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 Pd_2Si 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 Pd_2Si reaction product (a metal) has an electronic structure more like that of the noble metals than the transition metals, with an occupied 4*d* 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 (Pd_2Si-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 Pd_2Si compound formation.

The Si(111) samples were cleaned in UHV (base pressure ~1×10^{-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)]

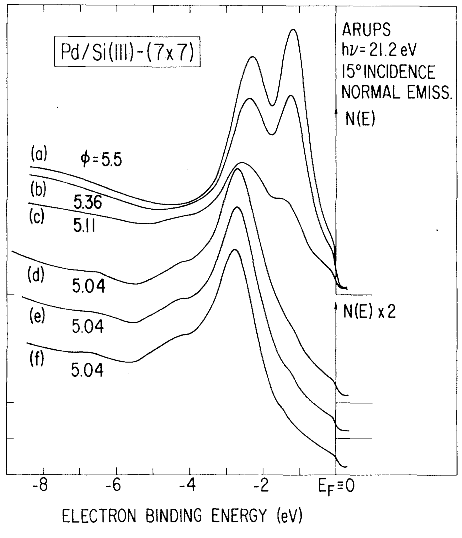

FIG. 1. (a) ARUPS spectra for ~300 Å Pd deposited on Si(111) at 25 °C; (b)–(f) subsequent spectra taken after stepwise annealing cycles of 30 sec at 150 °C.

was continuous and fully reacted to Pd_2Si, 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 Pd_2Si, which has $\varphi \cong 5.04$ 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 Pd_2Si 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 (~ 25 °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 Pd_2Si 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 ($\gtrsim$ 4–8 Å). TEM studies of films prepared as in Fig. 2(f) also showed continuous single-phase Pd_2Si, and *in situ* Auger composition analysis gave a Pd_2Si stoichiometry.[8] Thus Pd-Si(111) demonstrates a high degree of interface reactivity in the initial stages of compound formation, producing Pd_2Si readily at the metal-semiconductor interface even at room temperature.

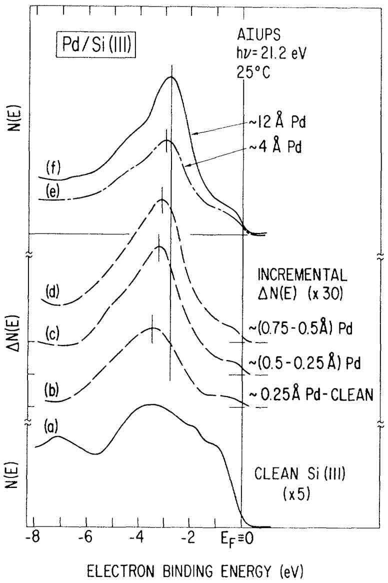

FIG. 2. (a) AIUPS spectrum for clean Si(111); (b)–(d) incremental difference spectra showing additional emission from ~0.25 Å added Pd (equivalent metal thickness) at 25 °C; (e) spectrum of ~4 Å Pd on Si(111) at 25 °C; (f) spectrum of ~12 Å Pd on Si(111) at 25 °C.

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 Pd_2Si 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 Pd_2Si 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 Pd_2Si 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 $\lesssim$ 1 Å.[8]

TEM lattice-constant measurements[10] were performed on three fully reacted Pd_2Si films and a fourth, partially reacted film [Pd metal on ~ 100 Å Pd_2Si 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 studies[11] show larger $a_0/2$ for "Si rich" than for "Pd rich" Pd_2Si (although stoichiometry was not quantified). In spite of these variations, the crystal structure of Pd_2Si is fixed, $a_0/2$ varies by $\lesssim$ 2%, φ varies by $\lesssim$ 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 Pd_2Si spectra strongly suggest that a Pd_2Si-like com-

TABLE I. TEM basal-plane lattice constants $a_0/2$ of Pd_2Si films as a function of equivalent Pd metal deposition thickness. Surface work function φ and *d*-band peak position E_{peak} ($E_F \equiv 0$) 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

[a] Unmeasurable: film surface unreacted so that Pd_2Si 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 Pd_2Si chemical environment as the film thickness reaches that of $\sim 2-3$ Pd_2Si unit cells (at $\sim 4-8$-Å coverage. The enhanced emission just below E_F may also be attributed to the metallic Pd_2Si-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 $\lesssim 1$ monolayer. Since $E_c - E_F = 0.79$ eV (Ref. 13) on the clean surface, the thin Pd_2Si 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 Pd_2Si. 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 Pd_2Si is formed; this could result from Si-rich Pd_2Si present at low coverage or simply from incomplete coverage ($\varphi_{\text{Si}} < \varphi_{Pd_2Si}$ dominates measurement). At higher annealing temperatures (~ 400 °C), we find that Si segregates to the surface of the Pd_2Si film, reducing the UPS intensity, the Pd-Si Auger intensity ratios, and φ (nearly to φ_{Si}), and changing spectral shapes.

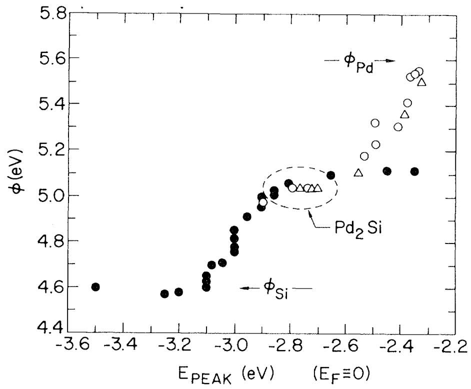

FIG. 3. Surface work function φ as a function of the position E_{peak} of the Pd_2Si d-band peak for Pd reaction on Si(111). Open circles and triangles: two separate measurements for 150 °C annealing cycles of thick Pd films on Si(111), proceeding from right to left (triangles correspond to the spectra 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.

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 interface[15]; instead, both the d-band peak and the emission just below E_F are more likely associated with formation of a Pd_2Si-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 states[2] 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., Pd_2Ga, PdGa, and $PdAs_2$),[17] and the UPS spectrum of 2–3 monolayers of Pd on GaAs(110)[18] is quite similar to that of Pd_2Si (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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Scattering of Neutral Atoms by an Exponential Corrugated Potential

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The integral equation of the scattering is solved exactly for a one-dimensional exponential corrugated potential. Numerical results are presented for a sinusoidal and a triangular profile of small amplitude. As the "slope" of the exponential increases the intensities given by the hard corrugated wall are approached. The finite slope of the potential has the strong effect of forcing the particles into the specular peak and tends to reduce the effect of multiple scattering.

In the scattering of light neutral atoms by a crystalline surface the diffraction-peak intensities calculated with use of a hard-corrugated-wall potential (HCWP) are successfully[1] compared with the experimental data. The HCWP is written as

$$V=\infty,\quad z<\varphi(\vec{R}),$$

$$V=0,\quad z>\varphi(\vec{R}),$$

where $\varphi(\vec{R})$ is the corrugation function or the surface profile, $\vec{R}$ and z being the parallel and perpendicular components of the surface position vector. The HCWP with a potential well having an attractive long-range part[2,3] (z^{-3}) gives a good picture of the structures (minima or maxima) observed experimentally in the diffracted peaks in the vicinity of condition for which resonance with bound states can occur.

On the other hand, these observed resonances allow the determination of the potential energy levels. Then one usually tries to deduce a potential shape or more precisely its zero-order Fourier component which gives the best fit to the bound-state energies. One generally finds that this can be well represented by a Morse[4,5] or a 9-3 potential.[6] Recently, more elaborate forms have been proposed, for instance, the shifted Morse hybrid potential,[7] so called because it is given by a Morse form at short distances and by an attractive z^{-3} form far from the surface.

In spite of the uncertainty which arises in a potential shape determined only by a limited number of bound-state energies one would expect that the