PHYSICAL REVIEW B VOLUME 22, NUMBER 10 15 NOVEMBER 1980

Chemical bonding and electronic structure of Pd_2Si

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(Received 28 March 1980)

The chemical bonding and electronic properties of Pd_2Si have been investigated by measuring ultraviolet photoemission spectroscopy and Auger electron spectroscopy transitions involving both core and valence electrons for Pd, Si, and Pd_2Si. The spectra have been interpreted based on partial state densities calculated for Pd-Si compounds. In the silicide, the *d* states of the Pd interact strongly with the *p* states of the Si. The resulting *p*-*d* hybrid complex is composed of Pd *d* states lying almost entirely below E_F with the central peak at -2.75 eV and two groups of Si states separated by ~ 5 eV. The lower-lying group of Si states forms the Si 3*p*–Pd 4*d* bonding levels, while the higher-lying group near E_F forms the corresponding antibonding states. The compound stoichiometry can change the position of the *d* peak as well as the occupation of the antibonding states, thus affecting the phase stability of the compound. Such stoichiometry variations are consistent with filling of the *d*-*p* complex in an almost rigid-band-like manner. The results obtained in this study can be used to account for the transport properties of Pd_2Si.

I. INTRODUCTION

The formation of silicide compounds at metal-Si interfaces is of current interest because of the potential device applications and the need for basic understanding of the properties of metal-semiconductor interfaces. Extensive studies have been carried out on the material properties of silicides,[1] such as phase identifications and formation kinetics; however, the electronic- or chemical-bonding characteristics of these compounds have not been systematically investigated. Knowledge of the electronic properties of the silicide and at the interface is important for understanding the formation mechanism of Schottky barriers and Ohmic contacts at silicide-Si interfaces. In this regard, it is relevant to distinguish interfaces where metal-Si compounds can be formed, e.g., Pd-Si and Pt-Si, from those where such compounds do not exist, e.g., Al-Si and Au-Si. The formation of a specific compound defines the local atomic and chemical environment in the silicide lattice and to a significant extent at the silicide-Si interface as well, whereby the electronic properties are largely determined. In contrast, most of the properties of the nonreacting interface may be characteristic of the discrete nature of the ideal metal-Si interface, e.g., metal-induced gap states.[2] In addition, compound formation proceeds at a reaction interface which is created continuously by atomic rearrangement resulting from material reactions. This tends to better preserve the intrinsic characteristics of the interface since it is less susceptible to interfacial-contamination effects than are the noncompound-forming interfaces. Indeed, we reported earlier in a study of the Pd-Si interface[3] that microscopic compound formation dominates the chemical and electronic properties of the Pd-Si interfaces.

We have completed a study of silicide formation at the Pd-Si interface using ultraviolet photoemission spectroscopy (UPS) and Auger electron spectroscopy (AES). The reason for choosing the Pd-Si system is threefold. First, we wish to explore the nature of the chemical bonding between the metal *d* and the Si *s*-*p* electrons underlying the mechanism for transition-metal silicide formation. Second, the basal plane of Pd_2Si and the Si (111) surface have an epitaxial relationship with less than 2% lattice misfit,[4] so the atomic structure of the interface is expected to be simple. Third, extensive data on silicide formation in the Pd-Si system show formation of only one compound, Pd_2Si, and that is stable up to 700 °C but can still be readily formed at 200 °C.[5] The compound stability and fast reaction kinetics suggest a strong chemical interaction between the Pd and Si atoms. All these factors facilitate our prototype study of the metal-Si interface.

Results of our study are reported in two papers. Here, the first one describes results for bulk Pd_2Si formed by reacting relatively thick (~100 Å) Pd overlayers with Si. The chemical bond and electronic characteristics of the compound are inferred by interpreting the spectroscopy data using calculated electronic density of states (DOS) for Pd, Si, and Pd-Si compounds. The sequel paper deals with the chemical bonding and reactions at the Pd-Si interface observed during the initial stage of silicide formation.

II. EXPERIMENTAL

All experiments were carried out on single-crystal Si substrates of 1- to 10-Ω cm resistivity.

Before Pd evaporation, the Si substrate was sputter-cleaned using Ar^+ ions of 1-keV energy and then annealed by direct resistive heating up to about 850 °C for about 10 min to remove the sputter damage. Low-energy electron diffraction examination of some sample surfaces showed the annealing procedure to be sufficient to produce the reconstructed (7×7) Si (111) surface or a (1×1) Si (111) surface [probably a disordered (7×7) structure]. Observations by transmission electron microscopy (TEM) revealed that the Pd_2Si formed on the Si (111) substrates after sputtering and annealing treatments was not epitaxial in all areas, indicating incomplete recovery of the surface sputter damage.[6] However, the features of the UPS and the AES spectra were independent of the degree of epitaxy of the Pd_2Si.

Pd evaporations were made by direct sublimation of a resistively heated Pd wire (0.25-mm diam) in the ultrahigh-vacuum chamber. During evaporation, the pressure rise was less than 2×10^{-9} Torr. Auger examination of the Pd surface usually revealed no detectable surface contaminants (i.e., less than 1% surface coverage). Pd thickness was measured by a thickness monitor (for UPS measurements) or calibrated according to the relative intensity changes of the Pd and Si Auger lines with different electron escape distances.[7] Data reported here were all obtained on samples with Pd thickness more than about 50 Å. For these samples, the conversion of Pd into Pd_2Si was carried out by annealing at about 200 °C where a few minutes were sufficient for a complete conversion (as confirmed by TEM phase identification).

Spectroscopy data were taken using a double-pass cylindrical mirror analyzer with an energy-band pass of 0.6%. UPS measurement used a differentially pumped He resonance lamp for photon excitation ($h\nu = 21.2$ eV) and electron-counting techniques. For AES measurements, the electron gun was operated at 5 keV and a beam-chopping method was used to obtain the undifferentiated $N(E)$ spectra directly. Measurements were made on the Pd $M_{4,5}VV$ and Si $L_{2,3}VV$ and KLL Auger transitions. The first two valence-state transitions were used to monitor changes in the valence electronic structure of Pd and Si as a result of silicide formation. There are two other Si valence transitions, the LLV and the KLV lines, which are simpler to interpret since only one valence level is involved. They were not used because of the LLV energy overlap with Pd lines and the weak intensity of the KLV line. The core KLL transition was used mainly to obtain the relative changes in the Auger line intensities in order to determine the composition and thickness of the silicide layer. Here it suffices to mention that the results presented in this paper were obtained from samples which have been identified by Auger composition calibration and TEM diffraction techniques to be the Pd_2Si compound.

III. RESULTS

A. Photoemission and auger spectroscopy

In Fig. 1 the angle-integrated UPS spectrum of Pd_2Si formed on Si (111) is compared with spectra from clean single-crystal Pd (111) and Si (111) surfaces. The considerably larger intensity in the Pd (111) and Pd_2Si spectra arises from the large Pd $4d$ photoionization cross section, which causes the Pd_2Si spectrum to be dominated by the Pd d states. Comparing the Pd (111) and Pd_2Si spectra, the $4d$ band is seen to be shifted toward lower energies as a result of silicide formation; the main Pd_2Si peak B appears about -2.75 eV below the Fermi level E_F. The width of the d band is not greatly changed but those empty d states in Pd metal (above E_F) now become essentially completely filled. These features indicate an electronic structure for Pd in the silicide more like that of the noble metals than the transition metals. The formation of Pd_2Si also brings forth new, but relatively weak, peaks at C and D. In addition, electronic states exist near E_F which produce a characteristic Fermi-level cutoff shape at E_F. This portion of the DOS (designated as A) gives a metallic character for Pd_2Si. The detailed nature of the electronic states contributing to these structures cannot be readily assessed on the basis of the UPS data alone, although it is expected that they involve not only the Pd but also the Si valence states. This will be discussed later in conjunction with results from AES measurements and band calculations.

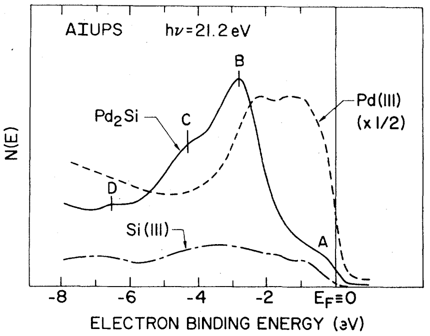

FIG. 1. Angle-integrated UPS spectra observed on Pd_2Si and on single-crystal Pd (111) and Si (111) surfaces. Note the difference in the intensity scales revealing the dominance of the Pd $4d$ states in the Pd_2Si spectrum.

In Fig. 2(a) we compare the Si $L_{2,3}VV$ spectrum for elemental Si with that in Pd_2Si. It is clear that the formation of the silicide significantly alters the line shape of the LVV transition, thus reflecting basic changes in the valence structure of Si. For clarity, we decompose the silicide LVV spectrum into two portions as shown in Fig. 2(b) with one portion scaled according to the LVV shape of elemental Si and the other showing the change in the spectrum. The silicide spectrum displays peaks at 79, 84, 89, and 94 eV. The origin of these peaks will be discussed later; at this point, it is interesting to note that these peaks are separated by about 5-eV energy differences.

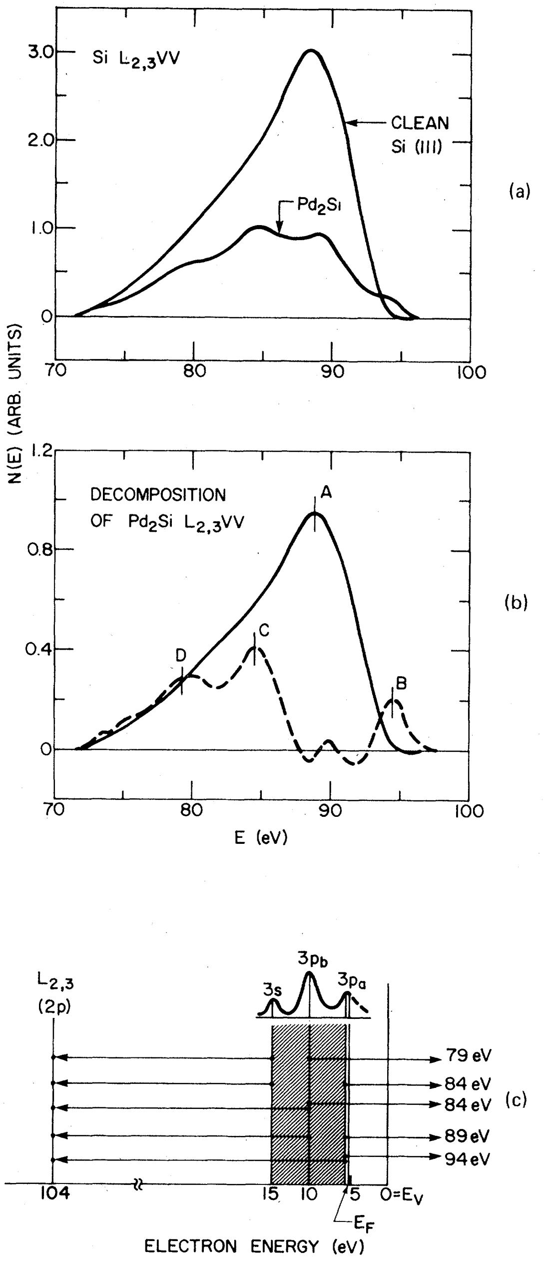

FIG. 2. (a) Comparison of the $L_{2,3}VV$ Auger spectra observed on Pd_2Si and Si (111) surfaces. (b) Decomposition of the Auger spectra into two portions with the solid-line portion proportional to the elemental peak and the dashed-line portion showing the change as a result of silicide formation. (c) Schematics of the Auger transitions for Si $L_{2,3}VV$ in Pd_2Si according to calculated state densities.

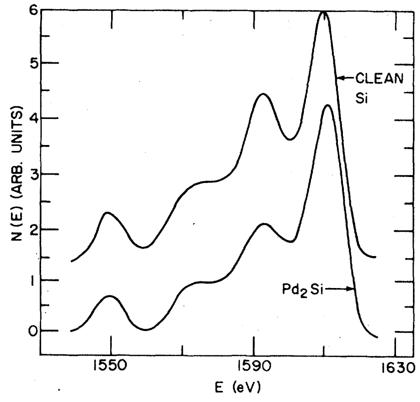

FIG. 3. Comparison of the Si KLL spectra observed on Si (111) and Pd_2Si surfaces. (Intensities normalized for the main peak.)

In contrast, the KLL Si line for Pd_2Si as shown in Fig. 3 exhibits little change from that of elemental Si. This leads to the obvious conclusion that the formation of silicide changes primarily the valence states of Si but does not change its core-level positions greatly (<1 eV.) In Fig. 4, the $M_{4,5}VV$ spectra for Pd obtained from a pure Pd film and from Pd_2Si are shown. The shape of the main doublet in the spectrum shows no visible difference as a result of silicide formation. The lower-energy peak A of this spectrum comes from transitions involving $3d_{5/2}$ core states and the higher-energy one (B) corresponds to transi-

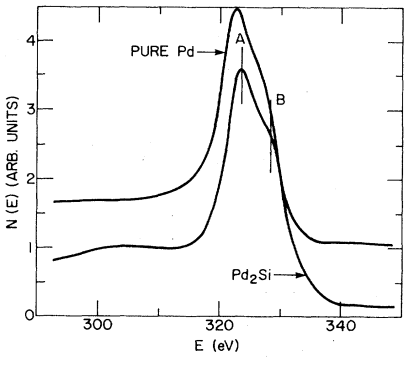

FIG. 4. Comparison of the Pd $M_{4,5}VV$ Auger spectra observed on a polycrystalline Pd surface and a Pd_2Si surface formed on Si (111) substrate. (Intensities normalized for the main peak.)

tions involving the $3d_{3/2}$ states. The separation of these two $3d$ peaks caused by spin-orbit splitting is about 5 eV in pure Pd as determined by XPS measurements.[8] The $M_{4,5}VV$ Auger transition has an energy separation between A and B still of 5 eV, so the relative levels of the two $3d$ states do not change upon the formation of silicide, and its linewidth of about 10 eV reflects the transition arising from self-convolution of the $4d$ valence states (5 eV wide). These features agree quantitatively with the results obtained in a similar spectroscopic study on amorphous Pd-Si metallic glasses.[8] In the amorphous-compound study, the high-energy peak of the compound was observed to shift about 1 eV toward lower energy. This magnitude of energy shift has not been ascertained in our measurements. In our Pd_2Si spectrum, a new broad peak appears at about 302 eV. The intensity of this peak was observed to increase with Pd layer thickness during the initial stage of silicide formation so it is associated with silicide formation. The origin of this peak is not clear at present.

B. Calculated state densities

The UPS and AES results indicate significant changes in the valence electronic structures of both Pd and Si upon silicide formation. Extracting information relevant to the bonding characteristics requires line-shape analysis of the spectra which is not straightforward. As noted earlier, although the UPS spectrum is dominated by Pd $4d$ contributions, Si contributions are also present, so that a distinction between these two cannot be made by UPS data alone. The Auger spectrum is specific to the local Si or Pd electronic structure but it involves a self-convolution of the valence-state densities; the multistate nature of the transition makes it difficult to deconvolute the valence density of states.

To facilitate the interpretation of the measured spectra, calculations of density of state were carried out for both Pd, Si, and several Pd-Si compounds (although here we will only show results of two compounds most relevant to our data interpretation). To describe the crystal structure used in the calculation, it is useful to examine first the lattice structure of Pd_2Si. This compound has an hcp structure with atomic arrangements for the two basic stacking layers[4] as shown in Fig. 5. The structure shows that each Si atom is encased by nine Pd atoms stacking in three equilateral triangles with 60° relative rotations. Probably the most important aspect of this structure in affecting the Si spectra is that the tetrahedral environment of elemental Si is completely eliminated; each Si is completely surrounded by Pd atoms. Limitations of our computer programs prevent us from studying Pd_2Si in the hexagonal structure. However, our self-consistent calculations for Pd-Si compounds in the Cu_3Au, CuAu, and CsCl structures reveal, we feel, the important properties of the Pd-Si bond, such as the role of stoichiometry, the importance of charge transfer, the strength of the bond, and the implications of depriving the Si atoms of the Si neighbors. In Fig. 5(b) we show the CuAu- and Cu_3Au-type crystal structure for PdSi and Pd_3Si. All three of the structures used in the calculations permit the Si atoms to be surrounded by Pd atoms. Furthermore, comparison of the results for the CsCl and CuAu structures provides an indication of the importance of the local geometrical structure. In all cases total-energy minimization was used to determine the lattice constant and to assess the bonding strength.

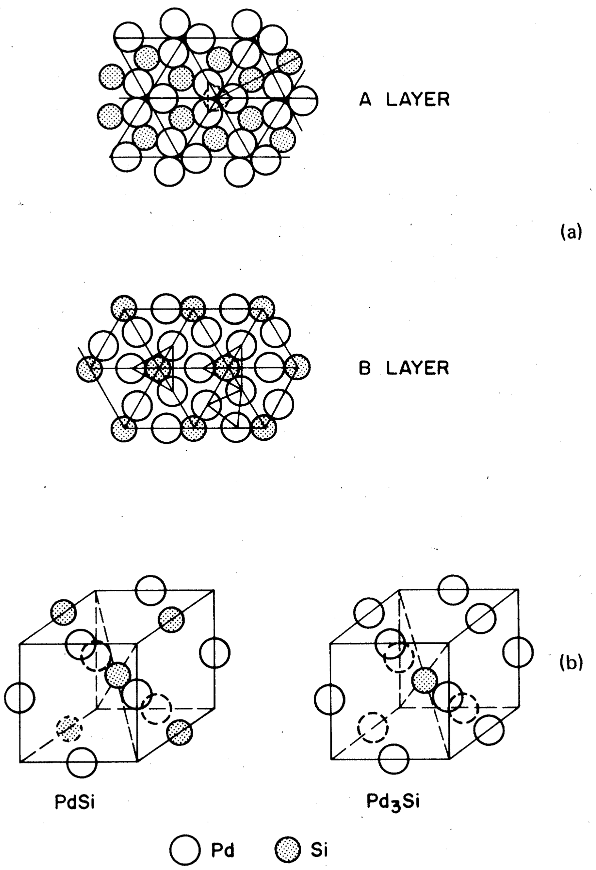

FIG. 5. (a) Atomic arrangements on the two basic layers forming Pd_2Si structure. The hcp Pd_2Si structure has a stacking sequence of *ABAB*. (b) The CuAu- and Cu_3Au-type crystal structures of PdSi and Pd_3Si used for calculating DOS of Pd-Si compounds.

The calculations employ the augmented-spheri-

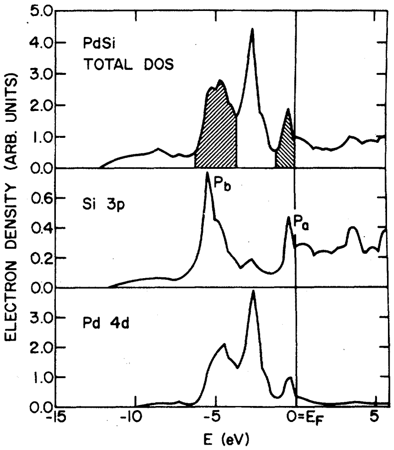

FIG. 6. Calculated total and partial state densities for Pd, Si, and PdSi compound. Note the difference in the vertical scales for the state densities. The shaded areas in the total DOS indicate the bonding and antibonding states.

cal-wave method.[9] The aspects of this method which are important in the present context are: (1) it is fully self-consistent (if charge transfer were important, we would see it); (2) calculated heats of formations agree well with experiment[9,10]; and (3) the only input to these calculations is the atomic numbers of the constituents and the crystal structure.

Figures 6 and 7 show the calculated DOS for PdSi and Pd_3Si in the CuAu and Cu_3Au structures (fcc-like). Also shown are the partial (projected) DOS corresponding to the Si and Pd sites. Several aspects of the state densities should be noted. First, the total state densities for PdSi and Pd_3Si are qualitatively similar, indicating that rigid-band theory is the appropriate perspective from which to consider stoichiometry changes. The principal difference between PdSi and Pd_3Si is the position of the Fermi level. Second, the *d* states of the Pd dominate the total state density. One should note, however, that the DOS near E_F is not exclusively due to the *d* states; rather the Si $3p$ states contribute about equally, and a similar situation exists in the tail portion of the *d* band at about 5.5 eV below E_F. Third, the density of Si *p* states indicates two well-defined groups of states which straddle the *d* band. These two groups reflect the formation of bonding and antibonding Si $3p$-Pd $4d$ hybrids. The bonding and antibonding hybrid states are observed in the UPS spectrum (Fig. 1) as the states at *C* and *A* positions, respectfully. The chemical bond in Pd_2Si does not seem to involve the Si $3s$ states since most of them remain about 10 eV below E_F. The large effect on the Si $3p$ states is not unexpected since these states are mainly responsible for the directionality in the covalent bond of Si, which is completely absent in the silicide.

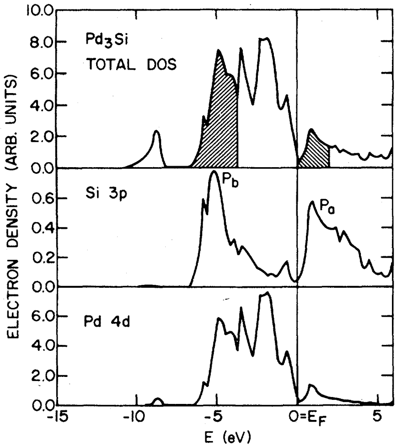

FIG. 7. Calculated total and partial state densities for Pd, Si, and Pd_3Si compound. Note the difference in the vertical scales for the state densities. The shaded areas in the total DOS indicate the bonding and antibonding states.

IV. DISCUSSION

In studying the UPS spectrum of amorphous PdSi compounds, Riley *et al.*[8] estimated the cross-section ratio $\sigma(\text{Si } 3p)/\sigma(\text{Pd } 4d)$ to be about unity. Judging from this ratio and the relative numbers of valence electrons for Pd and Si (20 vs 4 in Pd_2Si), the UPS spectrum for Pd_2Si is expected to reflect rather closely the total DOS with dominant contributions from the Pd *d* states. On this basis the UPS data and the calculated DOS are in good agreement, with both showing the Pd *d* band being completely occupied and the major *d* peak shifted to about -2.75 eV below E_F. Interestingly, the shift of the major *d* peak was not constant but rather was observed to vary from -3.5 eV at submonolayer Pd coverage to -2.75 eV in bulk Pd_2Si.[3] This shift and the stoichiometry dependence of the *d* peak and Fermi level separation (larger for higher Si concentration) seen in the calculated DOS (Figs. 6 and 7) suggest that early stages of the interface are Si-rich as compared to Pd_2Si. The implication of such stoichiometry effects on the interface properties will be discussed in the sequel paper.

The energy-band calculations indicate that the principal factor in the *d*-peak displacement is not charge transfer, but rather the formation of a hybrid complex resulting from the strong interaction of the *p* (Si) and *d* (Pd) states. The *d* component of this complex, while well defined in the photoemission spectrum, contains sufficiently fewer than ten electrons that its position below E_F does not imply significant charge transfer.

For AES, Sawatzky[11] showed that for transitions involving two valence states, the spectrum is quasiatomic if the Coulomb interaction between the two holes is much larger than the bandwidth; otherwise it resembles the self-convolution of the DOS of the valence band. Previous Auger studies[12,13] on d metals showed that the quasiatomic character holds in general for the $M_{4,5}VV$ transitions. Since the observed $M_{4,5}VV$ line shape was almost identical for Pd and Pd_2Si we infer that the Pd local charge density remains quasiatomic in the silicide lattice. This is really not surprising since the local Pd configuration in Pd_2Si is primarily of the nearest-neighbor Pd-Pd type.

Riley *et al.*[8] have also concluded from the peak shift of the Pd $M_{4,5}VV$ line that negligible charge transfer occurs between Pd and Si in the amorphous Pd-Si metallic glass. This is consistent with our observation of the Pd $M_{4,5}VV$ transition in Pd_2Si as well as with our calculated state densities.

In contrast, the Si $L_{2,3}VV$ transition satisfies the band-convolution criterion, and the line shape of this transition has been investigated and successfully understood for elemental Si in a number of theoretical studies.[14-16] The conclusion generally reached is that the spectrum is dominated by the p-p-type transitions involving two $3p$ valence states, which account for most of the intensity for the 89-eV peak. As for the other transitions, the s-p types represent only about 10%, contributing mainly to the tail portion of the spectrum, and the s-s transitions are negligibly small. These weightings are attributed to matrix-element effects which suppress contributions from the overlap (bonding) charge density of the s-like atomic orbitals.

For Pd_2Si the observed $L_{2,3}VV$ spectrum can be qualitatively understood based on the Si DOS obtained from our calculations and schematics for the Si $L_{2,3}VV$ transitions in the silicide are shown in Fig. 2(c). The 5-eV splitting of the bonding (p_b) and antibonding (p_a) states can account for peaks at 94 eV (p_a-p_a), 89 eV (p_b-p_a), and 84 eV (p_b-p_b). Additionally, transitions involving the p_a, p_b, and $3s$ states contribute to the peaks at 79 and 84 eV, respectively. Evaluation of the line shape would require detailed calculation of the silicide spectrum which is currently under study[17]; however, Roth[18] has recently derived the Si valence DOS by self-deconvolution of the $L_{2,3}VV$ spectrum observed for Pd_2Si, and his results agree generally with our calculated DOS and the schematics of the transitions.

We found that the 94-eV peak was more readily observed at low Pd coverages than the 79- and 84-eV peaks, with its intensity reaching a relative maximum under about two monolayers (~3 Å) of Pd coverage. This reveals enhanced DOS existing in the band gap during the initial stage of silicide formation. (Details of this observation and its stoichiometry dependence will be discussed in the sequel paper.) Since the 94-eV peak originates from the p_a anitbonding states, which may be only partially occupied in the initial state of Pd_2Si, we speculate that some of the empty antibonding states can also contribute to the Si $L_{2,3}VV$ Auger spectrum because they are the states constituting the screening charge brought to the Si site by the core hole responsible for the Auger transitions. (The initial state from the viewpoint of the Auger transitions is the fully screened final state of the core-hole-creation process.[19,20])

Summarizing the AES and UPS results, the formation of Pd_2Si is found to affect both the Pd- and Si-derived states: for Pd, the d states become "filled" and shifted to about -2.75 eV below E_F; for Si, the $3p$ states are split into two peaks about 5 eV apart, while the $3s$ states remain about 10 eV below E_F and not much affected. The chemical reactions responsible for Pd_2Si formation involve Pd $4d$–Si $3p$ bonding states at about -5.5 eV and antibonding states near E_F. These overall features of the chemical bond for Pd_2Si crystalline compound are quite similar to those observed for amorphous $Pd_{81}Si_{19}$ metallic glass.[8] The calculations demonstrate that stoichiometry can affect compound stability by varying the occupation of the antibonding states. This is also reflected in the calculated heat of formation which shows a sharp variation with the stoichiometry. All these results indicate that the stable stoichiometry is determined by the energy benefit of positioning E_F below the antibonding state, so the silicide in the Pd-Si system tends to contain more Pd than the 50:50 ratio in order to improve its phase stability.

Finally, the electronic structure of Pd_2Si as deduced here can be used to account for its transport properties. Wittmer *et al.*[21] measured the transport properties of Pd_2Si from the Hall mobility and the electrical conductivity. They concluded that Pd_2Si is metallic with negative charge carriers of average mobility but were unable to explain the low conductivity value which amounts to only about $\frac{1}{6}$ of the mobile charges in pure Pd. We have already pointed out the metallic character of Pd_2Si. Significantly, our results show also that in Pd_2Si, most of the d band is shifted about 2 to 3 eV below E_F so these d electrons do not contribute to the transport properties; thus the mobile charges come only from the small portion of the total electrons located near E_F as observed by these authors in their conductivity measurements of Pd_2Si. Interestingly, these electrons are also responsible for part of the chemical bond between Pd and Si atoms in Pd_2Si.

ACKNOWLEDGMENTS

We wish to thank Dr. K. N. Tu and Dr. J. L. Freeouf for valuable discussions during the course of this work and Dr. T. Y. Tan for his TEM phase identification of the Pd_2Si. This work was supported in part by the Office of Naval Research.

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