

Microscopic Compound Formation at the Pd-Si(111) Interface

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Photoemission studies of Pd on clean Si(111) surfaces show that formation of the Pd₂Si compound dominates the microscopic chemistry and properties of the Pd-Si interface. No evidence is found for interface dipoles or occupied metal-induced interface states in this system. The Pd₂Si reaction product (a metal) has an electronic structure more like that of the noble metals than the transition metals, with an occupied 4d band located ~2.75 eV below the Fermi energy.

Phenomena intrinsic to the abrupt metal-semiconductor interface can in principle determine the Schottky barrier height (SBH).¹ Recent experimental results have been interpreted as evidence for some of these phenomena, including metal-induced gap states,² interface dipole formation,^{2,3} etc. These experiments have also demonstrated that chemical interactions strongly affect these phenomena, but characterizing these interactions is difficult.²⁻⁴

We have chosen to study a particular metal-Si interface,⁵ Pd-Si(111), because extensive thin film results establish that reaction at up to 700 °C yields a single product (Pd₂Si-Si).⁶ We find no evidence for the formation of occupied interface states or interfacial dipole layers. Instead, the evolution of the electronic structure (density of states and work function) from submonolayer metal coverage to thick metal contacts on Si(111) can be fully understood simply on the basis of Pd₂Si compound formation.

The Si(111) samples were cleaned in UHV (base pressure $\sim 1 \times 10^{-10}$ Torr) by ion bombardment and annealing (via resistive heating) at up to 850 °C. Pd overlayers were evaporated by direct sublimation from a resistively heated Pd wire. Estimated Pd coverages are given in terms of equivalent Pd metal thicknesses. Surface electronic structure was measured by angle-resolved and angle-integrated ultraviolet photoemission spectroscopy (ARUPS and AIUPS, respectively) complemented by Auger, low-energy electron diffraction, and transmission electron microscopy (TEM) studies. Studies on both the (7×7) reconstructed Si(111) surface and a (1×1) Si(111) surface [probably representing a disordered (7×7)] were carried out and gave essentially the same results. The silicide reaction product was approached by (i) sequential annealing cycles of relatively thick metal films on Si(111) and (ii) sequential depositions of thin (submonolayer) metal films onto the Si(111) surface.

Figure 1 presents ARUPS results for sequential annealing cycles of a thick Pd film (~300 Å) deposited at 25 °C on clean Si(111). Normal emission spectra before annealing [as shown in Fig. 1(a)] are nearly identical to those for Pd(111) (Ref. 7) [TEM studies of a similar film showed strong (111) texture], indicating unreacted Pd metal exists at the film surface (away from the Pd-Si interface). Three successive 150 °C annealing steps (30 sec each) strongly modify the ARUPS spectral shape [Figs. 1(b)–1(d)] and reduce the work function ϕ (photon energy $h\nu$ minus the width of the UPS spectrum); two subsequent anneals [Figs. 1(e) and 1(f)] shift the dominant peak near -3 eV slightly toward lower energy without changing ϕ or the overall spectral shape. (The ARUPS spectra at this point are insensitive to $h\nu$, angle of incidence, or angle of emission variations, in contrast to those for the deposited Pd film.) TEM studies established that this film [Fig. 1(f)]

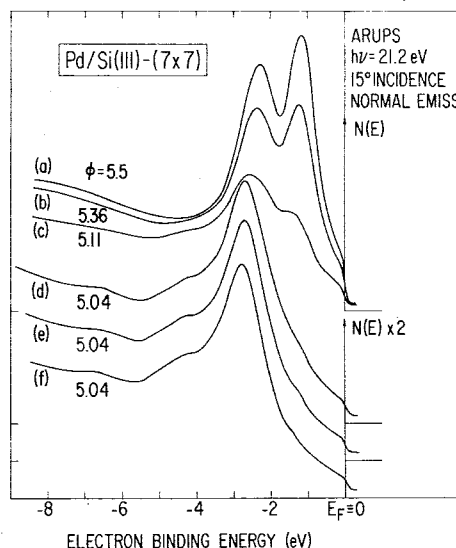


FIG. 1. (a) ARUPS spectra for ~300 Å Pd deposited on Si(111) at 25 °C; (b)–(f) subsequent spectra taken after stepwise annealing cycles of 30 sec at 150 °C.

was continuous and fully reacted to Pd₂Si, with no other phases detectable. As explained below, we attribute the dominant peak near -2.75 eV in Figs. 1(d)–1(f) to the Pd-4*d* band of Pd₂Si, which has $\phi \approx 5.04$ eV.

AIUPS results for the sequential deposition of submonolayer quantities of Pd on clean Si(111) are shown in Fig. 2 and reveal the initial stages of Pd₂Si formation. The spectrum of clean Si(111) is shown [Fig. 2(a)] for comparison. The additional AIUPS emission for ~ 0.25 -Å Pd deposited at room temperature ($\sim 25^\circ\text{C}$) is shown by the dashed difference curve in Fig. 2(b), and incremental difference curves for two additional depositions are shown in Figs. 2(c) and 2(d). The spectral changes for submonolayer Pd coverage are very similar in shape to the spectra for Pd₂Si layers [Figs. 2(e), 2(f), and 1(f)] except that the *d*-band peak shifts with coverage from ~ -3.5 eV at low coverage to its final position at ~ -2.75 eV at higher coverage (≈ 4 –8 Å). TEM studies of films prepared as in Fig. 2(f) also showed continuous single-phase Pd₂Si, and *in situ* Auger composition analysis gave a Pd₂Si stoichiometry.⁸ Thus Pd-Si(111) demonstrates a high degree of interface reactivity in the initial stages of compound formation, producing Pd₂Si readily at the metal-semiconductor interface even at

room temperature.

These results present the first direct observation of the electronic structure and density of states of a well-defined metal silicide compound. We identify the strong asymmetric peak at ~ -2.75 eV in Pd₂Si as primarily the Pd 4*d* band. Both the UPS and the Pd *M*_{4,5}*VV* Auger spectra show that the Pd-4*d* bandwidth in Pd₂Si is similar to that in Pd metal but shifted to lower energy. Because the 4*d* band is well below E_F , the electronic properties of Pd₂Si should be more like those of the noble metals than of the transition metals. In contrast, the Si *L*_{2,3}*VV* Auger spectrum exhibits new structure characteristic of the silicide, indicating strong changes in the Si electronic structure,^{8,9} which may contribute to the shape of the UPS *d*-band peak. Difference curves for the Si *LVV* Auger spectrum show the characteristic silicide features for coverages ≤ 1 Å.⁸

TEM lattice-constant measurements¹⁰ were performed on three fully reacted Pd₂Si films and a fourth, partially reacted film [Pd metal on ~ 100 Å Pd₂Si on Si(111)]. As shown in Table I, the basal plane lattice constant $a_0/2$, work function, and *d*-band peak position varied with Pd thickness in a correlated fashion. Although lattice strain caused by the 6.65-Å Si(111) substrate spacing may partially explain the larger $a_0/2$ for thinner films, we believe stoichiometry variations also contribute to the changes in $a_0/2$: X-ray powder studies¹¹ show larger $a_0/2$ for "Si rich" than for "Pd rich" Pd₂Si (although stoichiometry was not quantified). In spite of these variations, the crystal structure of Pd₂Si is fixed, $a_0/2$ varies by $\leq 2\%$, ϕ varies by $\leq 1\%$, and the shape of the density of states persists even though the *d*-band peak shifts by up to ~ 0.75 eV.

The marked similarity between the low-coverage spectra [Figs. 2(b), 2(c), 2(d)] and the Pd₂Si spectra strongly suggest that a Pd₂Si-like com-

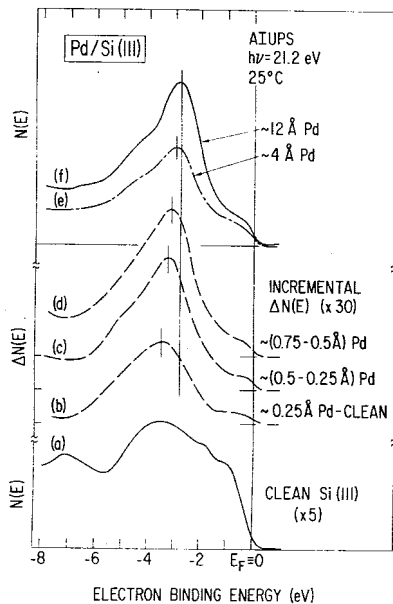


FIG. 2. (a) AIUPS spectrum for clean Si(111); (b)–(d) incremental difference spectra showing additional emission from ~ 0.25 Å added Pd (equivalent metal thickness) at 25°C ; (e) spectrum of ~ 4 Å Pd on Si(111) at 25°C ; (f) spectrum of ~ 12 Å Pd on Si(111) at 25°C .

TABLE I. TEM basal-plane lattice constants $a_0/2$ of Pd₂Si films as a function of equivalent Pd metal deposition thickness. Surface work function ϕ and *d*-band peak position E_{peak} ($E_F = 0$) are also given.

Thickness (Å)	$a_0/2$ (Å)	ϕ (eV)	E_{peak} (eV)
20	6.58	4.96	-2.93
80	6.54	4.99	-2.80
300	6.52	5.04	-2.76
300	6.47	a	a

^aUnmeasurable: film surface unreacted so that Pd₂Si not accessible to UPS.

pound is formed at submonolayer Pd coverage.¹² The shift of its d -band peak may be associated with the stoichiometry and/or lattice-constant variations mentioned previously, or possibly with the evolution of the complete Pd₂Si chemical environment as the film thickness reaches that of ~ 2 -3 Pd₂Si unit cells (at ~ 4 -8-Å coverage. The enhanced emission just below E_F may also be attributed to the metallic Pd₂Si-like compound formed at the interface.

As seen from the behavior of the bulk Si peak [~ -7.2 eV in Fig. 2(a)], the band bending is unaltered (± 0.1 eV) for thicknesses ≤ 1 monolayer. Since $E_c - E_F = 0.79$ eV (Ref. 13) on the clean surface, the thin Pd₂Si film has a SBH of 0.79 ± 0.1 eV, in good agreement with thick film results.⁵

The detailed behavior of ϕ with varying conditions of the reaction, as indicated by the d -band peak position E_{peak} , is shown in Fig. 3. Both thick-film annealing and thin-film deposition reach the same parameters to characterize Pd₂Si. The relation between ϕ and E_{peak} agrees with that in Table I. In the thin-film deposition, ϕ remains near ϕ_{Si} until about a monolayer of Pd₂Si is formed; this could result from Si-rich Pd₂Si present at low coverage or simply from incomplete coverage ($\phi_{\text{Si}} < \phi_{\text{Pd}_2\text{Si}}$ dominates measurement). At higher annealing temperatures (~ 400 °C), we find that Si segregates to the surface of the Pd₂Si

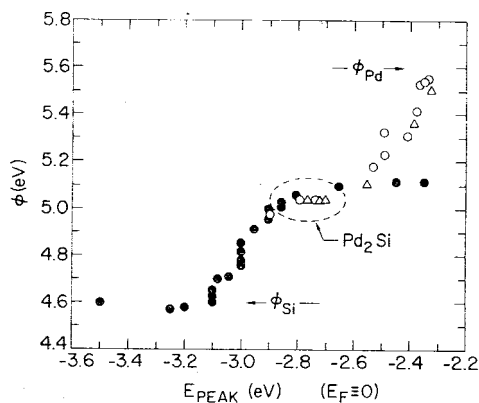


FIG. 3. Surface work function ϕ as a function of the position E_{peak} of the Pd₂Si d -band peak for Pd reaction on Si(111). Open circles and triangles: two separate measurements for 150 °C annealing cycles of thick Pd films on Si(111), proceeding from right to left (triangles correspond to the spectra in Fig. 1). Solid circles: sequential deposition of thin Pd layers on Si(111) at 25 °C proceeding from left to right and corresponding to the spectra in Fig. 2. For lower coverages E_{peak} is obtained from the incremental difference curves.

film, reducing the UPS intensity, the Pd-Si Auger intensity ratios, and ϕ (nearly to ϕ_{Si}), and changing spectral shapes.

We conclude that changes in the surface work function for Pd-Si(111) can be fully understood on the basis of changes in the chemical composition of the surface; we observe no anomalies in the behavior of ϕ requiring interface dipole formation.^{2,3,14} Furthermore, the UPS spectra for low coverages show no structure indicative of the metal-induced interface states believed intrinsic to the abrupt metal-semiconductor interface¹⁵; instead, both the d -band peak and the emission just below E_F are more likely associated with formation of a Pd₂Si-like compound at the interface. Although we cannot rule out some contribution from interface states and/or dipole formation, we observe no direct evidence for either and believe our results are much more simply and naturally understood without invoking such effects.

Although metal-induced interface states² and/or dipole formation^{2,3} have previously been inferred from new behavior of the electronic structure not characteristic of either metal or semiconductor, the systems studied were not well characterized chemically in terms of reaction products, kinetics, segregation, etc. We suggest the possibility that such chemical processes might equally well explain previous results.^{15,16} For example, reactions of Pd with GaAs are known to produce various compounds (e.g., Pd₂Ga, PdGa, and PdAs₂),¹⁷ and the UPS spectrum of 2-3 monolayers of Pd on GaAs(110)¹⁸ is quite similar to that of Pd₂Si (dominant peak has $E_{\text{peak}} \sim -2.5$ eV, full width at half maximum ~ 3 eV). Finally, surface segregation^{15,19,20} of compound semiconductors is complicated by the possibility of preferential segregation, with corresponding effects on surface spectra and ϕ .

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