Soft-x-ray photoemission study of Co—n-type InP(110) interface

T. Kendelewicz, R. S. List, M. D. Williams, K. A. Bertness, I. Lindau, and W. E. Spicer

Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

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The room-temperature interaction of Co overlayers with the cleaved InP(110) surface has been studied using soft-x-ray core-level photoemission spectroscopy. We show that Co strongly reacts with the surface to form phosphide. For small metal coverages the reacted overlayer grows in a laminar fashion. The pinning position for the 1.5-Å Co coverage is approximately 0.30 eV below the conduction-band minimum. For higher coverages the pinning is difficult to follow due to the uncertainty in accounting for the chemical reactions in the core-level spectra.

In this work we report a soft-x-ray photoemission study of the formation of the Co—n-type InP(110) interface. The problems of the characterization of the chemical reactions taking place at this interface and the evolution of the Schottky barrier height during the initial stages of the interface formation are addressed. Both these issues can be studied simultaneously with photoemission electron spectroscopy (PES). A detailed description of the application of PES to study interfaces is well documented in the literature.[1] The experimental procedures used in our studies of interfaces have been presented in prior publications.[2] The study reported here was performed on the ultrahigh-vacuum ($< 10^{-10}$ Torr) unpinned cleaved n-type InP(110) surface. The surface was then covered with controlled amounts of Co evaporated in submonolayer and monolayer increments from a resistively heated Co evaporator. The crystal used in this experiment was Sn doped with carrier concentration 5×10^{17} cm^{-3}. Synchrotron-radiation-excited In $4d$ and P $2p$ core-level spectra were taken with a double-pass cylindrical mirror analyzer with an energy resolution of 0.2 eV. The weak Co $3p$ spectra were also recorded with resolution 0.5 eV. We also measured the photoabsorption spectra close to the P $2p$ threshold. This was done with the constant final-state (CFS) photoemission mode with partial yield detection.[3]

Figure 1 presents the evolution of the In $4d$ and P $2p$ core-level spectra for increasing Co thickness. The first Co evaporation of 0.15 Å causes a nearly equal rigid shift of both core levels (0.19 eV for P $2p$ and 0.22 eV for In $4d$). This shift is nearly entirely due to the band bending. For higher coverages the line shapes of the spectra show modifications corresponding to chemical reactions at the surface. The chemically shifted peaks dominate the spectra for the highest coverages. A new contribution on the high kinetic energy (KE) side of the In $4d$ core level corresponds to the movement of the In released from the substrate into the overlayer (due to an interfacial reaction). The peak formed on the lower KE side of the P $2p$ is a clear indication of the formation of a Co phosphide. For both core lines the behavior is typical of strongly reactive InP interfaces.[4] As with most of these systems the Co/InP interface also shows a decrease of the integrated

P $2p$—to—In $4d$ intensity ratio at higher coverages.[5] The decrease of the In $4d$ core-level intensity is less pronounced due to limited solubility of In in the Co overlayer. A strong reaction between Co and P is confined to the region close to the interface. This reaction limits the P out-diffusion.[5] The shape of the high-coverage P $2p$ core-level spectra suggests that the reaction is complex in the sense that more than one phase of the Co-P compound seems to be present at the interface. This is seen from the large width of the 15- and 20-Å spectra which indicate some emission close to KE of 51.5 eV far from the main chemically shifted peak which develops around 50.5 eV. We suggest that the higher KE emission is not related to the attenuated "substrate" peak which is dominant at smaller coverages. This suggestion is supported by an inspection of the In $4d$ core level which does not show such a substrate contribution at higher coverages. A more quantitative assignment of the products of the chemical reaction at the interface is difficult from PES spectra alone.

It is worth noting that the Co-P glassy systems attracted a great deal of interest in the literature due to its magnetic properties. In most of these works the amorphous samples are prepared by an electrodeposition on some substrate. It is well documented that upon annealing one observes the nucleation of Co$_2$P.[6] It is also known that metal deposition on clean surfaces of semiconductors like Si, GaAs, or InP usually causes chemical reactions at room temperature (RT) much below the bulk thermodynamics eutectic temperatures. In particular, nucleation of stoichiometric silicides is often observed at RT at the metal-Si interfaces.[7] A similar room-temperature formation of phosphides with well-defined stoichiometry may also take place for the InP interfaces.[8] However, for these latter interfaces no analytical studies of the interfacial reactions have yet been performed. Because of this, assignment of the chemically shifted peaks to Co$_2$P or any other phase would be at present highly speculative. The other known binary bulk phases for the Co-P system are CoP and CoP$_3$. All Co phosphides have much larger heats of formation than InP (after Kubashewski[9] the experimental values of heat of formation are -44.8, -30.0, -48.9, and -18.0 kcal/mol for Co$_2$P, CoP, CoP$_3$, and InP,
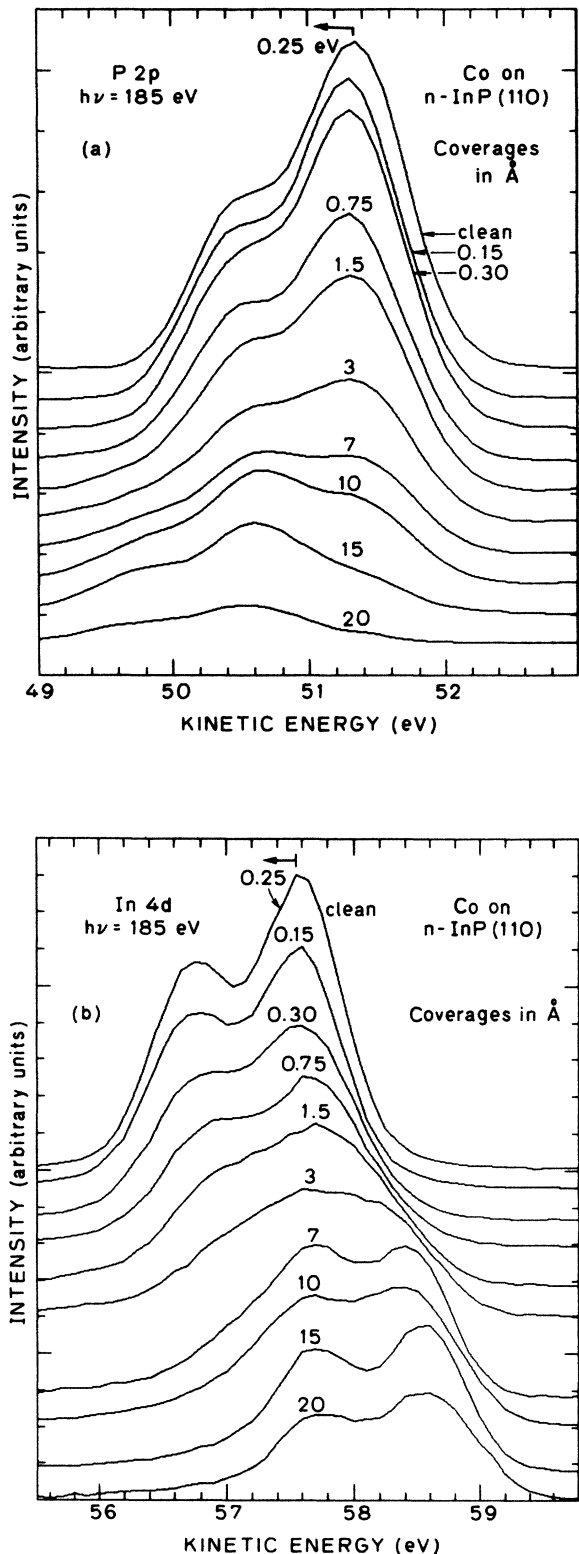
FIG. 1. Photoemission spectra of (a) In $4d$ and (b) P $2p$ core levels taken at photon energies of 80 eV and 185 eV, respectively, and normalized to incident photon flux. To avoid overlapping, the spectra of the clean substrate are shifted by 0.25 eV to higher kinetic energies. (The actual values of the band bending are shown in Fig. 3.)

respectively). Large heats of formation for Co phosphides are consistent with theoretical calculations of Niessen and Miedema.[10] These calculations also indicate that formation of Co-In alloys is highly unfavorable due to very small heats of formation. This, together with the known fact of limited solubility of In in Co, well support the trends of the reaction observed in our PES spectra. We conclude that the pattern of reaction at the interface observed in the data indicating formation of Co phosphide and phase segregation of metallic In is consistent with the predictions of bulk thermodynamics.

The core-level spectra of Fig. 1 also provide information on the evolution of the Schottky barrier height for thin metal overlayers. In order to follow this band-bending-related shift for coverages larger than 0.3 Å, a separation of different contributions is necessary. For these coverages the core-level spectra are affected by the presence of chemically shifted components. For kinetic energies accessible in our experiment the spectra are strongly surface sensitive and thus strongly affected by chemistry. We will show that the substrate components which provide the best estimate of band bending can be followed only up to the coverage of about 1.5 Å.

In order to follow the band-bending shift of the substrate component we curve fitted the spectra corresponding to coverages between 0.75 and 10.0 Å of Co using two components—a substrate component, represented by the line shape of the core-level spectra for the clean semiconductor, and an additional component from the reacted phases at the interface represented by the 15-Å spectra. The P $2p$ spectrum for 20 Å is strongly reduced in intensity and too noisy to be used in the curve fitting. The 15-Å spectra have negligible substrate contributions. The latter approximation is recognized as being subject to considerable error in particular for P where more than one reacted species may be present. For all coverages analyzed the intensities and binding energies of these components were treated as adjustable parameters. Figure 2 presents an example of the fitting for coverages of 1.5 and 7 Å of Co. It is worth noting that satisfactory fits were obtained for both P $2p$ and In $4d$ spectra at all coverages. Figure 3 presents the energy shifts of the substrate components. Since these should be equal to the band bending, one expects them to be equal for both P $2p$ and In $4d$. However, our analysis shows quantitatively different shifts. The band bending established from the P $2p$ core level for coverage of 10 Å is 0.32 eV. A corresponding shift deduced from the In $4d$ core level is 0.24 eV larger. Especially large differences in In $4d$ and P $2p$ shifts are observed above 3 Å of Co, although for all coverages the shift of P $2p$ is smaller. The reason for this anomalous behavior is not clear at present. We note that the difference in the band-bending shift of the studied core levels seems to be independent of the type of unfolding scheme applied in the data analysis. For example, the data fitted with a series of Gaussians shows a similar trend. It is possible that our model of the chemical reaction allowing for only a few phases is too simple and that the data should be fitted with more than two components. This would imply that our good fits obtained with two components were fortuitous. The problem of interpretation of
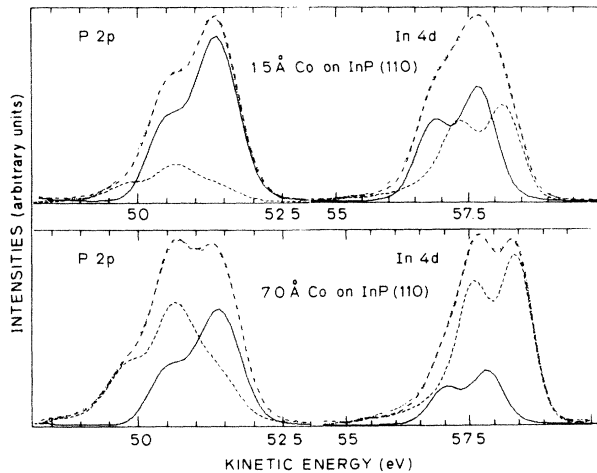
FIG. 2. Some examples of the curve fitting of the In $4d$ and P $2p$ core-level spectra. The spectra of 1.5 Å and 7 Å (dotted lines) are decomposed into substrate contribution and chemically shifted contribution represented by the spectra of clean substrate (solid lines) and spectra with 15 Å of Co (dashed lines), respectively. The sums of these two contributions for the best fit are presented as dashed lines.

the core-level spectra in terms of the band bending requires further attention. We note that for relatively small coverages on the order of 1.5 Å when the differences between In $4d$ and P $2p$ shifts are not large (although still present) the data indicate a barrier height of about 0.3 eV. The same value is consistent with the band-bending shifts of P $2p$ for the entire range of the coverages studied. It would be interesting to compare values of the band bending provided by the PES spectra for small metal coverages with the barrier heights measured on diodes with thick metal overlayers (for unpinned cleaves of a highly doped semiconductor the band bending is equal to the Schottky barrier height). Unfortunately, at present such data are only available for Co diodes grown on chemically prepared InP(100) wafers.[11] On these diodes Hokelek and Robinson measured the current-voltage (I-V) barrier of

0.45 eV. These authors argue that the Co/InP interface is nonreactive.[11] This latter statement is clearly in disagreement with our PES results and available thermodynamic data.

There are some indications that a shift of P $2p$ provides a more reliable estimate of the band bending:

(1) Our fitting shows that the chemically shifted component has constant binding energy. This is an indication of some stable, although possibly complicated, product of the chemical reaction at the interface. Contrary to this, the binding energy of the "segregated" In $4d$ peak is strongly changing. This may be due to some alloying, islanding, or other yet to be specified mechanism. In this case, approximating the total In $4d$ spectrum with only two doublets may be an oversimplification.

(2) The tunability of the synchrotron source provides a possibility to study near edge structure close to the P $2p$ photoionization threshold. Examples of the data taken in the CFS mode are presented for few coverages in Fig. 4. In the same spectra we also record the photoemission P $2p$ core-level sweeping through the analyzer window set at KE of 4 eV, for $h\nu$ a few eV above the absorption threshold. The data show that the excitonic enhanced absorption structure is not changing in energy with increasing Co coverage while the core level shifts by the value of the band bending. From this result we conclude that the bottom of the conduction band is shifted by the energy of the band bending. This result provides a self-consistent test
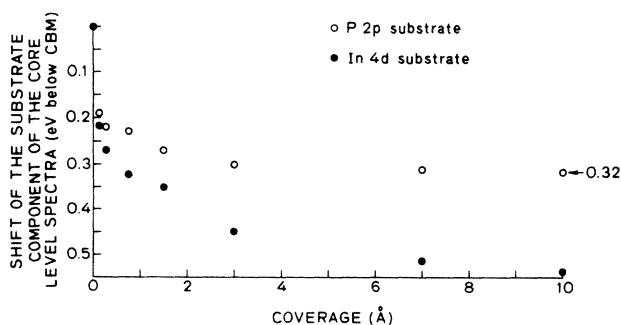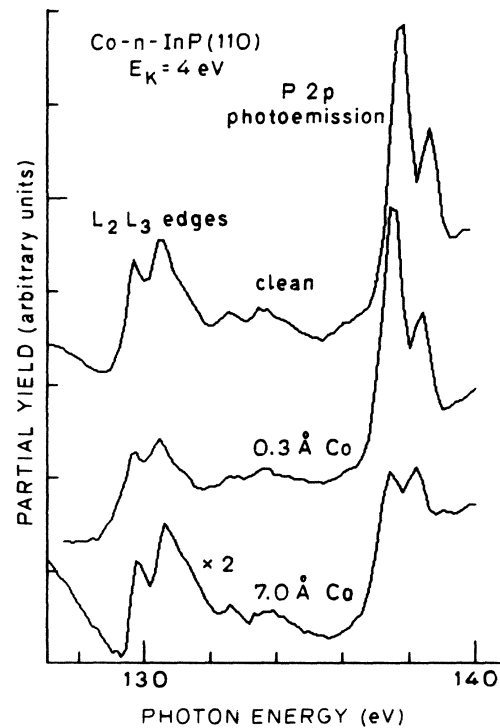

FIG. 3. Apparent shifts of the substrate components of the P $2p$ and In $4d$ core levels for increasing coverage of Co. CBM denotes conduction-band minimum.

FIG. 4. Near edge structure close to the P $2p$ threshold. The peak at 139 eV represents the P $2p$ core-level photoemission which sweeps through the analyzer window set at the kinetic energy of 4 eV.
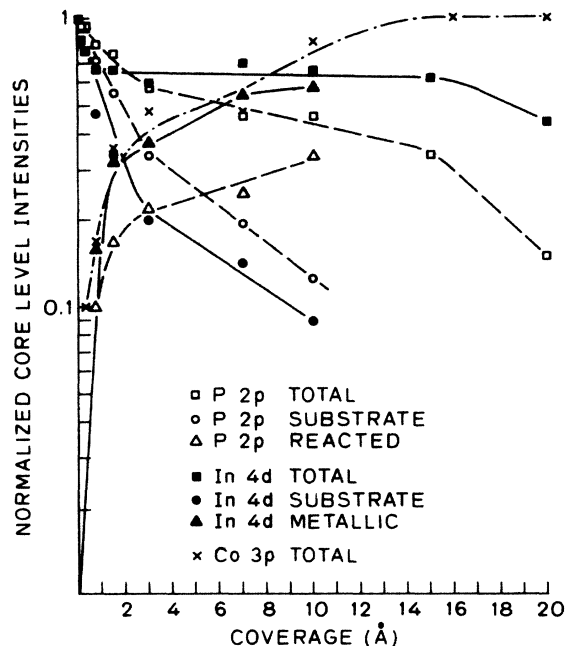
FIG. 5. Intensity profiles of the P $2p$ and In $4d$ core levels. Also included are intensities of different contributions obtained from the curve fitting as described in the text and presented in Fig. 2.

FIG. 6. Photoemission spectra of Co $3p$ core level taken at the photon energy of 115 eV normalized to the same height.

that the shift of the P $2p$ is indeed related to the band bending.

(3) We observed the discrepancy between band-bending-related shifts of P $2p$ in our previous experiments on transition-metal—InP interfaces.[12] In these cases pinning obtained from the P $2p$ core levels was consistent with the barrier heights measured with electrical techniques on thick diodes.[13]

The change of intensities from the deconvolution of the PES spectra provides important information on the mode of the interfacial overlayer growth. Figure 5 presents changes of the total intensities of the total P $2p$, In $4d$, and Co $3p$ core levels with the increasing Co coverage. Note that the P $2p$ and In $4d$ intensities are attenuated less than exponentially. This is due to outdiffusion related to chemical reactions. However, the substrate contribution presented separately in Fig. 3 shows a much faster decrease and decays by $1/e$ for coverage of 3 Å of Co. This value is comparable with the typical values of the escape depth from metals. (The actual thickness of the reacted layer is larger than the absolute metal coverage.) This result clearly shows that at the beginning of the interface formation the overlayer is growing in a laminar fashion. For higher coverages the decrease of the substrate contributions is less than exponential indicating some possible variations of the overlayer thickness. This may be an indication of the Stranski-Krastanov type of
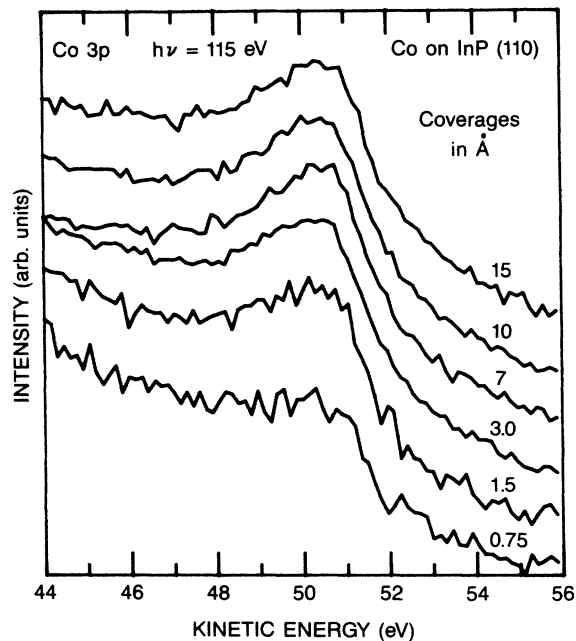
the overlayer growth in which a layer by layer growth is followed by islanding.

In Fig. 6 we include for completeness the evolution of the Co $3p$ spectra with increasing Co thickness. No change in the binding energy of the Co $3p$ core level was observed in the coverage range studied.

Our PES data clearly show the presence of a strong room-temperature chemical reaction on the Co/InP interface. The pattern of the reaction is in general agreement with the predictions of bulk thermodynamics. The reacted overlayer is growing in a laminar fashion at the beginning of the interface formation. Some islanding is possible for higher coverages. The barrier height for coverages on the order of 1.5 Å is estimated to be 0.3 eV. For higher coverages core-level spectra are dominated by chemically shifted components and the band bending cannot be reliably followed.

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