

## Si(111)-Pt interface at room temperature: A synchrotron radiation photoemission study

G. Rossi, I. Abbati,\* L. Braicovich,\* I. Lindau, and W. E. Spicer  
*Stanford Electronics Laboratory, Stanford University, Stanford, California 94305*  
 (Received 24 August 1981)

We present extensive results on synchrotron-radiation angle-integrated photoemission from Si(111) surfaces onto which increasing amounts of Pt (coverages  $\Theta$  from 0.07 to 40 monolayers) were deposited. Both core lines (Si  $2p$  and Pt  $4f$ ) and valence-band states have been measured. In the latter case we present results taken at a photon energy of  $h\nu=80$  eV where the Pt  $5d$  contribution is dominant and at  $h\nu=130$  eV where the Cooper minimum effect reduces the Pt  $5d$  photoemission considerably so that information on the Si contribution to the valence states can be revealed. We show that submonolayer coverages ( $\Theta \geq 0.07$ ) of Pt disrupt the surface sufficiently to introduce considerable changes in the photoemission spectra with respect to that of clean Si(111). An interface with a photoemission spectrum resembling that of a silicide has developed at about 2–10 monolayers. At increasing  $\Theta$  the region explored with photoemission shows enrichment of the metal, but the situation at  $\Theta=40$  is still very far from that of the pure Pt metal, thus indicating a very strong chemical interaction at room temperature on the depth scale of tens of monolayers. Opposite chemical shifts of the Si and Pt core lines are seen (Pt towards lower and Si towards higher binding energies with increasing  $\Theta$ ) and, moreover, the shape of the Si  $2p$  core lines is modified towards that typical of a metallic phase. All these results are discussed in terms of the nature of the chemical bond between Si and Pt.

### I. INTRODUCTION

The study of semiconductor–transition-metal interfaces is becoming a central topic in solid-state surface physics both for fundamental and practical reasons. The fundamental interest in these systems lies in the connection between surface chemistry parameters and the electronic properties of the junction<sup>1–8</sup> whose low-barrier (Ohmic) or high-barrier (rectifying) characteristics are not completely understood in terms of the mechanism underlying the formation of different barriers.

A better understanding of the physical chemistry of different semiconductor– $d$ -metal interfaces also provides valuable information of practical use since low- and high-barrier junctions are highly utilized in the production of active devices.<sup>9</sup>

This article presents the first systematic energy-dependent photoelectron-spectroscopy study of the Si-Pt interface at room temperature. Special attention has been given to the low-coverage regime since the very first stage of the interface growth is probably determined by the semiconductor surface disruption caused by the metal adatoms as discussed in an earlier paper.<sup>10</sup> At increasing coverages, we have followed the evolution of the elec-

tron states of the Si(111)-Pt interface by taking full advantage of the unique tunability of synchrotron radiation (SR). In addition to extensive core-level spectroscopy data, we present valence-band photoemission spectra at two energies, one ( $h\nu=130$  eV) corresponding to the Cooper-minimum region for the Pt  $5d$  photoemission ( $h\nu=130–160$  eV), so that the information on the Si  $sp$  contribution to the energy distribution curves (EDC's) can be revealed. This method, introduced for the first time in an earlier publication,<sup>10</sup> has turned out to be very useful in understanding the nature of the chemical bond between Si and  $d$  metals.<sup>11–14</sup> In fact it allows us to make a scheme for the assignment of the Si– $d$ -metal chemical reactions on a pure experimental basis.

The  $h\nu$  dependence of the  $4d$ - and  $5d$ -electron photoionization cross section which shows a deep minimum in the region between  $h\nu=130$  and 160 eV (Cooper minimum) is of great advantage in interface photoemission studies where the density of valence states can be probed, tuning the sensitivity to the  $d$  contribution. The presence of Cooper minima in solids has been proved experimentally in a number of recent synchrotron-radiation photoemission works both for pure  $4d$  and  $5d$  metals<sup>15</sup>

and for *d*-metal compounds.<sup>10–13</sup> A theoretical analysis of the Cooper minimum effect for valence-band states is still lacking and possible deviations from the pure atomic levels have not been explored in detail. In this paper we will, therefore, not argue about the Cooper-minimum effect *per se* or try to make quantitative comparisons between our results and the calculated atomic cases because that could only be highly speculative at present and is beyond the purpose of this work on Si–*d*-metal interfaces. Of importance for the present work is that the reduced *d* emission at the Cooper minimum allows a detailed study of the *sp* contributions to the total density of states which are hidden at all the other energies where the *d* emission is the dominant feature in the EDC's.

The Si-Pt junction belongs to the so called Si–transition-metal reactive interfaces as do Si-Pd (Refs. 11, 16, and 17) and Si-Ni (Refs. 18 and 19). One characteristic of the Pt-Si system is that two stable bulk compounds are known: PtSi and Pt<sub>2</sub>Si, with the Si-rich silicide formed at higher temperatures.<sup>20</sup> Some spectroscopic information on these two phases of Pt (Ref. 21) as a function of the temperature<sup>22</sup> is already available in the literature.

In general, rather than being characterized by a single stoichiometric reaction product, the nonannealed reactive transition-metal–silicon interfaces present (Refs. 10–12, 16–19, and 21–23) a broad mixed region where semiconductor-rich and metal-rich phases clamp a silicidelike phase, with concentration gradients defining the boundaries between these phases. A sharp interface has been reported for Si(111)-Pd where a Pd<sub>2</sub>Si-like overlayer is formed<sup>11,16,17</sup> as a result of a solid-state reaction, although a concentration gradient is present in the metal-rich side.<sup>11</sup>

This paper adds new information to the previous theoretical and experimental literature on the physical chemistry of the reactive interfaces, which has implications for the Schottky-barrier formation process and for the derivation of the barrier height. Reference to this literature will be made throughout the paper and in particular to the empirical correlations of these properties to such macroscopic observables as the eutectic temperature<sup>7</sup> and the heat of formation of the semiconductor-metal bond.<sup>8</sup>

The paper is organized as follows. An account of experimental techniques is given in Sec. II and the experimental results are collected in Sec. III. The discussion in Sec. IV is carried out with reference to three coverage intervals [in units of mono-

layers (ML)] which have their own features: section A—low coverages ( $\Theta < 0.51$  ML), section B—medium coverages ( $0.5 < \Theta < 10$  ML), and section C—high coverages ( $\Theta > 10$  ML). In Sec. V, we summarize the main results in connection with the interface growth mechanism.

## II. EXPERIMENTAL

Medium-doped ( $10^{16}$  atoms/cm<sup>3</sup>) *n*-type Si samples were carefully cleaved *in situ* at a working pressure of  $4 \times 10^{-11}$  Torr. The cleaves produced highly reproducible angle-integrated valence-band photoemission spectra. This is an important point because the Si(111) photoemission spectra are very surface sensitive at the energies used ( $h\nu = 80$  and 130 eV), and the relative intensities of the different valence peaks can vary depending on the quality of the cleaves as will be discussed later. What typically happens for certain qualities of cleaves is that the two deepest structures of the Si(111) valence band are depressed in intensity with respect to the top of the valence band. Examples of these kinds of EDC's can be found in a paper published earlier.<sup>10</sup>

The Pt overlayers were deposited by evaporation from a thin Pt wire wound around a W filament wire. Resistive heating at a power level of about 50 W was necessary for the evaporation. This required a very careful outgassing procedure and a special design of the evaporator assembly, similar to a source for MBE (molecular beam epitaxial) growth. The evaporations were done at a pressure lower than  $1.5 \times 10^{-10}$  Torr. The deposition rate was controlled with a quartz oscillator located on the sample carousel and alternatively put in the sample position in order to avoid any geometrical correction factor and any heating from the evaporation filament. Very stable rates, typically 1 Å/min, were easily established and the desired coverages were obtained by operating a shutter in front of the Pt source. The evaporation rate was checked again immediately after the completion of the overlayer preparation. The accuracy of the total coverages should be better than 20% for the lowest coverages and slightly better for the thicker depositions. No traces of contaminants were detected using either x-ray photoemission or core-line SR spectroscopy.

The angle-integrated EDC's were taken with a double-pass cylindrical mirror analyzer (CMA) in the retarding mode in an ultrahigh vacuum (UHV)

system described previously.<sup>26</sup> The light source was the 4<sup>th</sup> beam line at the Stanford Synchrotron Radiation Laboratory (SSRL) equipped with a "grasshopper" monochromator providing intense monochromatic light in the range  $h\nu=65-500$  eV.<sup>24</sup> The surface of the sample was normal to the CMA axis and the light was impinging at grazing incidence (15°). The overall resolution was 0.5 eV which is sufficiently good for the purpose of this study.

### III. RESULTS

This section is a summary of the experimental photoemission results which will be discussed in Sec. IV. The main trends in the experimental data are given in representative plots. The valence-band dependence on the Pt coverage ( $\Theta$  in monolayer units) is summarized in Figs. 1 and 2 for  $h\nu=80$  and 130 eV, respectively. At  $h\nu=80$  eV the Pt 5*d* photoionization cross section is much greater than the Si *sp* (Ref. 25) so that already at submonolayer coverages ( $\Theta > 0.33$  ML), and Pt 5*d* emission is the

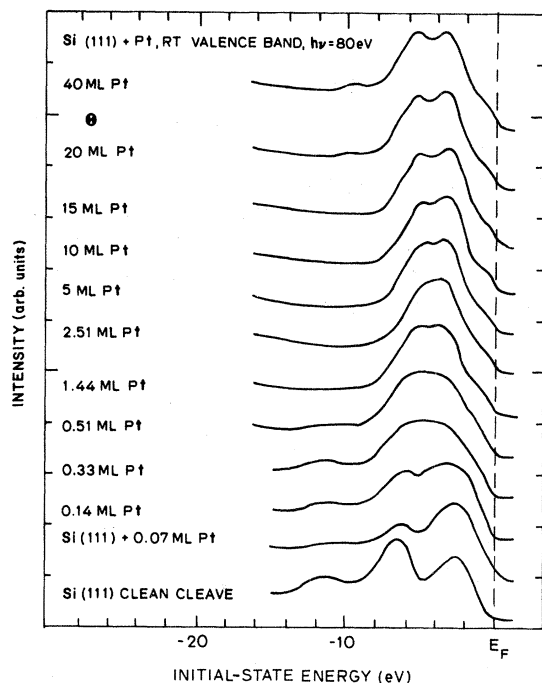


FIG. 1. Angle-integrated photoelectron energy distribution curves (EDC's) at  $h\nu=80$  eV for Si(111) and Pt at increasing coverages at room temperature. The Pt coverages quoted in the figure are in monolayer units where 1 ML =  $7.8 \times 10^{14}$  atoms/cm<sup>2</sup>, i.e., the surface density of the Si(111) substrate.

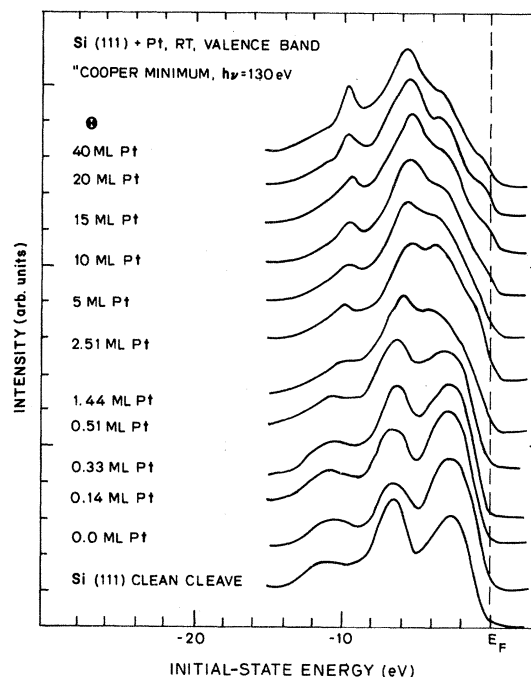


FIG. 2. Angle-integrated EDC's for Si(111) and Pt in the Cooper-minimum region for the Pt 5*d* photoionization cross section ( $h\nu=130$  eV). Coverages in ML.

dominant feature in the EDC's. On the other hand, at  $h\nu=130$  eV the Cooper effect (strong in Pt metal between 130 and 160 eV) reduces the emission and the evolution of the Si valence states are clearly revealed. The photon energy dependence is seen better in Fig. 3 where we contrast, at selected  $\Theta$ , the EDC's at the Cooper minimum and those with the dominant *d* contribution.

The Si 2*p* (unresolved doublet) core lines taken at a photon energy of 160 eV are plotted versus  $\Theta$  (at selected values) in Fig. 4. In the figure, the peaks are normalized to the same height to illustrate the shape modifications as a function of coverage. There is a very pronounced asymmetric broadening of the line towards higher binding energy with increasing coverage. The intensity variations of the Si 2*p* and Pt 4*f* levels versus  $\Theta$  are given in Fig. 5. From this plot alone, it can be deduced directly that the Si-Pt interface is not atomically abrupt but that some intermixing takes place since the Si and Pt peak intensities change over a much larger coverage interval than the electron escape depth (which is typically 5 Å at these energies.<sup>26</sup> The shift in binding energies for the same Si and Pt core lines as a function of coverage is shown in Fig. 6. The observed chemical shifts are fairly small and in opposite directions for Pt and Si.

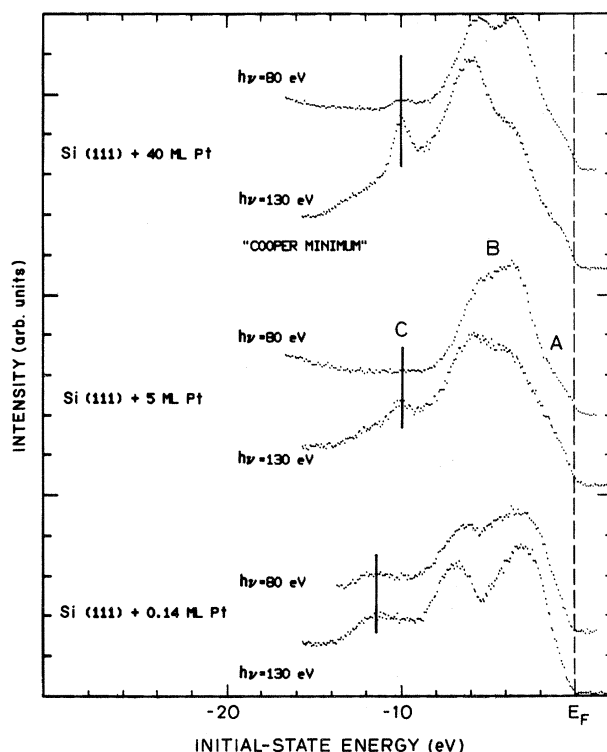


FIG. 3. Photon energy dependence of photoemission spectra for Si(111) and Pt: comparison between  $h\nu=80$  eV and the Cooper minimum ( $h\nu=130$  eV) at selected low, intermediate, and high coverages (in ML).

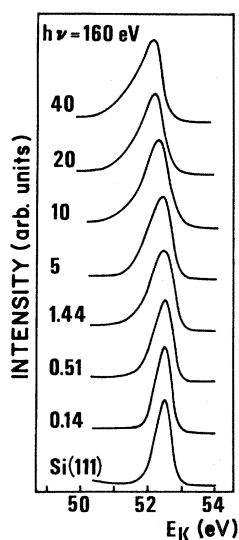


FIG. 4. Coverage dependence of Si  $2p$  core-line photoemission (unresolved doublet) at  $h\nu=160$  eV. The amplitude of the spectra has been normalized to the same value in order to follow the position and shape evolution. The spectra are plotted vs the kinetic energy of the photoelectrons; in fact, the absolute binding energy is uncertain by a factor of  $\pm 0.3$  eV because of the monochromator calibration.

It is noteworthy that all the photon energies used for the valence-band and core-level results shown in Figs. 1–4 give similar values for the electron kinetic energies, corresponding to the minimum of the escape depth.<sup>26</sup> This makes the core and valence information directly comparable since they refer to the same sampled depth of the Si-Pt interface (about 5 Å).

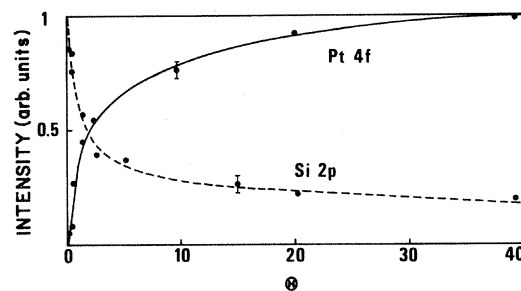


FIG. 5. Intensity profiles of Si  $2p$  and Pt  $4f$  core lines as a function of the coverage. The intensities are normalized to the maximum value of amplitude of the Si and Pt signals obtained in the experiment [i.e., the clean Si(111) surface and the  $\Theta=40$  Pt coverage, respectively].

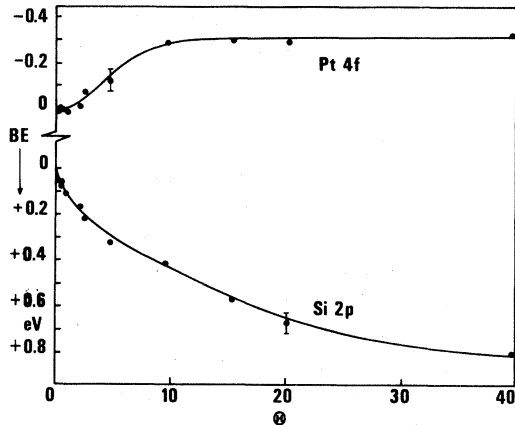


FIG. 6. Binding-energy variations for the Si 2*p* and Pt 4*f* core lines as a function of coverage. The curves are the best fits to the experimental points.

#### IV. DISCUSSION

In order to carry out a systematic analysis of the  $\Theta$  dependence of the spectra, it is important to note some general features present in the spectra of Figs. 1 and 2. The valence spectra never reach the shape typical of pure Pt even at the highest coverage ( $\Theta=40$ ) explored in the present research. This is evident by comparing the spectra shown in Fig. 7 for pure Pt (both at and away from the Cooper minimum) with the highest coverage spectrum ( $\Theta=40$ ) of the Si(111)-Pt interface in Figs. 1 and 2. It is clearly seen that even at very high coverages the Si(111)-Pt spectrum is very different with respect to that of pure Pt. This confirms the very strong chemical interaction at the Si(111)-Pt interface which has already been pointed out for lower coverages at room temperature in previous work by Abbati *et al.*<sup>27</sup> The pure Pt measurements were taken in a different run with the same SSRL beam line from a (111)-oriented clean Pt crystal.<sup>28</sup> The scaling factor between the two EDC's (80 and 150 eV) can be directly compared to those of the interface measurements. This comparison provides direct evidence for the reduction of *d* emission due to the Cooper-minimum effect also for *d* states involved in bonds with Si; the total counting rate in the spectra at  $h\nu=130$  eV is smaller by a factor variable between 10 and 3 with respect to the spectra at  $h\nu=80$  eV. It is apparent that relevant contribution from local density of states around Si can be deduced from the results at the Cooper minimum.

It is important to note that, in the intermediate

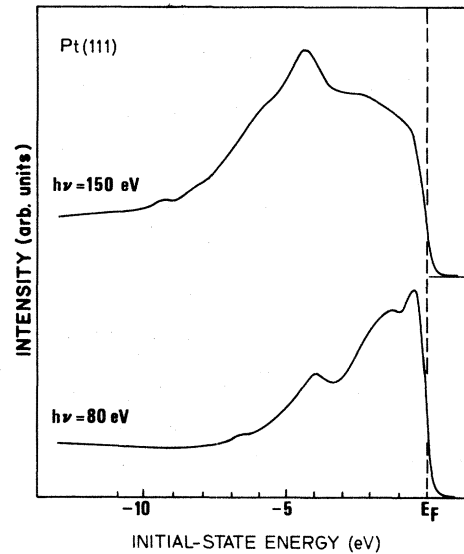


FIG. 7. Valence-band angle-integrated EDC's for pure Pt [Pt(111)] at  $h\nu=80$  eV and in the Cooper-minimum region ( $h\nu=150$  eV) (Ref. 28). The amplitude of the curves has been normalized to the same value; the counting rate ratio between the spectrum at  $h\nu=80$  eV and the spectrum at  $h\nu=150$  eV is  $I(h\nu=80 \text{ eV})/I(h\nu=150 \text{ eV})=8$ .

$\Theta$  region, the valence-band photoemission is already typically "silicidelike." For example, at  $\Theta=1.45$  and  $2.50$  the valence photoemission at  $h\nu=80$  eV is similar to that from Pt<sub>2</sub>Si and PtSi at  $h\nu=21.2$  eV as reported by Abbati *et al.*<sup>22</sup> Thus, at these coverages, the reaction has proceeded up to a silicidelike situation. This observation suggests a natural way to divide up the coverage regions into three intervals, which will be discussed separately below. In the submonolayer region ( $\Theta \leq 0.51$ ) there is not sufficient metal present to develop a silicidelike interface, while at high coverages ( $\Theta > 10$ ) there is a metal-rich phase, although some general features typical of silicides are still present. Of course there is not a clear-cut distinction between the three regions, and the selection of the coverage intervals is somewhat arbitrary; nevertheless, the division is of great help for the discussion.

##### A. The low-coverage region ( $\Theta < 0.51$ ML)

In this coverage region the most interesting result is the strong modification of the EDC when a very small quantity of Pt is deposited onto the surface ( $\Theta=0.07$ ). The Pt contribution to the

valence-band emission is very small (3–4% of the total signal at  $h\nu=80$  eV, as can be deduced by scaling from the high-coverage cases,  $\Theta=20$  and 40). Thus, in the absence of substrate modifications, the EDC is expected to be basically invariant. On the contrary a dramatic modification of the clean Si valence-band contribution is seen in Fig. 1 ( $h\nu=80$  eV) and in Fig. 2 ( $h\nu=130$  eV), mainly in the high-binding energy region of the valence band. This indicates that a small fraction of Pt atoms has a strong effect on the rearrangement of the Si(111) surface, most probably the top-most layer. This observation indicates that the interaction between Si and Pt is very strong so that Pt atoms with surrounding Si form very distorted localized regions which alter the long range properties of the clean Si surface. No systematic low-energy electron diffraction (LEED) studies are available on this subject but would obviously be of great value. The available results by Roth and Crowell<sup>29</sup> confirm that a small amount of several transition metals gives a strong background with a considerable attenuation of the  $(2\times 1)$  pattern. This is consistent with the strong effects seen in the present photoemission study which are direct evidence of a disruption of the Si surface from the very beginning of the interface formation.

As far as the nature of this disruption is concerned we can only present some speculations which should stimulate further research on this interesting problem. A first possibility is that the interaction with Pt induces a partial disordering of the surface. This would be consistent with the decrease of the photoemission intensity from the two deepest valence structures, since a trend of this kind has already been seen in the comparison between crystalline and amorphous Si (Refs. 30 and 31) (generally observed whenever the Si states become more localized). Another possibility is that the interaction with Pt induces changes in the relaxation of the top Si layer with a consequent modification of the surface back bonds which contribute to the deeper region of the valence band.<sup>32</sup> A qualitative comparison to the calculations by Pandey and Phillips<sup>33</sup> for the  $(1\times 1)$  Si surface shows that the modification of our EDC's is in agreement with a strong reduction of the relaxation. In this case the reduction should be originated by the metal atoms interacting with the surface lattice.

Of course the two processes can be present at the same time and further work is needed to assess the problem. In any case, this strong modification is

of crucial importance since it creates the surface which interacts with Pt deposited at increasing coverages.

The importance of this disruption mechanism is also confirmed by comparing the present results with our previous work<sup>10</sup> where the clean Si(111) spectrum is very similar to that obtained for 0.07 ml in the present experiment. This is most likely due to a different quality of the cleaves. Imperfections in the cleavage procedure probably have an effect analogous to the disruption induced by the very thin Pt overlayer. With these precautions in mind, there is no contradiction between the present results for the Si(111)-Pt interface and those reported earlier.<sup>10</sup>

When  $\Theta$  increases beyond 0.07, a small  $5d$  contribution is detectable and the deeper-lying Si states are modified, as can be seen from the spectra at the Cooper minimum, Figs. 1 and 2. This is the first evidence for the formation of mixed orbitals between Pt  $5d$  and Si  $sp$  states, which is also confirmed by the progressive chemical shifts of the Si and Pt core lines in opposite directions (see Fig. 6). At these coverages the situation is not yet that typical for silicides, but the chemical shifts of the core lines indicate the presence of a chemical reaction and a starting trend towards a silicidelike situation.

#### B. The intermediate-coverage region ( $\Theta=1-10$ ML)

The intermediate-coverage region presents a high degree of stability for the shape of the valence-band EDC's both at  $h\nu=80$  and 130 eV and can be characterized as the silicidelike region of the interface. In fact the energy position of the major peak and its width<sup>34</sup> are typical for silicides as already observed in the ultraviolet photoemission spectroscopy (UPS) experiments at  $h\nu=21.2$  eV,<sup>27</sup> and for other reactive Si-transition-metal interfaces such as Si-Pd (Refs. 11, 16, and 17) and Si-Ni.<sup>18</sup> The stability over such a broad interval of coverages is the result of a chemical reaction involving the deposited Pt atoms and the Si substrate, leading to a silicidelike phase several monolayers wide. In fact, for the highest coverages in this region (5 and 10 ML), the unreacted Si surface is at least 10–15 Å beyond the depth sampled by photoemission (5 Å).

Before discussing the details of this coverage regime, we recall the interpretation scheme for the Si-transition-metal bond introduced by Riley

*et al.*<sup>35</sup> and lately applied to Pd-Si,<sup>10</sup> based both on experimental results and theoretical calculations of the orbital contributions to the various EDC structures. The scheme is in agreement with that obtained independently by Rubloff *et al.*<sup>16</sup> The three main features of the valence states due to a Si-transition-metal bond are (compare Figs. 1 and 2): (i) a structure *A* around 0.5 eV below the Fermi level containing mixed orbital contributions from Si *p* and metal *d* electrons having antibonding character; (ii) the main structure *B* containing dominant Si *p* and Pt *d* hybrid-bonding contributions extending between  $-0.45$  and  $-2.5$  eV, being typical (with respect to the Fermi level) of the silicide bond and having a stronger Pt *d* character in the peak region ( $-2$  eV), and (iii) a deeper structure *C*, less involved in the bonding, due to Si *s* electrons with a minor contribution of metal *d* states. The bonding scheme is discussed in detail by Rossi *et al.*<sup>10</sup> and the reader is referred to this work for further information.

The stability of the bond involving hybridization between Pt *d* and Si *p* states is evident throughout this coverage region as shown by the presence of only minor changes in the EDC shape at  $h\nu=130$  eV (Fig. 2). On the other hand, the details of the valence-band emission at both photon energies, as well as the core-line spectroscopy results, indicate a change in composition of the silicidelike phase as the Pt coverage is increased. The leading peak in the EDC's at  $h\nu=80$  eV shifts towards lower binding energies for increasing Pt coverages. This is consistent with the changes observed for increasing Pt depositions in a silicidelike interface, as reported by Abbati *et al.* in Ref. 34 where temperature-dependent UPS results for Si-Pt were presented.

The analysis of the core-line intensities presented in Fig. 6 shows for this interval a strong decrease of the Si *2p* emission and an increase in the Pt *4f* emission. This accounts for a concentration gradient throughout the silicidelike phase. Additional information can be obtained by analyzing the chemical shifts of the core levels. The Pt *4f* level shift towards lower binding energies is completed within this coverage interval (for  $\Theta=10$ ), and the shifted peak remains stationary in energy in the high-coverage region, suggesting that the Pt atoms see gradually fewer Si near neighbors and are eventually no longer sensitive to the presence of dilute Si in the high-coverage region. The Si *2p* core lines, on the other hand, keep shifting towards higher binding energies with increasing Pt coverage which is consistent with a trend towards higher di-

lution.

It should be noted that the chemical shifts seen in the present system and in related systems are very small. Thus, their interpretation merely in terms of a charge-transfer mechanism is open to difficulties since other processes are also expected to contribute to core-line shifts. Such contributions may come from the change of the atomic configuration due to Si-Pt bond formation, the renormalization of atomic levels due to variations of the volume available per atom, and the variation of relaxation energy as a function of  $h\nu$ . The discussion of the charge transfer must wait for accurate theoretical accounts of these effects and the present data can constitute a valuable experimental basis for such theoretical work.

Here we note only that a trend of core-line shifts as in Fig. 6 with a monotonic and opposite behavior of Si and Pt levels is not compatible with a model based uniquely on charge transfer.

Another important point in this coverage region is the modification of the Si *2p* line shape, which broadens gradually and has a growing tail on the high-binding energy side of the unresolved doublet. The broadening can be interpreted as the simultaneous presence in the sampled depth [ $\sim 6$  Å for electron kinetic energies of 55 eV (Refs. 26 and 30)] of Si atoms in slightly different surroundings while the presence of the skewed line shape, much more enhanced in the high-coverage region as discussed in the next section, is related to the metallic nature of the interfacial compounds in which Si is present. We note that this is the first time that the development of the skewing of the Si *2p* line shape is clearly followed experimentally, step by step, as a function of coverage.

### C. High coverages ( $\Theta > 10$ ML)

When increasing amounts of Pt are deposited onto Si at room temperature, departure from the typical silicidelike situation is observed, and the region explored with photoemission becomes richer in the metal as seen from Fig. 5. It is noteworthy in this case that the EDC never reaches that of pure Pt, thus indicating that the fraction of Si present in the region explored with photoemission is of paramount importance in determining the valence states (compare Figs. 1 and 2 with Fig. 7). Furthermore, it is important to note that the structure *C* (around  $-10$  eV) is still present (Figs.

1–3). This indicates that the gross features of the chemical bond between Si and Pt are basically the same although the system is richer in the metal than at intermediate coverages. This structure increases in intensity when  $\Theta$  increases and provides evidence that some metal contribution is also present in C. This result is analogous to what was seen previously for the Si-Pd interface and is consistent with the Si–Pt and Si–Pd bond calculations by Abbati *et al.*<sup>34</sup> However, this paper provides a new insight, namely that the structure C is observed not only at the Cooper minimum, but also at  $h\nu=80$  eV for  $\Theta=40$  and thus must contain *d*-electron character as suggested by calculations on silicides.<sup>25,34,35,37</sup>

Another important point is the modification of the EDC shape at increasing  $\Theta$ . In the *d*-band region the deepest states give a stronger contribution to the photoemission spectra, mainly at the Cooper minimum, than the most shallow ones. This trend is also found in pure Pt (see Fig. 7) where the deeper states give a smaller Cooper effect. In the interface this trend would seem to be enhanced.

The presence of Si in the region explored does not imply that Si is present at constant concentration in the overlayer. Strictly speaking, we cannot exclude that something similar to the Si-Au case<sup>38</sup> takes place, where an intermediate Au-rich layer is found beneath a Si-enriched surface layer. This point deserves further investigation with depth-profiling techniques. But it is very likely that the strong energy gain in the Si-Pt reaction, as compared to the small one for Si-Au, does not lead to a Pt-rich layer with Si segregated on top.

In the metal-rich phase seen at high  $\Theta$  a strong change is seen in the Si 2*p* emission, both in energy position and in line shape, enhancing the trends already mentioned for the intermediate  $\Theta$  region in Sec. IV B. The line-shape change is of the Sunjic-Doniach type observed for core levels in metals when hole-pair formation around the Fermi level accompanies the photoemission excitation.<sup>39</sup> Of course we cannot exclude the fact that energy-loss mechanisms can also contribute to the line-shape modification. The skewed line shape (see Fig. 8) for higher coverages ( $\Theta=20$ ) is consistent with the Sunjic-Doniach model, which predicts this will happen with the increase of available states in the  $E_f$  region when the system becomes metal rich. The same results have been found for the Si-Pd interface at high coverages.<sup>11</sup> Therefore, it is probably a reliable characteristic of the change from a Si-rich to a metal-rich situation.

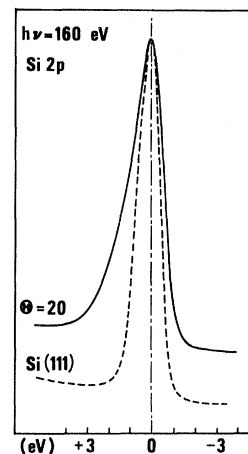


FIG. 8. Si 2*p* core line-shape evolution between the clean Si(111) case and  $\Theta=20$  ML of Pt onto Si(111). The peak positions have been aligned in order to demonstrate the broadening and the change in line shape. For the binding-energy shift between  $\Theta=0$  and 20, see Figs. 4 and 6.

## V. SUMMARY OF INTERFACE GROWTH AND CONCLUSIONS

The current work is the first extensive study of the Si-Pt interface at room temperature by means of the Cooper-minimum photoemission technique. Here we summarize schematically the results concerning the interface growth when increasing amounts of Pt are deposited onto the Si(111) surface.

(1) At submonolayer coverages the major effect is a dramatic change of the relative intensities of the Si(111) valence-band peaks indicating that a very small number of Pt atoms have long-range-order effects on the surface and can change the surface relaxation even before silicelike bonds are formed.

(2) At increasing coverages the Si-Pt reaction leads to a wide silicelike interface with a bonding configuration of strong Si *p*–Pt *d* hybridization. This region has a concentration gradient leading gradually to a metal-rich mixed phase. The chemical reaction proceeds with small chemical shifts of the Si 2*p* and Pt 4*f* core levels towards higher and lower binding energies, respectively.



(3) A metal-rich phase, containing diluted Si, is eventually reached at high coverages; this phase still has silicelike bonding characteristics and a valence band markedly different from pure Pt. In this region the Si  $2p$  core lines have a typical asymmetric line shape.

A more detailed analysis of the present data will be possible when theoretical treatments of the Cooper effect in transition-metal compounds and of core lines (both chemical shifts and line shapes) will be available together with more experimental structural information. The present paper will hopefully stimulate further work in this direction.

#### ACKNOWLEDGMENTS

This work was supported by the Advanced Research Projects Agency of the Department of Defense under Contract No. NO0014-79-C-007s and by the Gruppo Nazionale di Struttura della Materia of the Consiglio Nazionale della Ricerca, Italy. The experiments were performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the National Science Foundation under Grant No. DMR77-27489 in collaboration with the Stanford Linear Accelerator Center and the Department of Energy.

\*Permanent Address: Istituto di Fisica del Politecnico di Milano, 20133, Italy.

- <sup>1</sup>J. C. Phillips, *J. Vac. Sci. Technol.* **11**, 947 (1974).
- <sup>2</sup>S. G. Louie and M. Cohen, *Phys. Rev. B* **13**, 2461 (1976).
- <sup>3</sup>H. I. Zhang and M. Schluter, *Phys. Rev. B* **18**, 1923 (1978).
- <sup>4</sup>L. J. Brillson, *J. Vac. Sci. Technol.* **16**, 1378 (1979).
- <sup>5</sup>J. L. Freeouf, *Solid State Commun.* **33**, 1059 (1980).
- <sup>6</sup>J. E. Rowe, G. Margaritondo, and S. B. Christman, *Phys. Rev. B* **15**, 2195 (1977).
- <sup>7</sup>G. Ottaviani, R. N. Tu and J. W. Mayer, *Phys. Rev. Lett.* **44**, 284 (1980).
- <sup>8</sup>J. M. Andrews and J. C. Phillips, *Phys. Rev. Lett.* **35**, 56 (1975).
- <sup>9</sup>E. H. Rhoderick, *Metal-Semiconductor Contacts* (Clarendon, Oxford, England, 1978).
- <sup>10</sup>G. Rossi, I. Abbati, L. Braicovich, I. Lindau, and W. E. Spicer, *Solid State Commun.* **39**, 195 (1981).
- <sup>11</sup>I. Abbati, G. Rossi, L. Braicovich, I. Lindau, and W. E. Spicer, *J. Vac. Sci. Technol.* **19**, 636 (1981).
- <sup>12</sup>I. Abbati, G. Rossi, L. Braicovich, I. Lindau, and W. E. Spicer, *J. Appl. Phys.* **52**, 6994 (1981).
- <sup>13</sup>G. Rossi, I. Abbati, I. Lindau, and W. E. Spicer, *Appl. Surf. Sci.* (in press).
- <sup>14</sup>G. Rossi, I. Abbati, L. Braicovich, I. Lindau, and W. E. Spicer, *Surf. Sci.* **112**, L765 (1981).
- <sup>15</sup>L. I. Johansson, I. Lindau, M. H. Hecht, and E. Kallne, *Solid State Commun.* **34**, 83 (1980), and references quoted therein.
- <sup>16</sup>G. W. Rubloff, P. S. Ho, J. F. Freeouf, and J. E. Lewis, *Phys. Rev. B* **23**, 4183 (1981).
- <sup>17</sup>P. S. Ho, P. E. Schmid, and H. Foll, *Phys. Rev. Lett.* **46**, 782 (1981).
- <sup>18</sup>I. Abbati, L. Braicovich, V. del Pennino, B. de Michelis, and S. Valeri, in *Proceedings of the Fourth International Conference on Solid Surfaces and the Third European Conference on Surface Science, Cannes, 1980*, edited by D. A. Degras and M. Costa (Societe Francaise du Vide, Paris, 1980),

Vol. III, p. 1023.

- <sup>19</sup>P. J. Grunthaner, F. J. Grunthaner, and J. W. Mayer, *J. Vac. Sci. Technol.* **17**, 924 (1980).
- <sup>20</sup>*Thin Film Interdiffusion and Reactions*, edited by J. M. Poate, R. N. Tu, and J. W. Mayer (Wiley, New York, 1978).
- <sup>21</sup>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).
- <sup>22</sup>I. Abbati, L. Braicovich, B. de Michelis, V. del Pennino, and S. Valeri, *Solid State Commun.* **35**, 12 (1980).
- <sup>23</sup>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).
- <sup>24</sup>F. C. Brown, R. Z. Bachrach, and N. Lien, *Nucl. Instrum. Methods* **152**, 73 (1978).
- <sup>25</sup>I. Abbati, L. Braicovich, B. de Michelis, O. Bisi, C. Calandra, V. del Pennino, and S. Valeri, in *Proceedings of the Fifteenth International Conference on the Physics of Semiconductors, Kyoto 1980*, edited by S. Tanaka and Y. Toyozawa [*J. Phys. Soc. Jpn.* **49**, Suppl. A, 1071 (1980)].
- <sup>26</sup>P. Pianetta, I. Lindau, and W. E. Spicer, in *Quantitative Surface Analysis of Materials, A Symposium Sponsored by ASTM Committee E-42 on Surface Analysis, Cleveland, 1977*, edited by N. S. McIntyre, ASTM Special Technical Publication 643 (American Society for Testing and Materials, Philadelphia, 1978), p. 105.
- <sup>27</sup>I. Abbati, L. Braicovich and B. de Michelis, *Solid State Commun.* **36**, 145 (1980).
- <sup>28</sup>M. L. Shek, private communication.
- <sup>29</sup>J. A. Roth and C. R. Crowell, *J. Vac. Sci. Technol.* **15**, 1317 (1978).
- <sup>30</sup>J. O. Joannopoulos and M. L. Cohen, *Phys. Rev.* **7**, 2644 (1973).
- <sup>31</sup>W. E. Spicer, in *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors, Garmish-Partenkirchen, 1973*, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), Vol. II, p. 499.

- <sup>32</sup>J. A. Appelbaum and D. R. Hamman, *Rev. Mod. Phys.* 48, 479 (1976).
- <sup>33</sup>K. C. Pandey and J. C. Phillips, *Phys. Rev. Lett.* 34, 1450 (1975).
- <sup>34</sup>I. Abbati, L. Braicovich, B. de Michelis, O. Bisi, and R. Rovetta, *Solid State Commun.* 37, 119 (1981).
- <sup>35</sup>J. D. Riley, L. Ley, D. Azoulay, and T. Terakuta, *Phys. Rev. B* 20, 776 (1979).
- <sup>36</sup>H. Gant and W. Monch, *Surf. Sci.* 105, 217 (1981).
- <sup>37</sup>J. H. Weaver, V. L. Moruzzi, and F. A. Schmidt, *Phys. Rev. B* 6, 2916 (1981).
- <sup>38</sup>L. Braicovich, C. M. Garner, P. R. Skeath, C. Y. Su, P. W. Chye, I. Lindau, and W. E. Spicer, *Phys. Rev. B* 20, 5131 (1979).
- <sup>39</sup>S. Doniach and M. Sunjic, *J. Phys. C* 3, 285 (1970).