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Bulk silicides and Si-metal interface reaction: Pd_2Si

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We report synchrotron-radiation photoemission studies of cleaved Pd_2Si in which we use $4d$ Cooper minimum and $4p \rightarrow 4d$ resonance techniques to identify the bonding Si p—Pd d states 3.5—6.5 eV below E_F, the Si s states at 9.3 eV, the nonbonding Pd $4d$ states centered at 2.5 eV, and hybridized Si-Pd or Pd sp states within 1.5 eV of E_F. The resonant photoemission technique was shown to yield detailed information about the orbital character of the valence states and to be applicable in principle to all Si—d-metal systems. Comparison of bulk Pd_2Si with palladium silicide thermally grown on Si(111) shows the main $4d$ emission feature at 2.8 eV shifted 0.3 eV to higher binding energy relative to bulk Pd_2Si, an increased full width at half maximum (2.5 versus 1.5 eV), and substantially greater emission from Si p—metal d bonding states. This confirms that the palladium silicide formed on Si is Si rich near the silicide-vacuum interface and shows that the electronic structure of the uppermost silicide layers differs from that of bulk Pd_2Si.

INTRODUCTION

The interface between two dissimilar materials frequently exhibits structural and electronic properties which are different from those of either material. These interfaces are of great fundamental and technological importance because of their role in Schottky barrier formation, proximity effects for superconductors, ohmic contacts, coherent modulated structures, etc. Major experimental and theoretical programs are presently underway which examine atomic diffusion, interface morphology, and electronic structures.[1-9]

To characterize the reactions which occur at interfaces requires a thorough understanding of Si-metal chemical bonding in bulk silicides. The electronic structure of Pd_2Si has been the subject of intense interest in connection with Si-Pd interface reaction.[6-8] However, all the data available so far concern silicides obtained by metal-film reaction on Si(111) following heat treatment that enhances surface segregation and causes composition gradients at the silicide-vacuum interface. The present study concerns bulk Pd_2Si samples cleaved *in situ* and represents the first systematic study of the *bulk* electronic structure of Pd_2Si, as emphasized by the relevant differences observed with respect to the previous literature.[6-8] To study the character of the electronic valence states, we systematically applied to Pd_2Si Cooper minimum and resonant-photoemission techniques. While both techniques have been previously applied to other systems for analyzing the electronic density of states, this is the first application to a bulk Si-metal compound. The present results clearly demonstrate the potential of such techniques in understanding the Si-metal chemical bonding and directly reflect on the modeling of the Si-Pd interface. Resonant photoemission obtains complementary information with respect to the Cooper minimum technique and allows investigation of the different contributions to the electronic density of states in the Si—$3d$-metal system where the other technique is not applicable.

EXPERIMENTAL

Bulk samples of Pd_2Si were prepared by comelting high-purity palladium and silicon under an argon atmosphere in the water-cooled copper hearth of a nonconsumable arc furnace. The resulting buttons were zone refined to enhance grain growth. X-ray diffraction studies showed the $C22$ hexagonal (Fe_2P-type) structure of Pd_2Si with $a = 6.493 \pm 0.003$ Å and $c = 3.440 \pm 0.004$ Å.[10] Clean surfaces suitable for photoemission studies were obtained by fracturing the samples in the ultrahigh vacuum photoelectron spectrometer at operating pressures of $\sim 3 \times 10^{-11}$ Torr. Immediately after fracturing, the samples were positioned at the common focus of the monochromatic synchrotron-radiation beam and the electron-energy analyzer. Spectra were recorded for $15 \leq h\nu \leq 140$ eV using synchrotron radiation from the 240-MeV electron storage ring Tantalus at the University of Wisconsin-Madison. The radiation was dispersed with a $3m$ toroidal grating monochromator. The overall resolution (electrons plus photons) ranged from 0.4—0.6 eV for core studies and for valence-band studies for $h\nu < 100$ eV, to about 1 eV for valence-band studies in the range $100 < h\nu < 140$ eV. Details of the experimental system can be found in Ref. 11.

RESULTS AND DISCUSSION

Bulk Pd_2Si

Representative valence-band energy distribution curves (EDC's) for Pd_2Si are shown in Fig. 1 for $16 \leq h\nu \leq 130$ eV, together with the Si $2p$ core level measured at $h\nu = 130$ eV.[12] The EDC's are plotted in arbitrary units, normalized to the intensity of the main emission feature at 2.5 eV. Two features can be identified in each EDC at about 2.5 and 4.4 eV below E_F (labeled B and C). A shoulder can be seen at 1.9 eV (labeled A) and a second weak feature appears at ~ 5.2 eV (labeled D) at low photon energy. At high energy a fifth structure is visible at 9.3 eV (E). As shown, there is very little dispersion of the experimental features with photon energy[13] but there is considerable variation in their relative intensities. Hence they can be associated with features in the density of occupied states, modulated in intensity by the $h\nu$ variation of their partial photoionization cross sections. EDC's taken at $h\nu = 80$, 110, and 130 eV are shown in Fig. 2 to emphasize the variation of the relative intensity of the experimental features. The most evident $h\nu$ variation is seen in the relative enhancement of structure C near 50 eV (Fig. 1) and of structures C, E, and the emission within 1.5 eV of E_F for $h\nu \gtrsim 100$ eV.

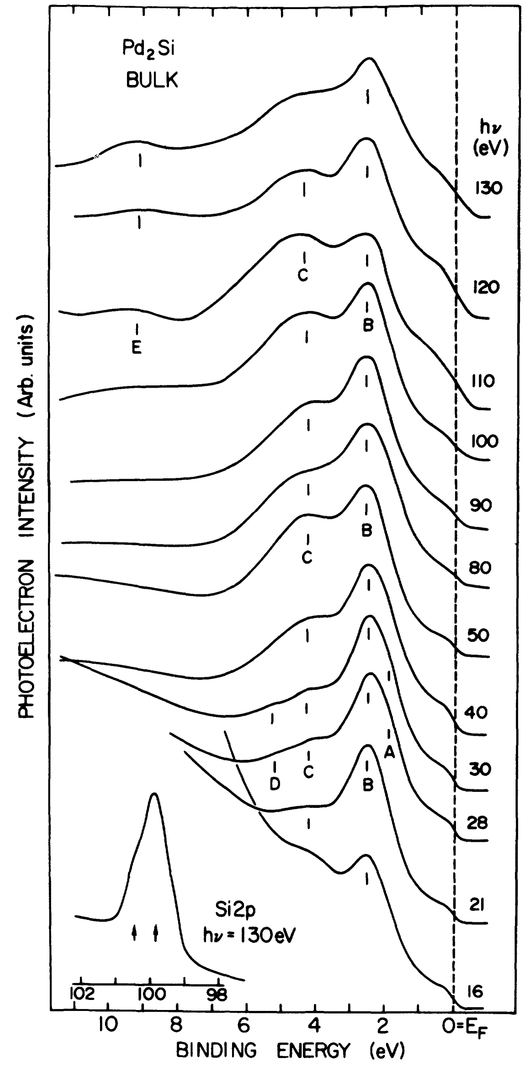

FIG. 1. Representative EDC's for the valence-band emission of Pd_2Si and for the Si $2p$ core levels measured at 99.83 ± 0.15 eV (Ref. 12) at $h\nu = 130$ eV. Structures A, B, C, D, and E are associated with features in the density of occupied states. The modulation of their relative intensity in the experimental photon energy range reflects the $h\nu$ variation of their partial photoionization cross sections through the Pd $4p \rightarrow 4d$ resonance ($40 < h\nu < 60$) and at the Pd $4d$ Cooper minimum ($h\nu > 100$).

In Fig. 2 we reproduce the total density of states (DOS) for Pd_2Si (solid line) and the Si-derived s-p partial DOS calculated by Bisi and Calandra.[14] These semiempirical linear combination of atomic orbitals extended—Hückel-theory calculations have been found to be in good agreement with first-principles calculations and reproduce the experimentally observed trends in chemical bonding in silicides.[6,15,16] The vertical bars in Fig. 2 mark the experimental features A—E identified in Fig. 1. The calculations indicate that the states between E_F and 4 eV are Pd $4d$—derived with only minor contributions from Si-derived orbitals and that these metal states are not directly involved in the bond with Si, i.e., are nonbonding d states. On the other hand, mixed Pd $4d$—Si $3p$ states are found 4—6.8 eV below E_F and correspond to the bonding states. The corresponding antibonding orbitals extend from near E_F to well above E_F. A band of nearly pure Si s character is predicted 9—10 eV below E_F.

Comparison of theory with experiment (Fig. 2) suggests that feature E at 9.3 eV corresponds to the Si s DOS feature and that structure C at 4.4 eV reflects the important Si p—Pd d bonding feature predicted near 4.3 eV. Theory does not show a similar one-to-one correspondence for the other experi-

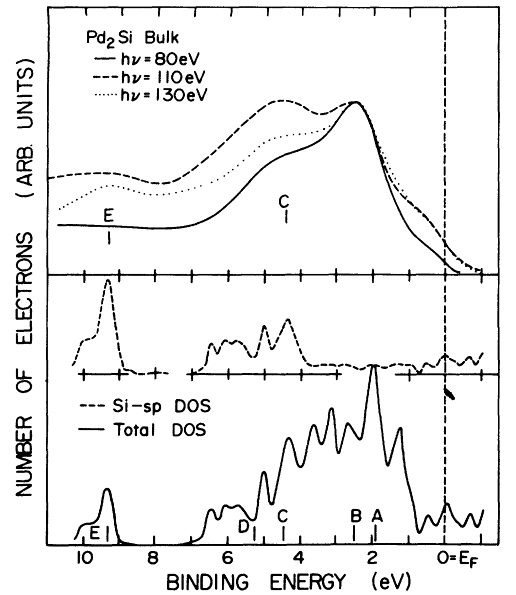

FIG. 2. EDC's for the valence-band emission of Pd$_2$Si at $h\nu = 80$, 110, and 130 eV are shown (top) normalized to the main 4*d* structure. In the lower part of the figure we show, for comparison, the total DOS (solid line) and the Si-derived *s-p* partial DOS as calculated by Bisi and Calandra in Ref. 14. The vertical bars mark the experimental features *A*–*E* identified in Fig. 1. Experimentally, the suppression of the Pd-derived *d* emission at the 4*d* Cooper minimum ($h\nu > 100$ eV) results in the emergence of the Si-derived *s* states at 9.3 eV and of the Si *p* states in bonding combination with metal *d* orbitals 3.5–6.5 eV below E_F. Theory does not show a similar one-to-one correspondence for the other experimental features but the qualitative agreement suggests that structures *A* and *B* arise from 4*d* nonbonding states. The emission within 1.5 eV from E_F is strongly enhanced at the Cooper minimum but the nature of the corresponding states is less clear. Either a substantial amount of metal *s-p* character is present near E_F or the antibonding Si *p*—metal-*d* orbitals are partially occupied.

mental features but the qualitative agreement suggests that structures *A* at 1.9 eV and *B* at 2.5 eV arise from 4*d* nonbonding states, possibly those predicted at 1.3 and 2.0 eV.

These tentative assignments can be verified through synchrotron-radiation photoemission measurements because the Si *s*, the nonbonding 4*d*, and the hybridized Si *p*—Pd *d* states have markedly different photoionization cross sections. Two complementary techniques are available to examine the character of the experimental DOS features. The first uses the Cooper minimum[17] for the Pd 4*d* electrons to suppress the Pd *d* character. The second makes use of resonant photoemission[17] associated with the $4p \rightarrow 4d$ transition to alternately reduce and then enhance the 4*d* character.

The Cooper minimum method has been used by Abbati *et al.*[18] and Miller *et al.*[19] to study the Si(111)-Pd interface and is applied here for the first time to a bulk silicide. The method stems from the observation by Hecht and Lindau[20] of a rapid decrease of the photoionization cross section for the valence-band emission of Pd metal at photon energies above 100 eV with a relatively flat photon energy dependence for $120 \leq h\nu \leq 150$ eV. This energy dependence was ascribed to the Cooper minimum because of the analogy with the results of atomic $d \rightarrow f$ transitions of Ref. 17.

The EDC's in Figs. 1 and 2 show a dramatic increase of structures *C* and *E* and of the emission within 1.5 eV of E_F for $h\nu \gtrsim 100$ eV. These structures also exhibit different photon energy dependences. In particular, the relative intensity of feature *C* and of the emission in the (3.5–6.5)-eV binding-energy range reaches a maximum at $h\nu = 110$ eV, i.e., some 105 eV above threshold, and decreases rather sharply at higher photon energy. The emission within 1.5 eV of E_F is also strongly enhanced at $h\nu = 110$ eV but shows virtually no variation in the photon energy range $110 \lesssim h\nu \lesssim 130$ eV. Structure *E*, instead, increases comparatively slowly in intensity above $h\nu = 100$ eV and reaches maximum intensity relative to feature *B* at the limit of the photon energy available to us here (140 eV).

The identification of the Si *s* character of structure *E* and of the Si *p*—metal-*d* bonding character for features of binding energies $6.5 \leq E_B \leq 3.5$ eV is clearly supported by these Cooper minimum measurements and is in agreement with what is suggested by Abbati *et al.*[18] and Miller *et al.*[19] for Si-Pd interface phases. The nature of the states within 1.5 eV of E_F is less clear. Either a substantial amount of metal *s-p* character is present near E_F or the antibonding Si *p*—metal-*d* orbitals are partially occupied. Bisi and Calandra[14] forecast the antibonding states to start just above E_F and the Pd-derived *sp* features to appear more than 1 eV above E_F, but the accuracy of the tight-binding calculations may suffer in this range because of the increasingly extended character of the wave functions. Grunthaner *et al.*[21] and Rossi *et al.*[19] for Si-Pd phases argue in favor of a Si-Pd antibonding origin for the states closer to E_F.

An independent check of the *d* character of the spectral features can be obtained in resonant photoemission studies where the photon energy is swept through the energy of the Pd $4p \rightarrow 4d$ transition. The 4*d* emission is first reduced (antiresonance) and then enhanced (resonance), as has been discussed by Dietz *et al.*[22] for the $3p \rightarrow 3d$ resonance in Ni and extended by Davis and Feldkamp[23] to the other 3*d* transition metals. Weaver and Olson[24] suggested

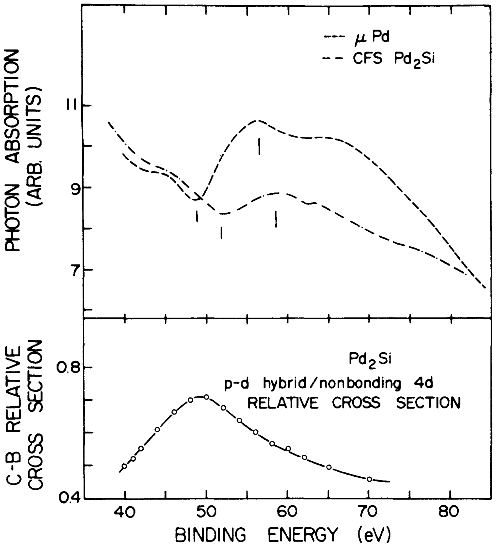

FIG. 3. Optical-absorption coefficient of Pd metal [dashed line, from Weaver and Olson (Ref. 24)] exhibits a Fano resonance line shape broadened by multiplet splitting and autoionization processes (Ref. 24). The partial yield spectrum of Pd_2Si (dotted-dashed line, kinetic energy 4 eV) is expected to show structure analogous to the optical-absorption features of Pd_2Si (Ref. 27) and comparison with the topmost spectrum confirms the common $4p \rightarrow 4d$ origin of the experimental features. Antiresonance and resonance (vertical bars) appear shifted 2—3 eV to higher photon energy in Pd_2Si, consistent with the expected chemical shift of the $4p$ core level in Pd_2Si compared to Pd (Ref. 28). In the lower part of the figure we plot (solid line) the ratio of the cross sections for features *C* and *B* in the same photon energy range as determined from the partial photoionization cross sections for initial states with binding energies of 4.4 eV (feature *C*) and 2.5 eV (feature *B*). The relative cross section *C-B* peaks in the antiresonance region, reflecting the suppression of the $4d$ character and the partial Si-derived character of the states near 4.4 eV.

that the same *p-d* mechanism applies to the $4d$ metals and showed that the optical-absorption coefficients for $4d$ transition metals do, indeed, show a minimum followed by enhancement qualitatively consistent with the Fano line shape.[25] According to this mechanism, the $4p \rightarrow 4d$ atomic excitation leads to a $4p^5 4d^6 5s^2$ state that decays into $4p^6 4d^4 5s^2\ \epsilon f$ through a super-Coster-Kronig transition.[26] This process would have the same initial and final states as the direct excitation $4p^6 4d^5 5s^2 + h\nu \rightarrow 4p^6 4d^4 5s^2\ \epsilon f$ so that quantum interference terms appear that can be analyzed through the Fano formalism.[25]

The optical-absorption coefficient of Pd metal exhibits a broad $4p$-$4d$ absorption feature that extends 20—30 eV above the $4p$ edge, as shown in Fig. 3

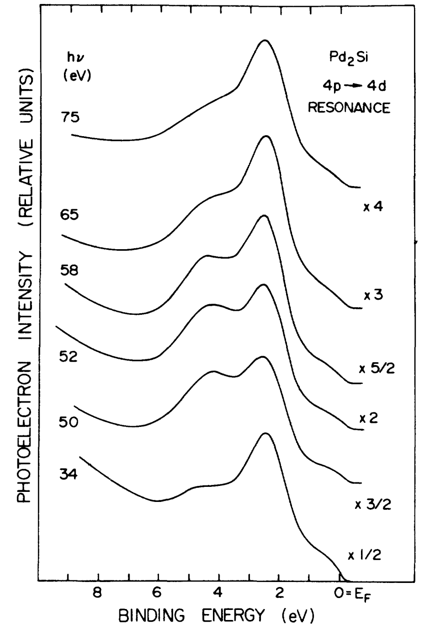

FIG. 4. Representative spectra of the valence-band emission of Pd_2Si for photon energy near the $4p \rightarrow 4d$ resonance. The spectra were normalized for monochromator output (Ref. 29) and are given in relative units. The modulation of the relative intensity of the experimental features reflects the suppression of the $4d$ character at antiresonance, where the Si-derived states are more visible ($h\nu \sim 50$ eV), and the following reenhancement at resonance (see Fig. 3). Resonant photoemission represents an important tool for analyzing the different orbital contributions to the valence states and, unlike the Cooper minimum technique, can in principle be applied to all *d* systems.

(from Weaver and Olson[24]). The line shape is qualitatively consistent with a complex Fano resonance broadened by multiplet splitting and autoionization processes. For comparison we show in Fig. 3 a partial yield or constant final-state energy spectrum for Pd_2Si (at kinetic energy of the photoelectron of 4 eV), which is expected to exhibit a structure analogous to those observed in the optical-absorption coefficient of Pd_2Si.[27] The close similarities of the two spectra confirm the common $4p$-$4d$ origin of the features observed in Pd and Pd_2Si. Vertical bars in Fig. 3 mark the position of a relative minimum and maximum in the absorption spectra (antiresonance and resonance, respectively). These appear shifted 2—3 eV to higher photon energy in Pd_2Si (58.5 and 52 eV, respectively), and such a shift is qualitatively consistent with the expected chemical shift of the $4p$ core level in Pd_2Si compared to Pd.[28]

To quantitatively examine the $h\nu$ dependence of features *B* and *C* at the $4p \rightarrow 4d$ resonance, we measured valence-band EDC's in (1—2)-eV increments

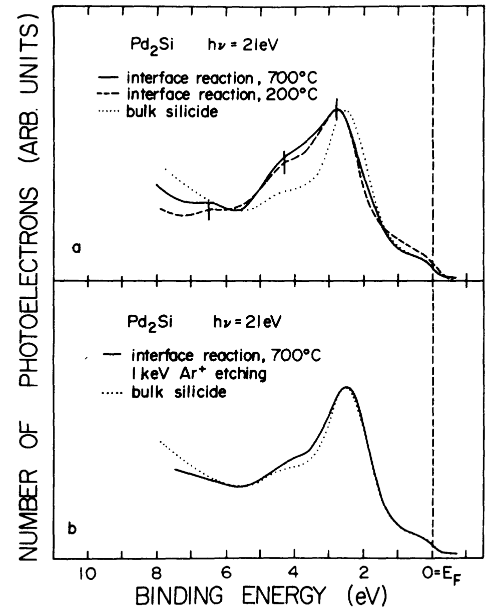

FIG. 5. EDC's at $h\nu=21$ eV for the valence-band emission of bulk Pd_2Si (dotted line) and for Pd_2Si grown on Si(111) at 200 °C (dashed line, Ref. 6) and 700 °C (solid line, Ref. 8). The sample obtained by thin-film reaction consistently have a 0.3-eV shift of the main 4d emission, substantially enhanced emission from the Si p—Pd d bonding states, and a feature 6.5 eV below E_F that is absent in the bulk samples. We associate these differences with the Si-rich layer that is present at the silicide-vacuum interface for all samples grown on Si (Refs. 33—35). This surface layer can be removed by ion sputtering, as can be seen in the lower part of the figure. Light ion sputtering with 1-keV Ar$^+$ ions (solid line, from Ref. 8) results in valence-band emission nearly identical to that of bulk Pd_2Si (dotted line, Ref. 36).

for $35 \leq h\nu \leq 85$ eV. A few representative spectra are shown in Fig. 4.[29] From these we determined[30] the partial photoionization cross sections for initial states with binding energies of 2.5 eV (feature B) and 4.4 eV (feature C). The ratio of the cross sections for features C and B is plotted in Fig. 3. The relative cross section C-B increases with photon energy while approaching antiresonance, peaks in the antiresonance region, and then decreases. This provides further evidence that the states near 4.4 eV have partial Si-derived p character. The enhancement of structure C with respect to structure B seen in Figs. 1 and 2 for $h\nu \simeq 50$ eV thus reflects the suppression of the 4d character at antiresonance so that the Si-derived states are more visible. Resonant photoemission, in conclusion, yields information complementary to that obtained through the Cooper minimum technique, with the important advantage that the technique can be applied to 3d systems that do not have a Cooper minimum.

Comparison of bulk and thin-film reacted Pd_2Si

In Fig. 5 we compare EDC's at 21 eV from this work with spectra for silicides epitaxially grown on Si(111) at 200 °C (dashed line, Ref. 6) and 700 °C (solid line, Ref. 8). The bulk compositions and structure were characterized by Rutherford backscattering (RBS) and channeling,[8] and by transmission-electron microscopy.[6] As shown, the samples obtained by thin-film reaction consistently have a 0.3-eV shift of the main 4d emission feature to higher binding energy, substantial enhancement of emission in the energy region around 4.3 eV, and a feature 6.5 eV below E_F that is absent in the bulk samples. Further, the full width at half maximum of the primary structure in Fig. 5 is 2.4—2.5 eV for the thin-film reaction data and 1.5 eV for the bulk samples. Such differences must correspond to different surface conditions since they are only apparent when surface-sensitive techniques are employed.[31] Bulk sensitive analysis (Rutherford backscattering and x-ray diffraction) indicate that the thermally grown silicide is identical to a metallurgically prepared bulk sample.[32]

Oura *et al.*[33] and Okada *et al.*[34] interpreted low-energy electron diffraction and Auger studies of Pd_2Si growth on Si as indicating an ordered Si overlayer at the silicide surface at ~200 °C. The layer thickness, estimated to be ~3 Å, showed little dependence on the reaction temperature.[34] Recently, Tromp *et al.*[35] performed a study of 20-Å Pd_2Si layers grown on Si(111) as a function of annealing temperature and showed, through a combination of medium-energy ion scattering, channeling, and blocking, that the uppermost atomic layer of Pd_2Si becomes Si rich upon annealing at 200 °C while the RBS spectra do not vary within the experimental uncertainty.

We associate differences between the valence-band spectra from Refs. 6—8 (Fig. 5) and ours for bulk Pd_2Si with emission due to this Si-rich layer at the silicide-vacuum interface. Enhanced emission in the region of structure C relative to feature B reflects increased amounts of Si p—Pd d hybrid orbitals relative to the nonbonding d states. The fact that thin-film reaction at 200 and 700 °C yields identical valence-band emission supports the observation[34] that the thickness of the Si-rich layer depends only weakly on the reaction temperature. As expected, the Si-rich surface layer can be removed by light ion sputtering with 1-keV Ar$^+$ ions[8] and such sputtering results in valence-band emission nearly identical[36] to bulk Pd_2Si (Fig. 5).

Abbati *et al.*[37] deposited six monolayers of Pd at 300 K onto UHV cleaved Si(111) and obtained thin

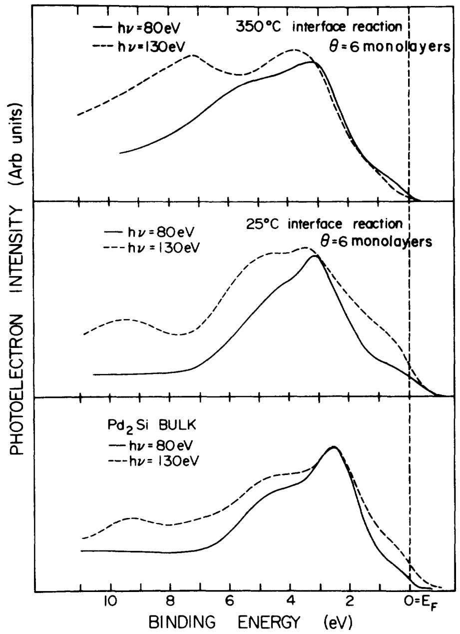

FIG. 6. EDC's at $h\nu = 80$ eV (solid line) and $h\nu = 130$ eV (dashed line) for the Si(111)-Pd interface (6 monolayers metal coverage) after reaction at 350 °C [topmost spectra, from Abbati *et al.* (Ref. 37)], for the same interface formed at room temperature ($\Theta = 6$ monolayers) (from Refs. 19 and 39), and for bulk Pd_2Si (bottom-most curve, this work). For both interfaces the nonbonding 4*d* states are shifted 0.6–0.7 eV to higher binding energy. The interface at room temperature shows also a higher density of Si *p*—Pd *d* bonding orbitals also shifted to higher binding energy, in agreement with what is expected for a Si-rich Pd_2Si interface phase suggested by several authors (Refs. 2, 4, and 30). Annealing at 350 °C produced a Si-derived dominant emission feature at about 7 eV that corresponds to an emission feature in the valence-band spectra of Fig. 5 (topmost curves, solid and dashed line) and therefore is related to the Si-rich phase at the silicide-vacuum interface.

intermixed Si-Pd phases.[2,3,38] While the stoichiometry of such silicidelike[2,3] interface phases is still controversial[2,38] and while their electronic structures show differences with respect to bulk Pd_2Si, annealing at 350 °C does appear to produce Si enrichment of the surface[37] and DOS changes qualitatively consistent with changes in the valence-band emission observed in Fig. 5.

The use of the 4*d* Cooper minimum technique in studies of bulk silicides and interface reaction products highlights the differences between the two phases. In Fig. 6 we compare our Pd_2Si valence-band results with EDC's for the Si(111)-Pd interface formed at room temperature (Refs. 19 and 39) and after 350 °C annealing (from Abbati *et al.*, Ref. 37). The quantitative differences are dramatic. First, the 4*d* nonbonding states are shifted toward higher binding energy relative to Pd_2Si for both interfaces. Second, for the interface at room temperature, a higher density of Si *p*—Pd *d* bonding orbitals is seen and these states also appear shifted to higher binding energies. Such differences are qualitatively consistent[40] with the presence of a Si-rich Pd_2Si interface phase, as suggested by several authors.[2,4,38] If we compare the emission spectra for the *annealed* interface to the bulk Pd_2Si results we see that thermal processing at 350 °C produces a dominant Si-derived emission feature at about 7 eV that does not correspond to any structure observed in the bulk Pd_2Si spectrum but that does correspond to an emission feature in the valence-band spectra of Fig. 5 (topmost spectra, solid and dashed lines). This feature was shown in the preceding section to be related to the Si-rich phase at the silicide-vacuum interface so that the present results support the interpretation of Abbati *et al.*[37] that annealing gives rise to dramatic Si enrichment of the interface phase.[41]

CONCLUSION

The task of modeling the interface reaction at Si-metal interfaces requires a full understanding of the chemical bonding as a function of composition. We have sought to show that systematic comparison of bulk and interface reaction data offers insight in this bonding. We hope that the present study will also stimulate more extensive use of the photon energy dependence of the electronic states because this $h\nu$ dependence offers a powerful tool for characterizing the modifications of chemical bonding.

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[29] The intensities were normalized for monochromator output, storage ring beam current, etc., but assuming the transmission of the analyzer to be constant, i.e., the point-source approximation.

[30] The cross sections were measured after substracting a secondary background linearly interpolated between 10 eV and E_F. The use of different criteria does not modify the qualitative trend shown in Fig. 4.

[31] Results obtained with x-ray photoemission (Ref. 7) with lower surface sensitivity are in better agreement with

our bulk studies. The Si $2p_{1/2}$ core emission appears at 99.83±0.15 eV in this study and at 99.72 eV in Ref. 7 after heat treatment at 200 °C of Pd films evaporated on Si(100).

[32] An alternative "bulk" effect, extending to the whole depth of the reacted phase, would be a composition difference below the detection limit of Rutherford backscattering, accomodated in a Pd_2Si lattice structure. J. L. Freeouf, J. Vac. Sci. Technol. 18, 910 (1981), noted that the phase diagram for Pd-Si shows that Pd_2Si is not in thermodynamic equilibrium with silicon so that the bulk stoichiometry of a Pd_2Si film in metastable equilibrium with Si is Si rich. This effect, however, is intrinsically less noticeable in our measurements than the Si enrichment at the silicide-vacuum interface observed by several authors (Refs. 2, 3, and 37) for Pd_2Si growth on silicon.

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[40] A Si-rich Pd_2Si-like phase will show an increase of Si p—Pd d hybrid orbitals at the expense of the $4d$ nonbonding orbitals. Also, the shift of the $4d$ emission to higher binding energy is expected from the systematics of DOS calculations for the Pd_2Si-PdSi series (Ref. 14) and of photoemission results for Pd_xSi_{1-x} disordered alloys. See J. D. Riley, L. Ley, J. Azoulay, and K. Terakura, Phys. Rev. B 20, 776 (1979); P. Oelhafen, M. Liard, H.-J. Guntherodt, K. Berresheim, and H. D. Polashegg, Solid State Commun. 30, 641 (1979).

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