eV}$ as typically observed for evaporated Pd metal. Normal emission spectra like that in Fig. 1(a) were nearly identical to those for a Pd(111) single-crystal surface²⁶ since the surface of the deposited film is unreacted metal and has strong (111) texture as shown by the TEM studies.

Three successive 150°C annealing steps ($\sim 30 \text{ sec}$ each) cause strong modifications in the ARUPS spectrum [Figs. 1(b), 1(c), and 1(d)] and reduce ϕ to $\sim 5.04 \text{ eV}$; at this point a single peak near -2.75 eV dominates the spectrum and a weak Fermi edge remains. Two further annealing steps shift this peak slightly toward lower energy without further changing ϕ of the overall spectral shape.

TEM analysis carried out after removing the sample from the UHV system determined that the overlayer film whose spectrum is shown in Fig. 1(f) was continuous and fully reacted to Pd_2Si , with no other phases detectable. As explained below, the surface properties (UPS spectrum and ϕ) for this film were also characteristic of the Pd_2Si bulk of the film. Thus Pd_2Si has $\phi \cong 5.04 \text{ eV}$; its UPS spectrum is dominated by a single peak [associated with the Pd(4*d*) electrons^{18,22}] near -2.75 eV .

The ARUPS spectra of this Pd_2Si film are insensitive to variations in $h\nu$ (16.8, 21.2, or 40.8 eV), angle of incidence, or angle of emission, in contrast to those for the deposited Pd metal film and for the clean Si surface. This lack of dispersion can be attributed to two factors. First, although thin-film studies have established that Pd_2Si can be formed epitaxially on the Si(111) surface,^{27,28} we found that a high degree of epitaxy is not readily achieved for Pd_2Si formation on the atomically clean and ordered Si(111) surface: although $\geq 95\%$ of the silicide could be made epitaxial, values near 30–50% were more typical. Without epitaxy, angular dispersion in ARUPS is expected to be lost. A second explanation for the insensitivity of the ARUPS spectra to angle and to $h\nu$ is that Pd_2Si has a rather large (9 atom) real-space unit cell,²⁷ and the correspondingly small unit cell in reciprocal space may therefore have many nearly flat bands and exhibit little band dispersion.

Finally, we note that the change in the UPS spectrum of the film surface is rather abrupt: although the annealing steps were all the same in Fig. 1, nearly all changes occur between curves 1(b) and 1(d) while

only a reduced emission intensity is seen from Figs. 1(a) to 1(b) and small changes from Figs. 1(d) to 1(f). This behavior indicates that the reaction front at which Pd is converted to Pd₂Si is rather sharp. As explained below, it begins at the Pd/Si interface (where Pd₂Si is formed): then the Pd₂Si/Pd interface proceeds through the Pd film toward its surface; when it comes within the UPS detection depth, the spectrum changes markedly.

B. Sequential deposition of thin films—UPS results

AIUPS spectra for sequential depositions of very thin Pd layers on the clean Si(111) surface at 25°C are shown in Fig. 2. The spectrum for the clean surface shows bulk Si peaks near -7 and -3.5 eV and intrinsic surface-state features²⁵ near -1.8 and -0.9 eV. The Si(111)-(7×7) surface is known to be metallic²⁵ [the associated metallic Fermi edge is not clearly observed here because of the modest energy resolution used (~0.35 eV) and the disorder of the superstructure which we believe is responsible for the (1×1) LEED pattern seen].

Upon Pd deposition the emission intensity increases significantly due to the considerably larger UPS cross section of Pd (from its 4*d* electrons) compared to that of Si. With increasing Pd coverage the intrinsic surface-state features are lost and metallic states appear much more clearly at E_F . The bulk Si features observed for ≤ 1 Å metal coverage exhibit no shift in energy, so that no evidence for band-bending changes is found. The work function increases by ~0.9 eV. A new peak arises near -3 eV (e.g., see the 1.0 Å curve) and shifts up in energy (toward E_F) slowly. The spectra for ~2–12 Å close-

ly resemble the ARUPS spectrum of Pd₂Si in Fig. 1(f), although relative intensities of various parts of the spectrum differ somewhat. The main peak of Pd₂Si in both AIUPS and ARUPS is asymmetric, sharper on the high-energy side and having shoulders near -4.5 and -6.3 eV on the low-energy side. Auger composition calibrations for films ~5–10 Å thick like those in Fig. 2 indicated the presence of a Pd-Si layer having about a Pd₂Si stoichiometry on top of the Si substrate. These AIUPS spectra are thus essentially characteristic of Pd₂Si compound.

Although the shift of the main *d*-band peak from ~2 to 12 Å Pd coverage is relatively small, comparable coverage increments from 12 to 22 Å and from 22 to 32 Å produce a more pronounced shift toward E_F . As discussed in detail later, we associate this with the presence of unreacted Pd metal near the surface in addition to Pd₂Si in the film (or possibly Pd-rich Pd₂Si). The AIUPS spectrum is then a combination of the Pd₂Si spectrum (*d*-band peak near -2.75 eV) and a Pd spectrum (center of mass of *d*-band structures near -1.75 eV) so that the main peak occurs somewhere in the middle (~-2.0 eV for 32 Å coverage). Since silicide formation begins at the Pd/Si interface and proceeds through the Pd film, progressively less reaction may have taken place at positions further from the interface (which are seen in the surface spectra for higher coverage).

In order to better understand and interpret the changes in the UPS spectra—especially for low coverage—we concentrate on “difference spectra.” Because the Pd cross section is much larger than that for Si, the difference curve obtained by subtracting the clean Si spectrum from the Pd-covered spectrum is nearly the same at the Pd-covered spectrum itself if the coverage is ≥ 4 Å. Corresponding difference curves for lower coverage show the electronic structure changes associated with all the deposited Pd present at that point. However, even more revealing information can be obtained from “incremental difference curves” such as those shown in Figs. 3(b), 3(c), and 3(d) for Pd/Si(111); these are representative of electronic structure changes associated with additional 0.25 Å Pd coverage increments deposited on top of whatever Pd was already present. These difference curves are compared to the spectra for clean Si(111) and those for 4 and 12 Å Pd/Si(111) in Fig. 3.

Although not at all obvious from the spectra in Fig. 2, the difference spectra in Fig. 3 show clearly that the electronic structure associated with sub-monolayer amounts of Pd deposited on Si(111) closely resembles that of Pd₂Si [Fig. 3(f)], with a weak Fermi edge and a strong asymmetric peak (high-energy side sharper) ~3 eV below E_F . This marked similarity leads us to conclude that chemical bonding at very low coverage is very similar to that in Pd₂Si (as seen by UPS), i.e., a Pd₂Si-like compound is

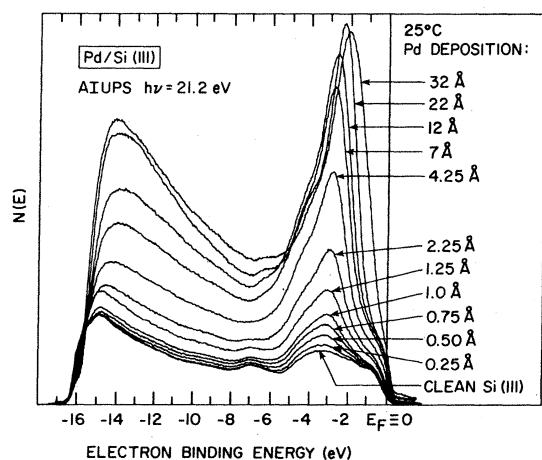


FIG. 2. AIUPS spectra for the clean Si(111) surface and for various Pd coverages deposited at room temperature.

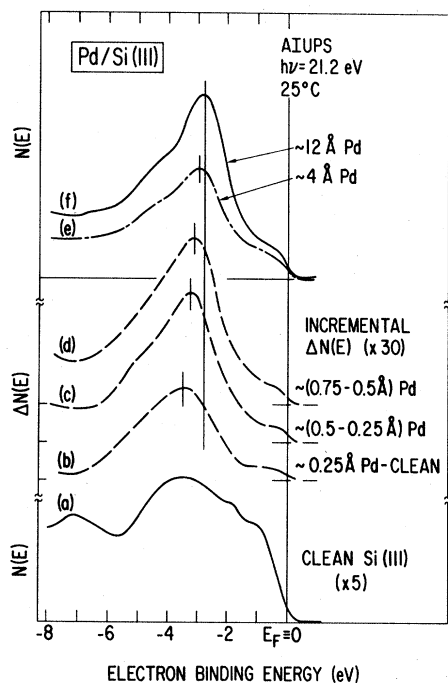


FIG. 3. AIUPS incremental difference curves for (b) 0.25 Å Pd-covered surface minus clean Si(111) surface, (c) 0.5 Å minus 0.25 Å Pd-covered surfaces, (d) 0.75 Å minus 0.5 Å Pd-covered surfaces, and AIUPS spectra for (a) clean Si(111), (e) ~4 Å Pd on Si(111), and (f) ~12 Å Pd on Si(111).

formed. We note, however, that there are some differences between the electronic structure at very low coverage and that of bulk Pd₂Si. The *d*-band peak shifts from an initial position at -3.5 eV [Fig. 3(b)] continuously toward E_F with higher coverage, reaching ~-2.75 eV in bulk Pd₂Si for ≥ 10 Å coverage. Furthermore, the intensity near E_F , i.e., in the Si band-gap region, appears somewhat enhanced at low coverage relative to the main *d*-band peak.

Corresponding AIUPS results for very thin Pd layers on the clean Si(100) surface are shown in Fig. 4. Intrinsic surface-state features exist²⁹ near -0.7 and -1.3 eV; the latter is seen clearly in Fig. 4(a) and gives rise to a marked dip at this energy in the difference spectra [Figs. 4(b) and 4(c)]. In spite of the differences between the initial clean Si(111) and (100) surfaces, the results are very similar. On the (100) surface, as on the (111) surface, the Pd₂Si spectrum is observed at ~12 Å Pd coverage. The low coverage difference spectra on Si(100) also show the essential Pd₂Si spectral characteristics, including a well defined Fermi edge, a strong *d*-band peak near -3 eV, and the shift of this peak from ~-3.5 eV at lowest coverage to a final position near -2.75 eV at higher coverage. Silicide formation thus occurs in a very similar way on Si(100) as on Si(111).

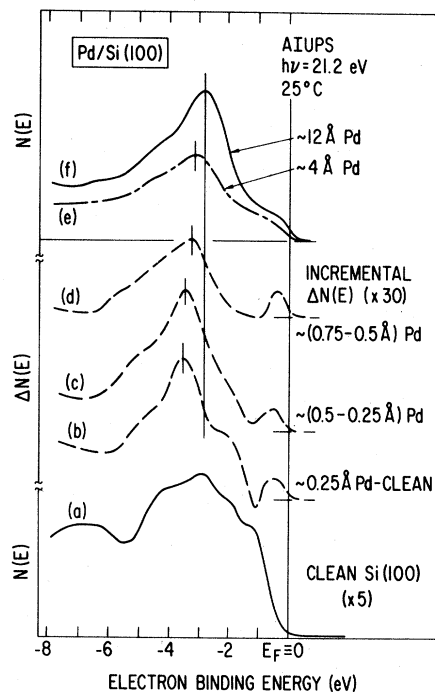


FIG. 4. AIUPS incremental difference curves for (b) 0.25 Å Pd-covered surface minus clean Si(100) surface, (c) 0.5 Å Pd-covered surfaces, (d) 0.75 Å minus 0.5 Å Pd-covered surfaces, and AIUPS spectra for (a) clean Si(100), (e) ~4 Å Pd on Si(100), and (f) ~12 Å Pd on Si(100).

The low-coverage UPS spectra are much more similar to those for bulk Pd₂Si than to those for very thin overlayers of pure transition metals. The UPS spectra for thin Pd layers on Ag (Ref. 30) and Pd alloyed with Ag (Ref. 31) show resonant *d* levels with widths and binding energies below E_F (~1 eV) which are ~2-3 times smaller than observed here for Pd on Si. Thin Pd(111) overlayers on Nb(110) exhibit *d* levels at ~-3.1 eV, again with a smaller width (~0.5 eV) than that for Pd/Si.³² In both cases the coverage-dependent shifts of the *d* level are much smaller (< 0.2 eV) than those seen here (~0.75 eV). Very thin (≤ 1 monolayer) Pd films on polar ZnO surfaces³³ do not react strongly with the ZnO; again the Pd *d* bands differ markedly from the low-coverage Pd/Si spectra, with ~2-3 times narrower peak width and with peak asymmetry of the opposite sign. Thus experimental UPS results provide no evidence favoring the presence of an elemental Pd film at low coverage. Such a hypothesis is also contradicted by the existence of epitaxy for Pd₂Si on Si(111) and by the formation of Pd₂Si observed directly at higher coverage.

On crystalline graphite surfaces the Pd *d* levels at low coverage (in He I UPS spectra) appear near -2.5

eV and shift somewhat (~ 0.5 eV) toward E_F with increasing coverage.³⁴ Their width is also comparable to that for Pd/Si. Thus the Pd d -band behavior at low coverage is similar on Si and graphite surfaces, but this could also result from similar chemical bonding and stoichiometry effects in a mixed Pd-Si or Pd-C interfacial material, especially because Si and C are isoelectronic.

We conclude that a Pd₂Si-like compound is formed at low coverage insofar as its electronic structure as seen in UPS is concerned.

C. Sequential deposition of thin films—AES results

The Si $L_{2,3}VV$ Auger spectrum provides a valuable measure of interface electronic structure because: (i) it is clearly sensitive to the chemical environment of the Si atom and its local valence bonding; (ii) its line shape is bandlike (i.e., revealing density-of-states information) rather than quasiatomic; and (iii) it is atom specific, showing local density-of-states properties at the Si site, in complementary relation to the UPS valence band spectra, which reveal mainly Pd d -band features. Other Auger transitions involving the valence band are either quasiatomic (e.g., the Pd $M_{4,5}VV$ near 330 eV) or otherwise not satisfactory for studies of the initial stages of interface formation because they are too weak (e.g., the Si KL near 1650 eV) or overlapping with other Auger transitions (e.g., the Si $L_{1L_{2,3}V}$ near 50 eV).

The Si $L_{2,3}VV$ AES spectra for the clean Si(111) surface and for thin Pd layers deposited at 25°C are shown in Fig. 5 [undifferentiated or $N(E)$ mode]. The spectra all have a common zero for $N(E)$. The dominant peak in the clean spectrum, at ~ 88.5 eV, is replaced by four new features at ~ 94 , 89.5, 85, and 80 eV, as Pd is deposited on the surface. Since this Si AES transition is observed for thicknesses ≥ 30 Å, which are large compared to its Auger escape depth (~ 7 Å in elemental Si), Si is present in the deposited overlayer. Auger composition analysis has demonstrated²⁴ that the stoichiometry of overlayers formed in this way for ≥ 3 –5 Å Pd coverage is essentially that of Pd₂Si, and TEM analysis of such samples confirms the existence of the Pd₂Si lattice structure. The spectrum in Fig. 5(f) thus represents that of bulk Pd₂Si. The interpretation of its features has been discussed previously;²¹ they involve mainly the Si($3p$)-Pd($4d$) bonding and antibonding valence states which determine the cohesive energy and phase stability of the Pd₂Si compound.

Because of the proximity of the Si 88.5-eV and the Pd₂Si 89.5-eV peaks (which are respectively suppressed and enhanced with Pd coverage), standard difference curves (Pd-covered minus clean surface spectra) and incremental difference curves (as used in the AIUPS results in Sec. III B) can be ambiguous in this

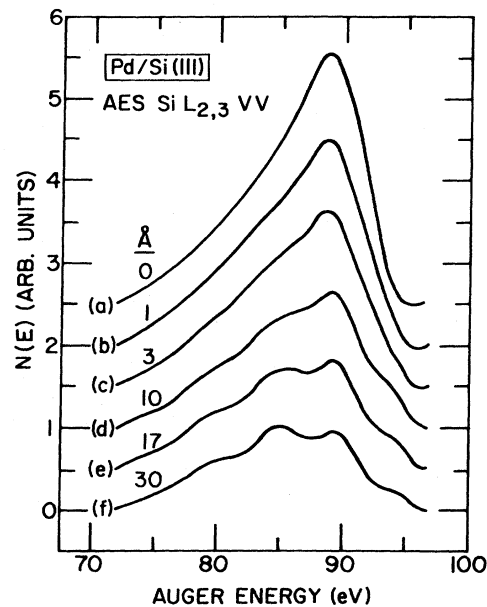


FIG. 5. Si $L_{2,3}VV$ AES $N(E)$ spectra for (a) the clean Si(111) surface and for increasing Pd coverages (b) 1 Å, (c) 3 Å, (d) 10 Å, (e) 17 Å, and (f) 30 Å.

range. We analyze the AES spectra for the initial stages of interface formation by decomposing the $N(E)$ spectra into a portion resembling elemental Si and an additional portion due to the Pd₂Si-like compound. Since the elemental Si part should correspond to Si below the overlayer, its shape should remain constant [that seen in Fig. 5(a)] while its intensity will decrease with overlayer thickness. Since there is no evidence for band-bending changes from UPS, we assume that the elemental Si contribution remains unshifted for decomposing the AES spectra.

The decomposition of the Si $L_{2,3}VV$ spectra in Fig. 5 into Pd₂Si and elemental Si contributions is shown in Fig. 6. Because a shape like that of elemental Si has been extracted from the data in Fig. 5, the spectra in Fig. 6(a) include notable contributions from the Pd₂Si 89.5-eV peak, which are correspondingly weakened in Fig. 6(b). Nevertheless it is clear that, as in the AIUPS results, the essential features of the bulk Pd₂Si spectrum dominate the interface electronic structure observed at very low Pd coverage (these AES results would be inconsistent with a hypothesis that a very thin elemental Pd film is formed at low coverage). However, some differences (as in the AIUPS results) are found between the low coverage spectra and the bulk Pd₂Si spectra. The 94-eV peak (and possibly the 79-eV peak) shift toward higher energy with increasing coverage. The intensity of states nearest E_F (reflected in the highest-energy AES

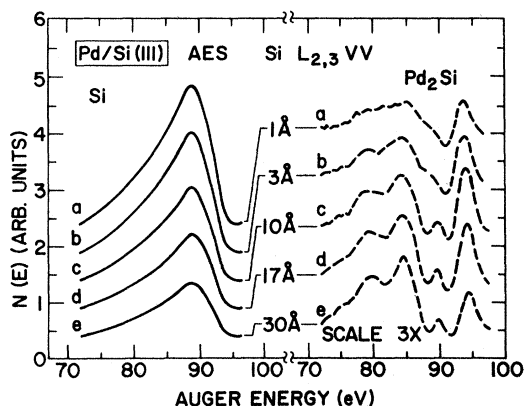


FIG. 6. Decomposition of the Si $L_{2,3}VV$ AES spectra for Fig. 5 into Pd_2Si and elemental Si-like contributions.

structure at ~ 94 eV) decreases with increasing coverage relative to the other peaks at lower energy. Like the AIUPS results, these spectra indicate that a Pd_2Si -like compound is formed in the initial states of interface formation.

D. Work-function measurements and Schottky barrier height

By monitoring the shift of the secondary electron cutoff (i.e., changes in the width of the UPS spectrum), work-function changes as small as ~ 30 – 50 meV could be detected. Since the Pd sublimation rate could be maintained constant over many thin-layer evaporations, the change in work function with coverage could be measured in considerable detail, as shown in Fig. 7. With increasing Pd coverage ϕ increases monotonically from its value for the clean

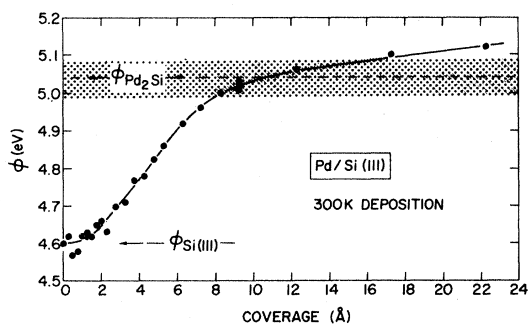


FIG. 7. Coverage dependence of the work function (measured by AIUPS) for Pd deposited on Si(111) at room temperature. The region of Pd_2Si work function is indicated by the shaded area.

Si(111) surface [4.6 eV (Ref. 25)] to that of Pd_2Si (~ 5.04 eV) in ~ 10 – 12 Å, then rises more slowly with further Pd coverage. The shaded ϕ region, ~ 5.0 – 5.1 eV, represents approximately the range of bulk Pd_2Si work functions, as described in Sec. III E. For Pd coverages above ~ 10 – 15 Å deposited at room temperature, ϕ increases toward that of Pd metal (~ 5.6 eV) due to the presence of incompletely reacted Pd metal at the surface of the overlayer. This is consistent with the coverage dependence of the main d -band peak position seen in AIUPS (Sec. III B).

The ϕ behavior in Fig. 7 shows a delayed onset of ϕ changes, and ϕ does not reach its Pd_2Si value until ~ 8 – 10 Å Pd coverage. Two factors may influence this behavior. First, the UPS measurement of the surface work function concentrates on the threshold or cutoff of the secondary electron distribution. If the surface consists of patches of material having different ϕ values (e.g., some clean Si and some Pd_2Si), the measurement will be much more sensitive to the lower ϕ material, which determines the actual cutoff. This fact may explain why the onset of work-function changes is delayed until ~ 2 Å Pd coverage. However, this effect appears incapable of explaining why the Pd_2Si work function is not obtained by ~ 3 – 5 Å coverage, since TEM observations for this coverage showed the overlayer to be continuous.

The second factor which could account for both the delayed onset of work-function changes and the delay in attaining $\phi = \phi_{Pd_2Si}$ is that the material produced at the interface—i.e., in the initial stages of interface formation—may differ somewhat from bulk Pd_2Si . This would be consistent with the differences (discussed in Secs. III B and III C) in the AIUPS and AES spectra for very low Pd coverages compared to those for bulk Pd_2Si . Since ϕ for a Pd-Si mixture or compound most likely scales monotonically with concentration between the work functions of the elemental constituents, a plausible interpretation of the delay in reaching ϕ_{Pd_2Si} is that the material produced near the interface has a larger Si-to-Pd concentration ratio than that in Pd_2Si —i.e., it is Si-rich Pd_2Si . This possibility is discussed more thoroughly in Sec. IV B.

It is interesting to compare the Schottky barrier height of these atomically clean interfaces with thick-film results obtained under more usual processing conditions. The barrier height of the contact is given by the value of the clean Si surface modified by the metal-induced change in band bending. For the clean n -Si(111) surface, we take the Schottky barrier height to be $E_c - E_F = 0.79$ eV (Refs. 35 and 36) (where E_c is the energy of the conduction-band minimum at the surface); for n -Si(100) it is similar²⁹ (0.75 ± 0.15 eV). The metal-induced change in band bending can in principle be obtained from the shift in a bulk Si UPS feature; using the bulk structures near -7 eV for the clean Si(111) and Si(100) surfaces, the

band bending is unchanged by Pd deposition (to ± 0.1 eV). (Above ~ 1 Å Pd this peak is not easily distinguished so that further band-bending changes are not measured). This would give a Schottky barrier height for the Pd₂Si film on both the clean Si(111) and Si(100) surfaces of $\sim 0.79 \pm 0.1$ eV, in good agreement with thick-film results.¹⁶ This agreement may result from the fact that the Pd/Si interfacial reaction occurs whether or not native oxides and/or contamination are present, producing regions of relatively clean Pd₂Si/Si interface which determine the electrical properties.

E. Interface and film reaction kinetics—effects on surface spectroscopies

It is worthwhile to emphasize the rapid reaction kinetics observed here for Pd₂Si formation. Although thin-film investigations have shown that 200 °C annealing is required to form Pd₂Si from ≥ 1000 Å Pd film deposited under modest vacuum conditions onto substrates prepared by standard processing techniques (wet chemical etch, etc.), we find spontaneous Pd₂Si formation within ~ 10 – 20 Å of the initial interface at 25 °C. In fact, we also carried out AIUPS experiments with the Si(111) sample held at ~ 180 K and obtained results essentially identical to those in Fig. 2, suggesting that silicide is formed even at low temperature in basically the same way as at room temperature.

The fast reaction kinetics observed here cannot be directly compared with standard thin-film studies for three reasons. First, the present studies concentrate on much thinner films, so that mass transport (believed to be the rate-limiting step in relatively thick Pd₂Si film growth) may be less important. Second, these experiments have been carried out on atomically clean and ordered Si surfaces under UHV conditions which allow Pd deposition without significant interface contamination, so that the kinetics of interface reaction steps in the Pd₂Si formation process may thus be much faster and could even be qualitatively different. Third, the present experiments concentrate in fact on the initial stages of silicide formation, in which at low coverage Pd₂Si is produced at the Pd/Si interface; in contrast, the Pd₂Si growth process for thicker films involves interface reaction steps at the Pd/Pd₂Si and the Pd₂Si/Si interfaces in addition to mass transport.

Since the silicide formation reaction originates at the Pd/Si interface, temperature dependence and thermal history will strongly influence what phases are present at various distances from the initial interface. In order to safely use the surface spectroscopy results, we must therefore be sure that the surface region from which spectra are obtained are composed of the phases we identified, e.g., for the full over-

layer film by TEM. The results of this analysis are especially important because we attempt to first identify the UPS and AES features characteristic of the bulk silicide product (Pd₂Si) and then to interpret the interface electronic structure (low-coverage spectra) on the basis of their comparison with the bulk silicide electronic structure.

An example of this problem was already shown and discussed in conjunction with Fig. 2. As the Pd coverage is increased above ~ 12 Å the main *d*-band peak of Pd₂Si appears to shift closer to E_F ; this is because at 25 °C the reaction has not gone to completion at the outer surface of the overlayer. Here unreacted Pd metal is mixed with Pd₂Si (or possibly the Pd₂Si is Pd rich), giving a composite surface spectrum with a *d*-band peak position between that of Pd₂Si and Pd metal.

Other examples of this “under-reaction” condition of the surface are illustrated by two dashed curves in Fig. 8, which correspond to different Pd coverages deposited at room temperature. It is clear that the *d*-band peak position can be varied continuously from ~ -3.5 to ~ -1.5 eV by changing the coverage for a 25 °C deposition temperature. In contrast, we found that a brief (\sim few minutes) annealing at ~ 200 °C returns surface spectra essentially to that of Pd₂Si, as indicated by the solid curve in Fig. 8 as well as the 12 Å curve in Fig. 2.

Figure 7 shows that the work-function behavior with coverage changes at $\phi \cong 5.0$ – 5.1 eV, indicating a ϕ value in this range for bulk Pd₂Si. Since both the work function and the *d*-band peak position E_{PEAK}

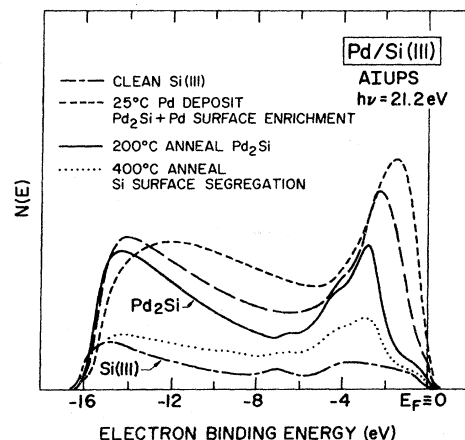


FIG. 8. AIUPS spectra: (i) dot-dash curve—the clean Si(111) surface; (ii) dashed curves—the “under-reacted” Pd₂Si surface, i.e., Pd₂Si enriched at the surface by excess unreacted Pd metal; (iii) solid curve—Pd₂Si (surface and bulk), formed by 200 °C annealing; (iv) dotted curve—the “over-reacted” Pd₂Si surface, i.e., Si-enriched by Si surface segregation.

are sensitive to and vary with Pd coverage (but in different ways), we used their correlation to determine ϕ and E_{PEAK} characteristic of bulk Pd₂Si. This relation is depicted in Fig. 9(a) for Pd/Si(111). The very-thin-film-deposition results are shown by solid dots, and E_{PEAK} in this case corresponds to the d -band peak position from the incremental difference curves. As also seen in Fig. 7, ϕ increases from the clean Si(111) value (4.6 eV) to ~ 5.04 eV as the E_{PEAK} increases. Once $\phi \cong 5.04$ eV is reached, ϕ increases only very slowly while E_{PEAK} shifts closer to E_F with the presence of additional unreacted Pd metal at the surface; this unreacted metal makes a direct contribution to shifting the peak but does not change ϕ significantly because $\phi_{\text{Pd}} \cong 5.6$ eV, considerably larger than $\phi_{\text{Pd}_2\text{Si}} \cong 5.04$ eV. This behavior is a clear indication that the surface is composed of Pd₂Si regions and unreacted Pd metal regions.

The thick-film annealing behavior is also depicted

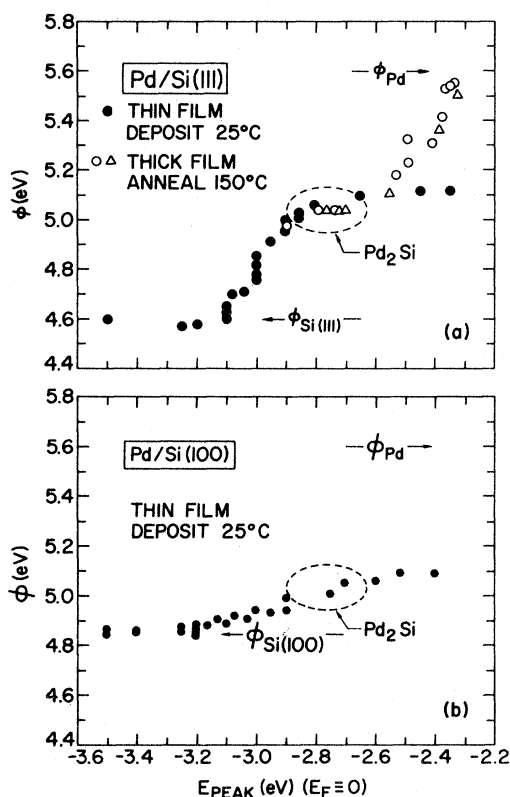


FIG. 9. Work function vs d -band peak position from UPS as obtained from thin-film deposition steps at 25°C (solid dots) and from thick-film annealing (150°C) steps (open circles and triangles). The plateau regions (surrounded by dashed line) near $E_{\text{PEAK}} = -2.75$ eV and $\phi = 5.04$ eV indicate where the surface is essentially Pd₂Si, like the underlying bulk.

in Fig. 9(a), by open circles and triangles. In this case ϕ starts from about the Pd metal value and decreases to the Pd₂Si value as the silicide formation reaction reaches the top surface. Note that in both the thick-film-annealing and thin-film-deposition results ϕ reaches a plateau at the same value, $\phi \cong 5.04$ eV. We therefore identify this as $\phi_{\text{Pd}_2\text{Si}}$. This state of the surface occurs for $E_{\text{PEAK}} \cong -2.75$ eV, which thus represents the d -band peak position for bulk Pd₂Si. The area enclosed by the dashed line in Fig. 9(a) indicates an approximate parameter space in which the surface region of a Pd₂Si film is essentially Pd₂Si, like the underlying bulk.

The ϕ vs E_{PEAK} results for Pd/Si(100) are shown in Fig. 9(b). The behavior is similar to that of Pd/Si(111) except that the initial work function for the clean surface is higher.

These results demonstrate that the “under-reaction” or Pd surface enrichment problem at the top surface occurs at 25°C only if the film is ≥ 10 –15 Å; at lower coverage the top surface is sufficiently close to the initial Pd/Si interface that all the Pd is converted into Pd₂Si form by the interface-driven reaction. With annealing for several minutes at 150–200°C, a thicker overlayer can be transformed completely into Pd₂Si.

Annealing at still higher temperatures like 400°C (or possibly much longer annealing times at ~ 200 °C) produces yet a different effect, as shown by the dotted AIUPS curve in Fig. 8. The line shape changes somewhat and the emission intensity is reduced considerably. The correlation between the AIUPS and the AES spectral changes, depicted in Fig. 10, demonstrates that the 400°C annealing cycle (“over-reaction” condition) decreases the Pd/Si concentration ratio at the surface dramatically.³⁷ It also returns the Si $L_{2,3}$ VV AES line shape to its elemental

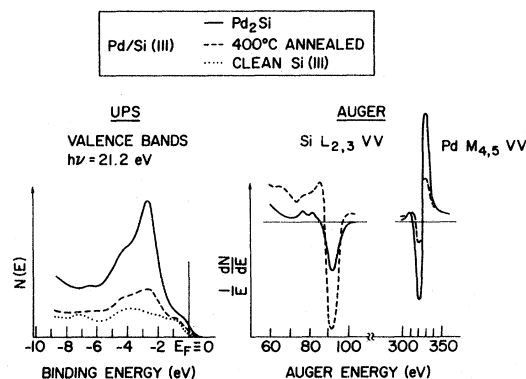


FIG. 10. Si surface segregation effects on Pd₂Si surface spectra induced by 400°C annealing (“over reaction”).

Si form, suggesting that the surface layer(s) may be relatively free of Pd and perhaps covalently bonded. Finally, we find that exposure of this "over-reacted" surface to oxygen produces an AIUPS spectrum like that resulting from oxygen exposure to the clean Si surface; in contrast, the Pd₂Si surface formed by 200 °C annealing is relatively inert to oxygen exposure.

Whereas the cause of the "under-reaction" condition (Pd surface enrichment) is clearly the fact that the silicide formation rate is lower further from the interface, the cause of the "over-reaction" condition (Si surface segregation) is less obvious. One possibility is that the solubility of Si in Pd₂Si is temperature dependent, so that at 400 °C more Si dissolves and must then segregate back into the Si or to the Pd₂Si surface upon cooling to 25 °C (at which the measurements were made). The possibility is being checked experimentally. Alternatively, the surface free energy may be reduced (for some unknown reason) by the presence of a Si layer at the vacuum interface.

IV. DISCUSSION

A. Reaction behavior

The UPS and AES spectra presented here demonstrate clearly that the clean Pd/Si interface is reactive. As emphasized by previous work,³⁻⁵ this implies that a meaningful understanding of the Pd/Si Schottky barrier requires detailed knowledge of the microscopic interfacial chemistry. By measuring the dependence on reaction parameters such as temperature, source supply (here Pd thickness), etc., it has been possible to determine how the state of the system varies with these parameters, then to deduce the surface spectroscopic properties of the Pd₂Si reaction product, and from this to have a basis for interpreting observations of the initial stages of interface formation.

Although some characteristics of the very low coverage results remain to be discussed in detail and evaluated below, it is clear from Sec. III E that a well defined Pd₂Si compound is formed at ~3–12 Å Pd coverage from ~180 K to ~room temperature. At higher coverage the surface of the overlayer becomes partially unreacted. The reaction product and processing temperatures are similar on the atomically clean Si(111) and Si(100) surfaces. The evolution of the partially unreacted surface for sufficiently thick films at ~25 °C demonstrates that the initial stage of the silicide formation reaction (Pd₂Si formation at the Pd/Si interface) proceeds considerably faster than the growth rate of thicker silicide films (i.e., after some Pd₂Si is present). This may be a consequence of the heat of adsorption of Pd on Si, the energy of which could be sufficient to promote the initial step spontaneously even at low temperatures.

B. Low-coverage reaction product

As discussed earlier, the evidence supports an identification of the interfacial material formed at low coverage as a Pd₂Si-like compound. First, the low-coverage UPS and AES spectra (difference curves) are strikingly similar in shape to those for bulk Pd₂Si. Second, this similarity holds both for the Si local density of states (as seen in the Si *L*_{2,3} *VV* AES spectrum) and for the Pd density of states (which dominates the UPS spectrum). Recent TEM vertical sectioning results^{38,39} for the buried interface show the lattice fringes of the Pd₂Si overlayer and the Si substrate continuing to an atomically abrupt interface. Identifying the low-coverage reaction product as a Pd₂Si-like compound provides a reasonable starting point for the abrupt buried interface, for the interface-driven character of the reaction, and for epitaxial Pd₂Si growth on Si(111). It also gives physical insight into the microscopic chemical origin of the interface electronic structure observed during the initial stages of interface formation; it says essentially that the metal-induced states at the interface are primarily those of the Pd₂Si-like compound formed.

C. Spectroscopically observed chemical shifts

However, the low-coverage spectra are not completely equivalent to those of bulk Pd₂Si. The *d*-band peak position in UPS appears ~0.75 eV further below *E*_F than in Pd₂Si and shifts smoothly with coverage. With increasing coverage, the highest-energy AES peak near 94 eV also shifts toward higher energy and decreases in intensity relative to the other AES peaks. As explained previously,²¹ this peak is associated with Si(3*p*)-Pd(4*d*) antibonding states, so that its energy shifts may be related to those of the main *d*-band peak observed in the UPS spectrum.

It is interesting to note that these chemical shifts seem to persist to Pd coverages considerably larger than both the first monolayer or so and also the screening length (~1 Å) in the metallic Pd₂Si film. In the AES spectra (Fig. 6), the position and relative intensity of the 94-eV peak continue to change even out to 30 Å Pd coverage. Since this particular feature of the Si *L*_{2,3} *VV* AES spectrum is associated specifically with those Si atoms bonded to Pd in silicide form, these variations are relatively free of complications from the "under-reaction" and "over-reaction" phenomena discussed in Sec. III E. In the UPS spectra (Figs. 3 and 4), the *d*-peak shifts are most dramatic in the first Å but are still clearly evident at ~12 Å coverage. The UPS shifts persist on fully reacted Pd₂Si films to ~100 Å,¹⁸ although a slight "under-reaction" or "over-reaction" condition could contribute to an apparent peak shift in these measurements. We recognize, however, that the smaller

peak shifts observed in the 10–100 Å coverage range are further complicated by the finite electron escape depth ($\sim 7\text{--}20$ Å), which can broaden the coverage range over which peak shifts are detected.

1. Interface strain

Strain caused by lattice mismatch at the interface could alter the electronic structure near the boundary and cause changes for tens of Å or more from the interface. For Pd/Si(111) (the epitaxial case) the Pd₂Si basal plane lattice constants were in fact found to increase at low coverage toward the Si(111) value, and at the same time the *d*-band peak shifted to larger binding energy. However, virtually identical *d*-peak shifts with coverage are observed (Fig. 4) for Pd/Si(100), where no epitaxial relationship exists and interface strains should be different. Unless the Pd/Si(100) interface would be drastically reconstructed to consist of Pd/Si(111) facets, it is difficult to accept interface strain as the explanation for the coverage-dependent chemical shifts.

2. Stoichiometry variations

An attractive explanation for these chemical shifts is stoichiometry changes within the Pd₂Si compound near the interface. The Si concentration gradient across an abrupt Pd₂Si/Si interface seems a logical driving force for motion of Si atoms across the boundary. In this way Si-rich Pd₂Si would be produced near the interface with a stoichiometry in the Pd₂Si graded over $\sim 10\text{--}100$ Å to reduce the local Si concentration gradient throughout the film. The low-coverage spectra would reflect the Si-rich stoichiometry of the Pd₂Si compound formed, and with increasing coverage the surface region measured would be further from the Pd/Si interface and thus less Si rich, presumably reaching exactly Pd₂Si for very thick, fully reacted overlayers.

Evidence supporting this explanation comes from three sources. First, self-consistent calculations for several Pd-Si compounds of different stoichiometry have revealed how density-of-states features in Pd-Si compounds change with stoichiometry.²¹ These calculations employed the augmented-spherical-wave method and treated Pd₂Si, PdSi, and PdSi₃ compounds in the Cu₃Au, CuAu, and CsCl structures, with lattice constants determined by total energy minimization. For Pd₃Si, the local Si environment (only Pd nearest neighbors) was close to that in Pd₂Si. Although details of the calculated density of states changed somewhat with crystal structure for a given compound, the essential qualitative features of the Pd-Si chemical bonding were unaffected, and overall energy positions of structure did not change

dramatically with reasonable variations in lattice constant. Furthermore, the calculated densities of states are consistent with more detailed self-consistent calculations of the real Pd₂Si compound carried out by Pandey.⁴⁰

These results illustrate the qualitative effects of stoichiometry changes clearly. The Pd-Si bonding occurs by the formation of Pd(4*d*)-Si(3*p*) bonding and antibonding states which lie, respectively, below and above the main Pd(4*d*) peak in the total density of states.²¹ With increasing Pd concentration, the antibonding states and the main Pd(4*d*) peak shift toward higher energy; in going from PdSi to Pd₃Si, the antibonding states become empty. Phase stability may be expected when a fraction of the antibonding states are emptied, so that from these calculations a stable stoichiometry might be anticipated somewhere between PdSi and Pd₃Si; this agrees with the fact that Pd₂Si is the stable compound. The observed UPS shift of the main *d*-band peak up toward E_F with increasing coverage and its interpretation as a decrease in the Si excess of the Pd₂Si (i.e., increased Pd concentration) is consistent with the trends predicted by these calculations, as is the shift of the Si $L_{2,3}VV$ 94-eV peak toward higher energy with coverage.

The second body of evidence that the chemical shifts arise from stoichiometry variations in the Pd₂Si film comes from measurements of the spectra^{41–44} of Pd_{1-x}Si_x metallic glasses, which occur over the range $x \sim 0.15\text{--}0.25$. For these Pd-Si mixtures, which are richer in Pd than is Pd₂Si, the main *d* peak occurs within ~ 2 eV of E_F , i.e., closer to E_F than observed here for Pd₂Si. Furthermore, the UPS line shape and work function ($\phi = 4.95 \pm 0.1$ eV, Ref. 42) are very similar to that for Pd₂Si. Finally, the *d* peak moves monotonically upward toward E_F with increasing Pd concentration of the metallic glass.⁴⁴ These observations are all consistent with the calculations²¹ and with our interpretation that the low-coverage Pd/Si spectra represent more Si-rich Pd₂Si than the truly stoichiometric compound and that the amount of Si excess in the well-defined Pd₂Si film decreases with coverage of distance from the interface. Extrapolating from the *d*-peak shift with concentration in the metallic glasses,⁴⁴ the apparent concentration seen by UPS at lowest coverage might be as high as $\sim 45\text{--}60\%$ Si; at higher coverage (≥ 4 Å) where smaller chemical shifts from bulk Pd₂Si positions are observed, the Si concentration should be not more than a few percent Si excess for unannealed samples.

The third source of evidence supporting stoichiometry variations in the Pd₂Si overlayer film comes from TEM measurements of the basal plane lattice constants $a_0/2$ of fully reacted Pd₂Si films on Si(111).¹⁸ These show that with increasing Pd₂Si film thickness from 20 to 300 Å the $a_0/2$ value decreases from 6.58 to 6.52 Å; at the same time the *d*-peak position shifts toward E_F from -2.93 to -2.76 eV.

X-ray powder studies⁴⁵ have indicated that larger $a_0/2$ values are obtained for "Si-rich" than for "Pd-rich" Pd₂Si, although measurements were confined to the range $a_0/2 = 6.50\text{--}6.52$ Å and stoichiometry was not quantified. This would suggest that at lower coverage, where larger d -peak binding energies and corresponding larger $a_0/2$ values are observed, the Pd₂Si is more Si-rich than at higher coverage.⁴⁶

Thus it seems reasonable to interpret the coverage-dependent chemical shifts as evidence that a Si-rich Pd₂Si-like compound is formed at very low coverage and that the amount of Si excess in the Pd₂Si overlayer decreases with distance from the interface. This inference forms a considerable part of the basis for a theory of silicide Schottky barriers proposed by Freeouf.⁴⁷ In this theory, the work function on the metal side of the contact is shifted from a silicide value considerably toward that of elemental Si by the Si-rich stoichiometry of the silicide at the interface; the Schottky barrier height, which scales with the work-function difference across the interface in a simple Schottky picture,⁴⁸ then exhibits considerably less variation with different metal silicides than would be expected from metal or metal silicide work functions.

3. Chemical environment and interface state effects

For the low-coverage regime there exist other explanations for the relatively large chemical shifts observed with coverage, based on the specific chemical environment of atoms nearest the interface. First, Pd–Si bonds in the silicide closest to the Si substrate may appear in these electron spectroscopy measurements to be in a Si-rich environment due to the elemental Si charge density which forms part of that environment. Second, some of the Pd–Si bonds may differ from those of the bulk silicide due to particular structural arrangements present only near the interface. Third, a high density of metal atom interstitials within the Si lattice could appear spectroscopically as a Si-rich silicide.⁴⁹ Differentiating between true stoichiometry variations, local chemical environment effects (effective stoichiometry variations), and altered interface bonding arrangements in the low-coverage regime represents a difficult semantic and conceptual, as well as experimental task, so we cannot at present suggest which of these pictures (if any) is more meaningful and accurate an explanation for the chemical shifts observed at low coverage.

Other electronic states in the band gap may be produced near the interface in addition to the metallic states of the bulk silicide. This can be inferred from differences between the low-coverage spectra and the bulk Pd₂Si spectra in the Si band-gap region. Besides the shift of the 94-eV peak (associated with states just below E_F) in the Si $L_{2,3}VV$ AES spectrum toward higher energy with increasing coverage (Fig. 6),

its intensity is enhanced at low coverage relative to other peaks in the spectrum (this effect has been noted previously by Roth and Crowell⁵⁰). That the enhancement is more readily seen in the AES spectra than in UPS may result from the fact that Si $L_{2,3}VV$ AES spectrum is specific to the local Si atom density of states (much of which is concentrated in the bonding and antibonding bands), while the UPS spectra are dominated by much stronger Pd d -electron contributions elsewhere in the spectrum. This enhancement of the density of states in the band gap region (near E_F) may represent additional states characteristic of the interface. Such states could provide an alternative explanation for the spectroscopically observed chemical shifts as well as for the enhancement of the 94-eV AES peak. This question deserves further detailed study in the future.

V. CONCLUSIONS

The main conclusions of this study may be summarized as follows:

(i) Silicide compound formation (Pd₂Si) dominates the microscopic chemistry and properties of the clean Pd/Si interface.

(ii) Consequently, the interface electronic structure in the initial stages of interface formation—and presumably for the thick metal contact (buried interface) as well—is primarily that of Pd₂Si: strong Pd($4d$) bands about 3 eV below E_F with bonding Pd($4d$)-Si($3p$) bands below and corresponding antibonding bands near E_F forming the conducting states of the metallic Pd₂Si compound.

(iii) Reactivity at the clean interface is very high: silicide formation occurs spontaneously at the interface even at temperatures as low as 180 K.

(iv) Coverage-dependent chemical shifts in the spectroscopy measurements can be interpreted as evidence for interface-driven stoichiometry variations (real or effective) in the Pd₂Si overlayer; these would consist of Si-rich Pd₂Si near the interface, with a graded stoichiometry (Si excess) which decreases with distance from the interface.

(v) The observed work-function behavior can be fully understood on the basis of Pd₂Si compound formation and the thin-film kinetics phenomena (Pd surface enrichment due to incomplete reaction, Si surface segregation by "over reaction") which occur. As a result, the ϕ behavior provides no direct evidence for interface dipole formation (although such a contribution cannot be ruled out); instead, it gives a very sensitive measure of the thin-film reaction kinetics and surface segregation phenomena.

(vi) As a consequence of interface reactivity, the reaction kinetics of the thin overlayer film becomes an important experimental complication, especially when surface-sensitive spectroscopic techniques like

UPS and AES are used. However, by studying the dependence on thermal history, it is possible to obtain reliable results from these techniques.

This study has produced a relatively simple picture of the microscopic chemical behavior at the Pd/Si interface, in which compound formation has been clearly identified and plays a dominant role in determining the interface electronic properties. This suggests the possibility that similar chemical processes might equally well explain previous results in other metal-semiconductor systems. For example, Pd-GaAs reactions are known to produce various compounds⁵¹ like Pd₂Ga, PdGa, and PdAs₂. The UPS difference spectrum for 2–3 monolayers of Pd on GaAs(110)⁵² is very similar to that of Pd₂Si: its dominant *d* peak occurs at ~ -2.5 eV with a full width at half maximum of ~ 3 eV. This suggests that compound formation may take place at the Pd/GaAs(110) interface, although the identity of the reaction product is not known.

The insight which has come from the present study of the Pd/Si interface partly results from the fact that the chemical reaction is simple, producing a single product—Pd₂Si. This characteristic was anticipated from previous thin-film studies (albeit under less controlled interface conditions) and played an important role in the choice of this particular reactive interface. Although some of the other silicide-forming interfaces may produce multiple products, rather extensive thin-film results are available for such systems.

In contrast, no bulk compounds are known for the simple metals (Al, Ga, and In) on Si. This makes it

difficult to characterize what (if any) chemical reactions may have occurred at the corresponding interfaces. Identifying reactions at compound semiconductor interfaces is made difficult by (i) the larger number of possible reaction products, (ii) the simultaneous presence of several reaction products, and (iii) the possibility of preferential surface segregation.^{53,54} This underscores the need for more thin-film investigations of reactions between metals and compound semiconductors. In spite of these problems, significant progress has been made in identifying chemical reactions at clean metal/III–V semiconductor interfaces, such as the exchange reaction for Al/GaAs.⁵⁵

The results presented in this paper have demonstrated that surface spectroscopy techniques can reveal the microscopic chemical processes occurring at the reactive metal/Si interface and display many aspects of the interface electronic structure. The further challenge is to develop reliable techniques for *in situ* monitoring of changes in the Schottky barrier height at low metal coverage and/or to correlate the interface electronic properties and microstructure with the electrical properties of the bulk contact, so that the mechanism(s) which really determine the Schottky barrier height can be identified.

ACKNOWLEDGMENT

Supported in part by the Office of Naval Research.

¹See, e.g., J. Vac. Sci. Technol. **11**, 935–1028 (1974).

²J. Bardeen, Phys. Rev. **71**, 717 (1947).

³G. Margaritondo, J. E. Rowe, and S. B. Christman, Phys. Rev. B **14**, 5396 (1976).

⁴J. E. Rowe, S. B. Christman, and G. Margaritondo, Phys. Rev. Lett. **35**, 1471 (1975); G. Margaritondo, S. B. Christman, and J. E. Rowe, J. Vac. Sci. Technol. **13**, 329 (1976).

⁵L. J. Brillson, J. Vac. Sci. Technol. **15**, 1378 (1978); Phys. Rev. Lett. **40**, 260 (1978); Phys. Rev. B **18**, 2431 (1978).

⁶R. Ludeke, Phys. Rev. Lett. **39**, 1043 (1977).

⁷H. I. Zhang and M. Schlüter, Phys. Rev. B **18**, 1923 (1978); J. Vac. Sci. Technol. **15**, 1384 (1978).

⁸V. Heine, Phys. Rev. **138**, A1689 (1965).

⁹J. Ihm, S. G. Louie, and M. L. Cohen, Phys. Rev. B **18**, 4172 (1978).

¹⁰J. C. Phillips, Phys. Rev. B **1**, 593 (1970).

¹¹J. C. Inkson, J. Phys. C **5**, 2599 (1972); **6**, 1350 (1973); J. Vac. Sci. Technol. **11**, 943 (1974).

¹²J. C. Phillips, J. Vac. Sci. Technol. **11**, 947 (1974).

¹³P. W. Chye, I. Lindan, P. Pianetta, C. M. Garner, C. Y. Su, and W. E. Spicer, Phys. Rev. B **18**, 5545 (1978).

¹⁴R. H. Williams, V. Montgomery, and R. R. Varma, J. Phys. C **11**, L735 (1978).

¹⁵K. 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.

¹⁶J. M. Andrews and J. C. Phillips, Phys. Rev. Lett. **35**, 56 (1975).

¹⁷G. Ottaviani, K. N. Tu, and J. W. Mayer, Phys. Rev. Lett. **44**, 284 (1980).

¹⁸J. L. Freeouf, G. W. Rubloff, P. S. Ho, and T. S. Kuan, Phys. Rev. Lett. **43**, 1836 (1979).

¹⁹J. L. Freeouf, G. W. Rubloff, P. S. Ho, and T. S. Kuan, J. Vac. Sci. Technol. **17**, 916 (1980).

²⁰G. W. Rubloff, in Proceedings of the 8th International Vacuum Congress, Cannes, France, edited by F. Abelès and M. Croset (Supplément à la Revue "LeVide, les Couches Minces" No. 201), Vol. I, p. 562.

²¹P. S. Ho, G. W. Rubloff, J. E. Lewis, V. L. Moruzzi, and A. R. Williams, Phys. Rev. B **22**, 4784 (1980).

²²(a) P. J. Grunthaner, F. J. Grunthaner, and J. W. Mayer, J. Vac. Sci. Technol. **17**, 924 (1980). (b) L. Braicovich, I. Abbati, J. N. Miller, I. Lindau, S. Schwarz, P. R. Skeath, C. Y. Su, and W. E. Spicer, J. Vac. Sci. Technol. **17**, 1005 (1980). (c) J. N. Miller, S. A. Schwarz, I. Lindau, W. E. Spicer, B. de Michelis, I. Abbati, and L. Braicovich, J. Vac. Sci. Technol. **17**, 920 (1980).

- ²³Commercially available as the IBM 7406 Device Coupler.
- ²⁴P. S. Ho, T. Y. Tan, J. E. Lewis, and G. W. Rubloff, *J. Vac. Sci. Technol.* **16**, 1120 (1979).
- ²⁵D. E. Eastman, F. J. Himpsel, J. A. Knapp, and K. C. Pandey, in *Proceedings of the 14th International Semiconductor Conference, Edinburgh, 1978*, edited by B. L. H. Wilson (Institute of Physics and Physical Society, London, 1979).
- ²⁶F. J. Himpsel and D. E. Eastman, *Phys. Rev.* **18**, 5236 (1978).
- ²⁷W. D. Buckley and S. C. Moss, *Solid State Electron.* **15**, 1331 (1972).
- ²⁸U. Köster, K. N. Tu, and P. S. Ho, *Appl. Phys. Lett.* **31**, 634 (1977).
- ²⁹F. J. Himpsel and D. E. Eastman, *J. Vac. Sci. Technol.* **16**, 1297 (1979).
- ³⁰D. E. Eastman and W. D. Grobman, *Phys. Rev. Lett.* **30**, 177 (1973).
- ³¹C. Norris, *J. Appl. Phys.* **40**, 1396 (1969).
- ³²S. Weng and M. El-Batanouny, *Phys. Rev. Lett.* **44**, 612 (1980).
- ³³W. Gaebler, K. Jacobi, and W. Ranke, *Surf. Sci.* **75**, 355 (1978).
- ³⁴W. F. Egelhoff, Jr., and G. G. Tibbetts, *Phys. Rev. B* **19**, 5028 (1979); G. G. Tibbetts and W. F. Egelhoff, Jr., *J. Vac. Sci. Technol.* **16**, 661 (1979).
- ³⁵G. Heiland and H. Lamatsch, *Surf. Sci.* **2**, 18 (1964).
- ³⁶Most reported measurements (derived mainly from UPS studies) agree with this value, including: F. G. Allen and G. W. Gobeli, *J. Appl. Phys.* **35**, 597 (1964); M. Erbudak and T. E. Fischer, *Phys. Rev. Lett.* **29**, 732 (1972); J. E. Rowe, *Phys. Lett.* **46A**, 400 (1974); J. E. Rowe, H. Ibach, and H. Froitzheim, *Surf. Sci.* **48**, 44 (1975); W. Monch, *ibid.* **63**, 79 (1977). The origin of the value 0.55 eV from UPS measurements given in Ref. 3 remains unclear. In contrast, much lower values have been deduced from surface photovoltage spectroscopy [0.36 eV, J. Clabes and M. Henzler, *Phys. Rev. B* **21**, 625 (1980)] and from photoemission threshold measurements [0.3 eV, C. Sebenne, D. Bolmont, G. Guichar, and M. Balkanski, *Phys. Rev. B* **12**, 3280 (1975)]. The source of these differences is not fully understood at present. For the purposes of discussion, we use the UPS value of 0.79 eV.
- ³⁷K. Oura, S. Okada, and T. Hanawa, *Appl. Phys. Lett.* **35**, 705 (1979).
- ³⁸P. S. Ho, H. Föll, J. E. Lewis, and P. E. Schmid, in *Proceedings of the 4th International Conference on Solid Surfaces, Cannes, 1980*, edited by D. A. Degras and M. Costa (Supplément à la Revue "Le Vide, les Couches Minces" No. 201), Vol. II, p. 1376.
- ³⁹H. Föll, P. S. Ho, and K. N. Tu, *J. Appl. Phys.* (in press).
- ⁴⁰K. Pandey (unpublished).
- ⁴¹S. R. Nagel, G. B. Fisher, J. Tauc, and B. G. Bagley, *Phys. Rev. B* **13**, 3284 (1976).
- ⁴²J. D. Riley, L. Ley, J. Azoulay, and K. Terakura, *Phys. Rev. B* **20**, 776 (1979).
- ⁴³P. Oelhafen, M. Liard, H.-J. Güntherodt, K. Berresheim, and H. D. Polaschegg, *Solid State Commun.* **30**, 641 (1979).
- ⁴⁴B. J. Wacławski and D. S. Boudreaux, *Solid State Commun.* **33**, 589 (1980).
- ⁴⁵A. Nylund, *Acta Chem. Scand.* **20**, 2381 (1966).
- ⁴⁶Since we have not measured $a_0/2$ versus thickness for Pd₂Si on Si(100), we cannot at present rule out the possibility that the $a_0/2$ variations on Si(111) result from strain at the epitaxial interface and are unrelated to the d -peak shifts. The d -band deformation potentials (energy shift per unit strain) in this case would have plausible values as compared to the range of optical (interband) deformation potentials of solids; see, e.g., M. Cardona, *Modulation Spectroscopy* (Academic, New York, 1969).
- ⁴⁷J. L. Freeouf, *Solid State Commun.* **33**, 1059 (1980).
- ⁴⁸W. Schottky, *Z. Phys.* **118**, 539 (1942).
- ⁴⁹N. W. Cheung and J. W. Mayer, *Phys. Rev. Lett.* **46**, 671 (1981).
- ⁵⁰J. A. Roth and C. R. Crowell, *J. Vac. Sci. Technol.* **15**, 1317 (1978); see also J. A. Roth, Ph.D. dissertation, (University of Southern California, 1979) (unpublished).
- ⁵¹J. O. Olowafe, P. S. Ho, H. J. Hovel, J. E. Lewis, and J. M. Woodall, *J. Appl. Phys.* **50**, 955 (1979).
- ⁵²D. E. Eastman and J. L. Freeouf, *Phys. Rev. Lett.* **34**, 1624 (1975).
- ⁵³A. Hiraki, K. Shuto, S. Kim, W. Kammura, and M. Iwami, *Appl. Phys. Lett.* **31**, 611 (1977).
- ⁵⁴I. Lindau, P. W. Chye, C. M. Garner, P. Pianetta, C. Y. Su, and W. E. Spicer, *J. Vac. Sci. Technol.* **15**, 1332 (1978).
- ⁵⁵L. J. Brillson, R. Z. Bachrach, R. S. Bauer, and J. C. McMenamin, *Phys. Rev. Lett.* **42**, 397 (1979).