Evidence of palladium phosphide formation at the Pd/InP(110) interface

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The bonding in the reactive Pd/InP(110) interface at room temperature has been investigated by valence-band and core-level photoemission in conjunction with photon-induced Auger spectroscopy. A dramatic change of the spectra identical to those previously reported for the Pd/Si interface strongly indicates formation of a stable palladium phosphide, most probably Pd_3P, at the interface in the Pd coverage range from ~ 2.5 to ~ 15 monolayers. It is suggested that such transition-metal-P compound formation may be a general phenomenon for transition metals on InP and other III-V compounds.

The interfaces between metals and semiconductors are of considerable fundamental and practical importance. The formation of compounds between Si and transition metals has long been recognized, studied fundamentally, and used in integrated circuits and other practical devices. In contrast, the formation of a silicidelike compound has rarely been considered for transition metals on III-V semiconductor compounds. It is the purpose of this paper to present the data showing formation of such a compound. The system used was Pd on the InP(110) surface at room temperature. Detailed examination of the electronic structure of the Pd/InP(110) interface and comparison with the properties of Pd silicide show the formation of an equivalent to the silicides, Pd phosphide, with In segregated out into pure metal inclusions. The choice of the Pd/InP system to perform these studies was motivated by the fact that Pd/Si, the system to which we compare our data, is probably the most thoroughly studied example of a silicide/Si junction. In particular, spectroscopic studies similar to those presented below have been used for the Pd/Si system and for the $Pd_{1-x}Si_x$ glasses by several experimental groups.[1-7] The similarity of the approaches enables us to compare directly the results for both interfaces and also to put our results into a more general context.

The experiments were performed using a standard ultrahigh vacuum apparatus (base pressure 3×10^{-11} Torr) equipped with a double-pass cylindrical mirror analyzer at the 4° beam line at the Stanford Synchrotron Radiation Laboratory. The junctions were prepared *in situ* by sequential evaporation of Pd overlayers onto cleaved p-InP(110) (Zn-doped $p = 3 \times 10^{18}$ cm^{-3}) surfaces at room temperature from a carefully outgassed and calibrated bead. The data reported here were selected to present different aspects of bond formation between Pd and P and include the energy dependence of valence-band (VB) features and changes of the P $2p$ core line shape as measured by photoemission spectroscopy as well as changes in the $P L_{2,3} VV$ Auger spectra.

Figure 1 shows the VB spectra for the Pd/InP interface for an increasing thickness of Pd overlayer [1 monolayer (ML) on InP(110) corresponds to 8.2×10^{14} atoms/cm^2 and for Pd is equivalent to 1.2 Å, as measured by the thickness monitor]. The spectra were taken at $h\nu = 80$ eV, where the ratio of the cross sections for Pd $4d$ versus that for the sp VB goes through the maximum, and also at 140 eV, close to the Cooper minimum (CM) for Pd $4d$ photoionization, where the ratio of the cross sections drops more than one order of magnitude and clearly reveals the sp contribution

otherwise swamped by Pd $4d$ emission. A similar study, taking advantage of the tunability of the synchrotron radiation source, has been performed previously for the Pd/Si interface.[3,4] First of all, we notice that all of our valence-band spectra collected in Fig. 1 show striking qualitative, and in some respects even quantitative, resemblance to similar results for Pd/Si,[3,8] indicating a similar mechanism of the redistribution of the density of states at both Pd interfaces. The Pd contribution, which in pure metal has a broad maximum close to 2 eV wide and is intersected by the Fermi level so that a high density of states is observed at E_F,[1,3] now changes shape and is shifted toward the higher binding energy. At the same time, we begin to observe a decrease in the emission near the characteristic shoulder, labeled A in Fig. 1. All features A, B, and C of the 80-eV spectra for Pd/InP are virtually identical both in structure and energy positions not only to the 80-eV soft x-ray photoelectron (SXPS) spectra[3] but also to the XPS (Ref. 5) and ultraviolet photoelectron spectra (UPS) (Ref. 1) taken for the Pd/Si interface or $Pd_{1-x}Si_x$ glass alloys.[6,7] In all the above cases, due to the high cross section, the spectra are dominated by the Pd $4d$ contribution. Increasing the photon energy to the CM at 140 eV reveals additional structure (labeled D) which is also easily observed at the CM for the Pd/Si interface but also has been resolved in both He I UPS and XPS. On the basis of this similarity in the data, it seems natural to extend the interpretation for the Pd/Si system[2,3,5,6] to the Pd/InP interface. In brief, we interpret the structures A and C on Fig. 1 as due, respectively, to antibonding and bonding Si $3p$-Pd $4d$ hybrids and view them as the fingerprints of a strong interaction between d states of Pd with the p states of the substrate. The central peak B is due largely to nonbonding $4d$ states located between the aforementioned rehybridized p states. The peak D is reminiscent of the sp band of the substrate. The above outlined model indicates that we may also expect a splitting of the Auger $P L VV$ line similar to that observed for the Pd/Si system.[2,6]

The $P L VV$ Auger spectra have been recorded using a photon beam of $h\nu = 160$ eV as the source of primary excitation. In Fig. 2, we compare a typical spectrum of $P L VV$ for the Pd/InP interface with that taken from phosphorous covalently bonded in InP. The difference curve allows a better presentation of the new structures by eliminating the background. The depressing of structure B, which happens to have at the interface an energy similar to that of the substrate peak, may be ambiguous (see also Ref. 1). Our data again show strong similarity to the results of experiments
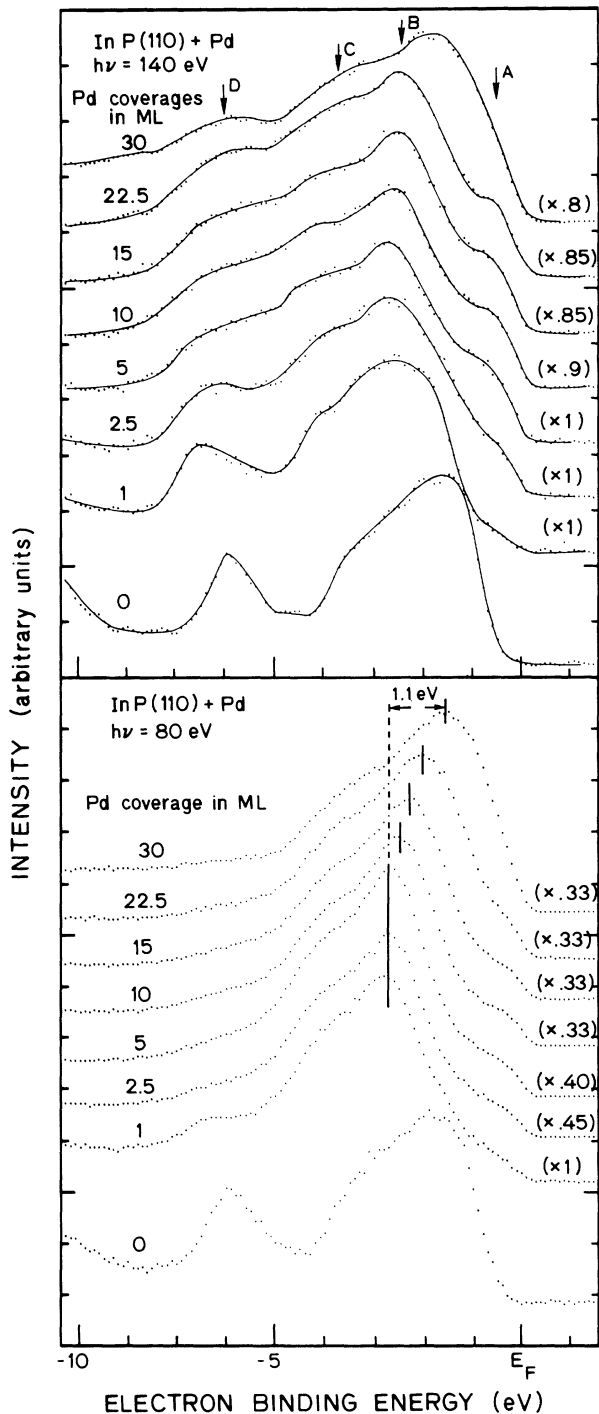
FIG. 1. Valence-band photoemission spectra for clean InP(110) and various Pd overlayers at room temperature for photon energies of 140 and 80 eV.

FIG. 2. $PL_{2,3}VV$ line shapes for InP + 15 ML Pd and clean InP(110).

performed for the Pd/Si interface where the change of the Si $L_{2,3}VV$ line has been recorded.[1,9] In fact, we clearly observe here the additional high kinetic energy shoulder (labeled A) that is responsible for the characteristic splitting of the spectra taken in the derivative mode.[2] We also observe the additional peak C well resolved for the Pd/Si interface. Three equidistant structures A, B, and C in Fig. 2 for Pd/InP and for Pd/Si represent a self-convolution of two peaks in the partial density of states in Fig. 1 associated with
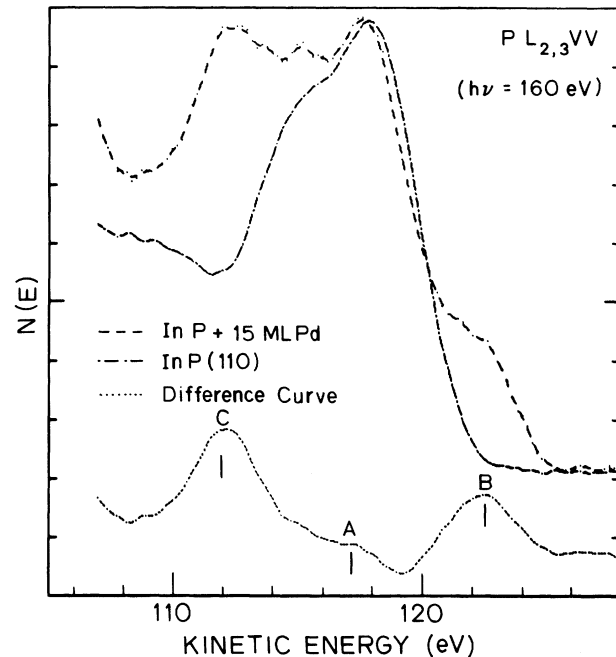
previously mentioned bonding and antibonding hybrids. We view splitting of the P $L_{2,3}VV$ to several components as direct evidence of the palladium phosphide formation. Comparing the spectrum of P at the interface with that of covalently bonded P, where the P LVV shows less structure, we argue that the nature of the new Pd-P bond is strongly different from that in covalently bonded semiconductors and similar to that in silicides.

The same conclusion can be reached on the basis of our P $2p$ core-level data shown in Fig. 3. As seen in the figure, 1 ML of Pd slightly decreases the P $2p$ emission and rigidly shifts the line toward higher binding energy without any change of the line shape. This shift represents the change of the band bending. As in the case of metal overlayers on GaAs, most of the change in the band bending is observed for the first small coverage (here 0.15 Å of Pd, not shown) where the role of the chemical reaction is at most marginal. The Schottky barrier height of 0.8 eV, established for 1-ML deposition as followed by the change of the $P_{3/2}$ component (labeled A in Fig. 3) of the P $2p$ line, increases only slightly for 2.5-Å deposition. The substrate P $2p$ peak is not resolved for coverages ≥ 10 Å of Pd. Starting from a 2.5-Å deposit, a new chemically shifted peak indicating a change of the P environment is observed and for intermediate coverages remains stable in shape, position, and intensity. It is worth noting that the chemically shifted peak has higher binding energy than for InP, again indicating that a more stable Pd phosphide has been formed. This result is coherent with previously discussed spectroscopic data and with results on the Pd/Si interface.[3] It is also worth noting that our data show a characteristic broadening of the line toward lower kinetic energy. A very similar skewed line shape of the core line was also observed for Si $2p$ in the Pd/Si interface.[3] This characteristic Doniach-Sunjic[10] line shape again indicates the metallic character of new bonds.
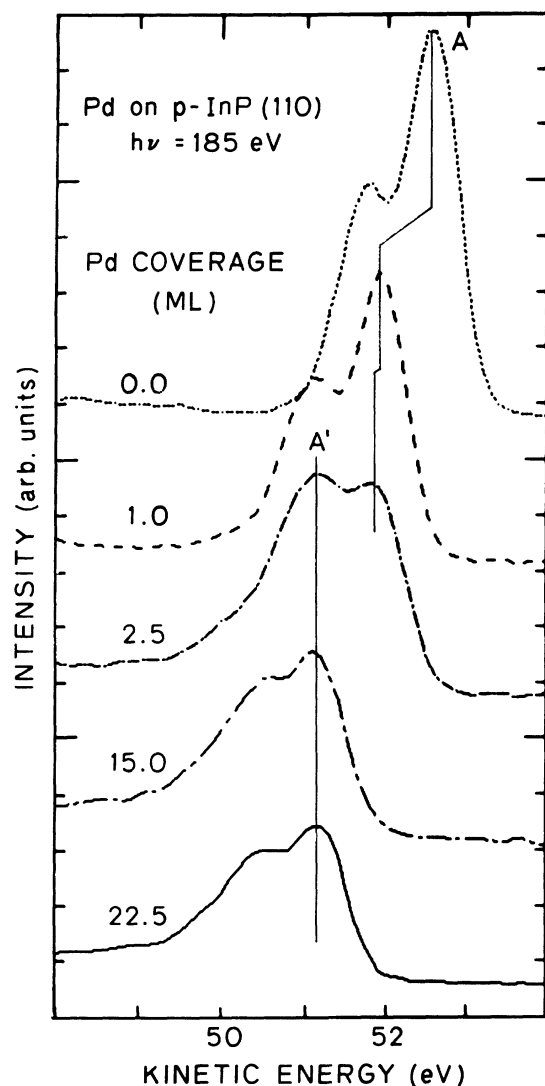
So far, little attention has been paid to indium. The

FIG. 3. P 2p core line spectra for some Pd exposures.

changes in the behavior of this component were monitored through analysis of the change of the In 4d core line. For this line, our data are in good agreement with previous reports indicating segretation of metallic In.[11] The influence of In removed from the covalent bond in the substrate on the electronic properties of these systems seems to be negligible in the first approximation.

Finally, we address the important question of the stoichiometry change of the phosphide produced at the Pd/InP interface. From Fig. 1, it is apparent that spectroscopic features representing the VB density of states distribution of the reacted layer are stable both in shape and energy over a reasonable range of Pd coverage. Since the Pd is deposited in InP at room temperature, the reaction is probably limited as the Pd thickness is increased. For 140-eV photon energy, a dramatic change of main peak B toward smaller binding energy is only observed for the 30-ML

coverage. The $h\nu = 80$-eV spectra, more sensitive to the 4d states, are stable up to 10–15 ML. Similar stability of the spectra for Pd/Si up to ~ 12 Å is generally interpreted as an indication of spontaneous room-temperature (and even below RT (Ref. 1)] formation of Pd_2Si. The shift toward E_F indicates the presence of a metal-rich phase or unreacted Pd metal in the upper layer of the interface. We note that a fast kinetic reaction similar to that for Pd/Si is observed for the Pd/InP interface.

Another problem not addressed so far is related to the composition of the compound produced in the "stable" phase of the interfacial reaction. We can address this question by comparing the theoretical atomic cross section for photoionization with experimental intensities of the Pd 3d [taken for $h\nu = 415$ eV (Ref. 12)] and P 2p ($h\nu = 185$ eV) peaks. From this analysis, which takes into account all experimental parameters such as the transmission function of the monochromator, the analyzer, etc.,[13] we conclude that the ratio of Pd to P atoms is 3 to 1 for the 15-ML sample. Under a further assumption (Fig. 1) that neither P nor Pd are bonded to In for this coverage, this result indicates that Pd_3P is formed at the interface. The phase diagram,[14] with the assumption that In segregates to form islands reducing the ternary phase diagram for the system to the Pd-P diagram, shows that such a compound indeed exists. Moreover, on the basis of the phase diagram, this phosphide seems to be the most likely candidate to nucleate first at the Pd/InP interface.[15] Although this assignment awaits checking by structural methods, we tentatively conclude that most probably Pd_3P is formed in the early stage of the Pd/InP barrier formation.

In conclusion, we note that for the first time for a nonelemental semiconductor interface, the detailed nature of the chemical bond has been studied by following the evolution of the VB, core lines, and analysis of the P LVV transition. Comparing our results with a system in which the role of interfacial chemistry is well understood, we provide spectroscopic evidence that Pd-phosphide formation and segregation of In dominates the microscopic chemistry and electronic structure of the Pd/InP interface. Similar results obtained by us for Ni on InP suggest that this is a general result for transition metals on InP and raises the importance for other III-V compounds.

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