# 3d transition metals on InP(110): A comparative study of reactive interface evolution

C. M. Aldao, I. M. Vitomirov, F. Xu, and J. H. Weaver

*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455*

(Received 5 November 1987)

Room-temperature formation of reactive $M$/InP(110) interfaces (where $M$ denotes the $3d$ transition metals Ti, Cr, Fe, and Co) have been studied using high-resolution synchrotron radiation photoemission. Detailed line-shape analysis shows that these metals disrupt the substrate to form phosphides and release In atoms to the free surface. For Ti and Cr depositions, there are also ultrathin transition regions or precursors to reaction, which are not observed for Fe and Co, but these precursors do not correlate clearly with Schottky barrier development or final height. Critical coverages of $\sim 7$ Å for Ti, $\sim 4$ Å for Cr, $\sim 2.7$ Å for Fe, and $\sim 1.6$ Å for Co are found which reflect morphology changes in the disrupted overlayer, namely, growth of metal-phosphide nuclei and expulsion of In from the region where compound formation dominates. For depositions greater than $\sim 22$ Å for Ti, $\sim 12$ Å for Cr, and $\sim 7$ Å for Fe and Co, the interface reactions become diffusion limited and the phosphide-rich regions are buried by metallic overlayers. At the same time, In atoms released during earlier stages continue to segregate because of their low solubility in these metals. Comparisons are made to GaAs-based interfaces where epitaxial growth of Fe and Co was observed.

## INTRODUCTION

Interface formation involving metals and semiconductors has been the subject of much experimental and theoretical work in the last several years.[1-9] Although the importance of controlling interface properties has long been recognized for microelectronic and other applications, there is no definite way to predict interface evolution. Many techniques, with varying degrees of sensitivity for chemical and structural order, have been used to characterize complex evolving interfaces. Among them, photoemission with synchrotron radiation has been popular because it combines the ability to examine changes in the chemical environment of species with very high surface sensitivity. Interest in metal-InP interfaces has resulted from the importance of metal/(III-V) compound semiconductor interfaces, in general, and from the development of specific InP-based devices.[2,6-8]

In this paper, we present a detailed room-temperature study of the evolving Ti/InP(110), Cr/InP(110), Fe/InP(110), and Co/InP(110) interfaces. We have used synchrotron radiation photoemission to obtain high-resolution core-level and valence-band energy distribution curves. In addition, we have used low-energy electron diffraction (LEED) to correlate chemical and structural changes. Our results show that these metal adatoms disrupt the substrate to form phosphides which remain confined to the buried interface region, in agreement with earlier studies by Kendelewicz *et al.*[8] Further, we have observed a critical coverage at which In is expelled from the region where $M$-P nuclei are growing. We have found no evidence for epitaxial growth, as occurs for Fe and Co overlayers on GaAs,[9] and we associate the differences with the heats of formation of the phosphides. Detailed line-shape analysis of the In $4d$ and P $2p$ core levels, quantitative measurements of core-level emission intensities, and comparisons of bulk- and surface-sensitive results have made it possible to model these evolving interfaces. This analysis resolves an issue raised in Ref. 8 concerning the evolution of the Schottky barrier. Comparisons with depth profiles based on Ar sputtering and x-ray photoemission provide confirmation of our model of reactive, diffusion-limited interface formation.

## EXPERIMENT

The photoemission experiments were carried out at the Aladdin electron storage ring at the Wisconsin Synchrotron Radiation Center using the facility Grasshopper Mark V monochromator and beamline. Photoelectron energy analysis was done with a double-pass cylindrical mirror analyzer. Monochromator bandwidths and analyzer pass energies were chosen to give a total resolution of $\sim 200$ meV for the In $4d$ core levels and $\sim 400$ meV for the P $2p$ core levels. Core-level spectra were measured for incident photon energies of 32 and 60 eV for In $4d$ and 140 and 170 eV for P $2p$ to give primary electron mean free paths of $\sim 4$ and $\sim 10$ Å for surface- and bulk-sensitive measurements.[10] As a result, the probed region at the interface ranged from $\sim 12$ to $\sim 30$ Å.

Posts of $n$-type InP (Sn-doped at $4 \times 10^{17}$ cm$^{-3}$) were cleaved *in situ* to produce mirrorlike surfaces measuring approximately 4 mm $\times$ 4 mm. The cleaved surfaces were judged visually and by inspection of the core level and valence-band spectra to assure high-quality, unpinned surfaces before performing the interface studies. The metals Ti, Co, and Fe were evaporated from resistively heated 5-mil tungsten boats; Cr was evaporated from a 30-mil W coil. The source to sample distance was $\sim 30$ cm and the evaporation rate, measured with a quartz crystal monitor, was about 1 Å/min. The measurements were done in a vacuum system which was optimized for

interface research. In particular, it was possible to move the sample from the evaporation position to the positions for photoemission and LEED with a simple rotation of a precision rotary motion feedthrough. The system operating pressure was $\sim 5 \times 10^{-11}$ Torr. After extensive degassing, the metals were evaporated at pressures of less than $4 \times 10^{-10}$ Torr. For Ti and Cr, the pressure during deposition was less than $7 \times 10^{-11}$ Torr. Operating pressures were reached within 2–3 min of the completion of an evaporation. The amount of deposited metal is expressed in angstrom units, as measured with the quartz crystal oscillator. Assuming that the overlayer grows in registry with the substrate, conversion from angstroms to monolayers yields 0.69 ML/Å for Ti, 1.01 ML/Å for Cr, 1.03 ML/Å for Fe, and 1.11 ML/Å for Co where 1 ML is the atom density of the InP surface. It is important to note that the amount of metal deposited differs from the actual thickness of the overgrowth since these systems are reactive and do not develop epitaxially.

Detailed line-shape analysis of the In $4d$ and P $2p$ core-level spectra was performed with an IBM RT computer using a nonlinear least-squares minimization procedure to achieve the best fit to the original data.[11] The line shapes of the spectra were well represented by convolving Lorentzian and Gaussian functions, the former describing the natural core-level linewidth and the latter arising from phonon broadening and monochromator and analyzer contributions. Line-shape asymmetry, observed in the In $4d$ emission and associated with final-state screening effects in the metallic environment of surface segregated In atoms, was described using Doniach-Sunjic line shapes,[12] the asymmetry factor being typically around 0.15. During interface evolution, we allowed up to three spin-orbit doublets, one representing the substrate and the other two interface reaction products. The variables used in our fits were the position and intensity of each of the pairs. However, the Gaussian linewidths for the reacted components were allowed to vary to account for broadening due to inequivalent sites. During the early stages of development of the Schottky barrier, we also allowed the width of the substrate component to vary to account for inhomogeneous pinning (e.g., for P $2p$ emission at 140 eV for Co/InP, there was a 20% broadening of the Gaussian of the substrate). This method of data analysis, described in detail elsewhere,[13] is essential for understanding the details of interface evolution.

## RESULTS AND DISCUSSION

We have used the tunability of the synchrotron radiation photon source in a detailed study of the In $4d$ and P $2p$ core-level line shapes for unpinned, cleaved InP(110) surfaces. These investigations were crucial for understanding the clean surface and were especially important for subsequent quantitative characterization of evolving interfaces. As noted above, parameters obtained for the clean surface were used for fits for the more complex interface line shapes.

As is now well known, differences in coordination number, bond length, and neighbor positions give rise to

core-level binding energies for atoms at the surface which differ from those of the bulk. Surface core-level shifts have been observed unambiguously for Ga, Sb, and As atoms in GaP, GaAs, and GaSb.[14] For In in InP(110), our fittings reveal a surface-related doublet at 0.30±0.01 eV higher binding energy than In in bulk InP. This is in good agreement with the tight-binding theoretical predictions of Priester et al.[15] More controversial, however, is the existence of a surface shift for the P $2p$ core levels. Such a shift was not predicted by Priester et al. but seems to be indicated by electrostatic interaction considerations of Mönch.[16] Our findings agree with the latter since considerably improved fits were obtained for the cleaved surface spectra by introducing a surface shifted peak 0.29±0.02 eV to lower binding energy. This has generally escaped observation because the P $2p$ spectra have been measured with poorer resolution than the In $4d$ features (in the present study this compromise is also evident because of flux limitations, giving $\sim 400$ meV total resolution for P $2p$ versus $\sim 200$ meV for In $4d$). As will be discussed, it is particularly important that the presence of a surface component be taken into account when considering changes in the Schottky barrier heights.

Further confidence in our assessment of In $4d$ and P $2p$ surface core-level shifts comes from calculations of the photoelectron mean free paths, $\lambda$, and the ratio of emission from the surface and bulk components as a function of electron mean free path (photon excitation energy). The distance between (110) crystal planes in InP is $d = 2.075$ Å and the expected surface-to-bulk ratio is given by $R = I_s / I_b = \exp(d/\lambda) - 1$. From this, we found experimental escape depths of 3.6 Å for In $4d$ electrons measured with high surface sensitivity at $h\nu = 60$ eV and 10 Å for the bulk-sensitive In $4d$ spectra taken at $h\nu = 32$ eV. These values agree with general trends outlined in Ref. 10.

The surface core-level contributions play an important role in determining Schottky barrier heights based on analysis of core-level shifts during early stages of interface formation. By neglecting them, a systematic error is introduced which is related to the amount of bulk core-level shift induced by the adatoms. This led in Refs. 8 and 17 to the unphysical conclusion that band bending shifts were different for bulk P and In atoms in InP. In the present study, we have used photoelectrons with low kinetic energy to follow band bending shifts in the substrate component caused by successive metal depositions. By maximizing the probe depth in this way, it was possible to measure the substrate signal with high reliability up to $\sim 4$ Å of metal deposition. The total band bending changes found at approximately that coverage were 0.31 eV for Ti, 0.63 eV for Cr, 0.45 eV for Co, and 0.32 eV for Fe (uncertainty ±20 meV). In Fig. 1 we can see the evolution of the Fermi-level position for these metals, as determined by core-level shifts of the In $4d$ substrate component at $h\nu = 32$ eV. In all cases, the heats of phosphide formation are large and this correlates well P trapping at the interface and segregation of In atoms to the free surface. Despite the overall similarities, the Schottky barrier heights are found to have very different
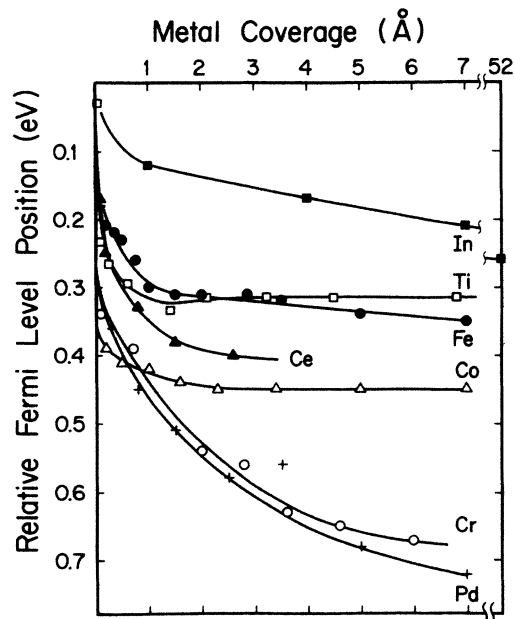
## Metal Coverage (Å)



FIG. 1. Fermi-level position referenced to the conduction-band minimum for different metal overlayers, plotted as a function of amount of metal deposited. The band-bending changes were determined from the In $4d$ core-level shifts as measured at $h\nu=32$ eV for Ti, Cr, Fe, and Co, and 40 eV for Pd, and at 60 eV for Ce and In.

values. Note that the most reactive transition metals, Cr and Ti, present the highest *and* the lowest band bendings of the four cases studied here. As we will show, these early transition metals also have a precursor stage for reaction, but we find no correlation between this precursor and the Schottky barrier variation. Also shown in Fig. 1 are results for Ce, In, and Pd overlayers on InP(110). These are included for comparison because Ce exhibits substantial reaction, In exhibits cluster formation with no reaction, and Pd shows preferential P surface segregation. For In/InP(110), the barrier is not established until very high coverage. Examination shows that there are different final positions for each of these metals. The results are not consistent with a final position which neglects the influence of the metal adatoms or their reactivity.

In Fig. 2 we summarize our surface-sensitive In 4d core-level results for Ti and Cr. The bulk-sensitive In results for Fe and Co overlayers are summarized in Fig. 3. For visual clarity, these spectra have been normalized to constant height and have been offset to account for Schottky barrier changes. (Quantitative information about variations in intensity is found in the attenuation curves of Figs. 6–8.) Representative line-shape decompositions are shown on the right of Figs. 2 and 3 to emphasize similarities and differences for the different systems and to show the effect of varying the probe depth. Similar analysis has been done for all of the surface and bulk spectra for Ti, Cr, Fe, and Co, including coverages and entire sets of data not shown, since they provide the quantitative information necessary to determine how the

various chemical environments change with metal deposition. The labels 1 and 2 identify the bulk and surface components, respectively. For the clean surface, the surface contribution is ~18% of the total In signal for $h\nu=32$ eV and 43% for $h\nu=60$ eV. The deposition of reactive adatoms leads to its rapid disappearance (e.g., 0.35 Å of Fe reduces the surface component three times). This reflects disruption of the substrate by adatom-anion reactions. At the same time, a reaction-induced In $4d$ doublet grows on the low-binding-energy side of the substrate feature. This shoulder becomes more distinct and develops into a peak which dominates the spectrum at coverages above ~5 Å for Ti, and ~2 Å for Cr, Fe, and Co. At lower coverages, it exhibits a poorly defined shape and is shifted ~0.4 eV from the substrate. At high coverages, it becomes a sharp, well-resolved feature (full width at half maximum of 0.34 eV for 80 Å of Ti) while shifting constantly to lower binding energy. The results of Figs. 2 and 3 further show that the In $4d$ core-level emission develops a distinct asymmetry as the metal deposition increases. Such asymmetries have been associated with final-state screening of the core hole and reflect metalliclike surroundings for the emitting atom.[12]

Since the development of the asymmetric line shape could indicate the formation of metallic clusters on the surface, we measured the coverage-dependent In $4d$ line shape for In/InP(110) and In/Co interfaces. Those results showed that small amounts of In atoms on Co exhibit different core line shapes than those arising from In clusters grown on InP(110).[18] Moreover, the In $4d$ core line shapes observed for high metal coverages of Ti, Cr, Fe, and Co on InP resembled those seen at low In coverages on clean Co. We conclude that the dissociated In atoms do not cluster but remain dispersed on the surface. The continual shift of the In $4d$ peak to lower binding energies supports the idea of a monotonic change in the environment of In atoms rather than the formation of In clusters of distinct character.

These observations about In indicate that the reaction-induced In $4d$ feature does not correspond to a well-defined compound. Instead, the gradual sharpening of the new feature is caused by atomic redistributions at the interface.[18] In particular, In atoms, which are initially in a disordered array on the surface where nuclei of metal phosphides are appearing, are ejected to the surface of an increasingly metallic overlayer. They persist in this environment, although some are metastably trapped or taken into solution as additional adatoms of metal are deposited. This behavior for In is analogous to that of Ga at $M$/GaAs interfaces and is consistent with what has been reported for other systems as well. In these cases, the heats of formation for metal-anion compounds favor anion-based compounds over cation-based compounds and the cations are the residue of the heterogeneous reactions (see next paragraphs). We conclude that the In behavior and the mechanisms of trapping and segregation are common in these systems.

The generalization about similar behavior for In atoms for these systems can be only partially extended to their P counterparts. The most striking differences are reflected in the existence of two reacted components of P $2p$ core

lines for Ti and Cr overlayers compared to a single react-ed component for Fe and Co. An important common as-pect is that P is trapped close to the buried interface and does not appear in the surface region of thick films.

In Fig. 4 we present background-subtracted, bulk-sensitive P 2p core-level spectra for the Co/InP(110) in-terface taken with a photon energy of 140 eV. Line-shape decompositions on the right show the substrate component and a surface component shifted 0.29 eV to lower binding energy [surface-to-bulk intensity ratio of 25% because $I_s = 0.2I_{total}$ and $I_b = 0.8I_{total}$ for the cleaved (110) surface, consistent with the In results]. The deposition of 1 Å of Co results in the growth of a shoul-der at higher binding energy and quenches the surface contribution. The reaction product, labeled 3 in Fig. 4, grows with further Co deposition, dominates by a cover-age of 5 Å, and shows a well-defined binding-energy shift of + 0.73 eV. Since this structure always appears at the same binding energy, the experimental spectra could be fit at any coverage by varying only the substrate, surface,

and reaction-product intensities, without change in fitting parameters. We therefore associate the third component with a distinct Co-P compound[19] which forms when Co is deposited and results in the release of In. With increased Co deposition, a condition is reached when reaction to form Co-P is impeded by the reacted layer. Thereafter, overlayer growth is dominated by formation of Co metal with dissociated semiconductor atoms in solution and segregated to the surface. Comparison of these results with those for Fe/InP(110) shows strikingly similar P 2p behavior and a Fe-P feature which appears at 0.66 eV higher binding energy than in the substrate. All of the evidence points to parallel growth patterns for Fe and Co overlayers on InP(110).

Our LEED studies for clean, cleaved InP(110) showed sharp (1×1) diffraction patterns.[20] However, the deposi-tion of Co induced a high background intensity and fad-ing of LEED spots. By 2.3 Å, the LEED pattern disap-peared. In no cases did we find evidence for epitaxial growth of the overlayer, consistent with the high heats of
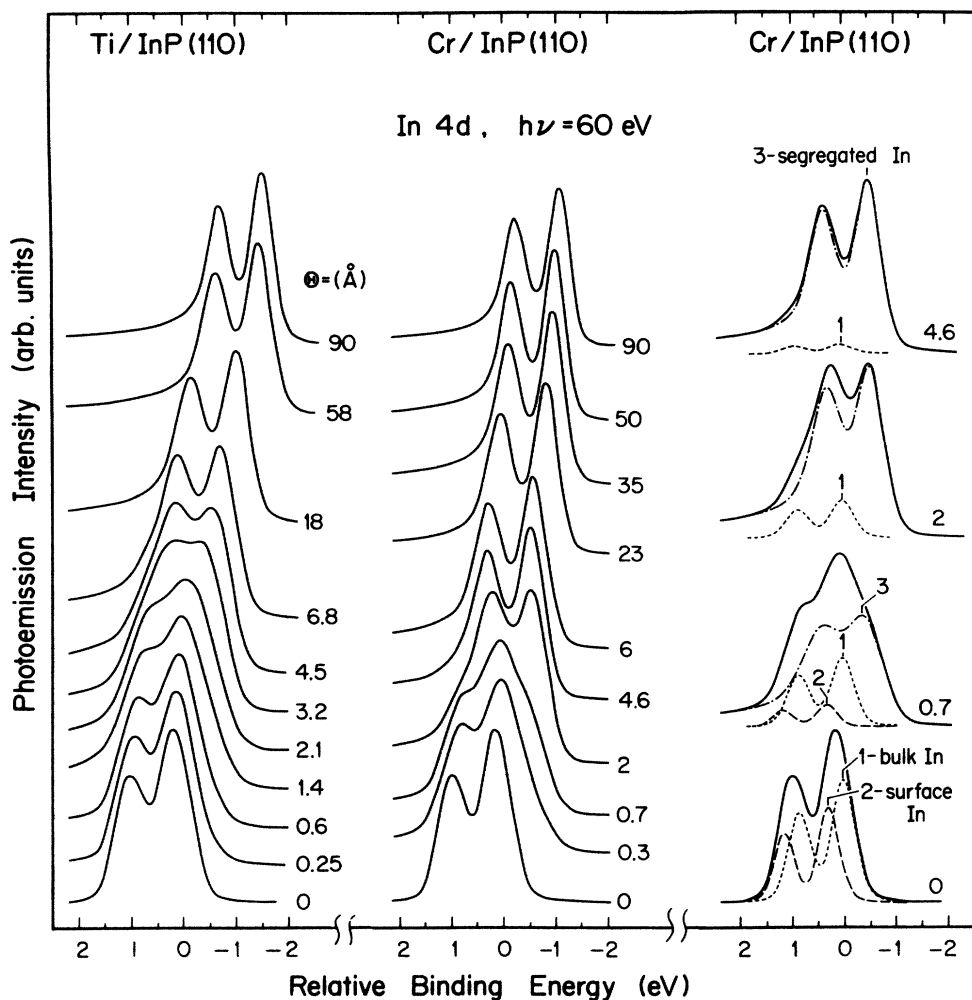


FIG. 2. Development of the In 4d core levels, taken at $hv = 60$ eV, upon Ti and Cr deposition. The results of line-shape analysis shown on the right for Cr/InP(110) indicate the existence of a surface shifted component (labeled 2) in addition to the substrate com-ponent (labeled 1). At low coverage, the surface component is rapidly attenuated. The doublet labeled 3 is associated with In atoms expelled from the reacted region and dominates the spectra for coverages above ~5 Å for Ti and ~2 Å for Cr, Fe, and Co.

formation of the phosphides, although the bcc-fcc lattice match is very good. The epitaxy of Fe and Co on GaAs then represents a delicate balance where an epitaxial relationship is possible and the chemical driving forces for extensive disruption are weak.[21]

The Ti/InP(110) and Cr/InP(110) interfaces yield considerably more complex P $2p$ core-level line shapes than for Fe and Co, but, as for Fe and Co, there are internal consistencies for Ti and Cr. In Fig. 5 we show the P $2p$ evolution for Cr/InP using surface-sensitive spectra taken at $h\nu = 170$ eV. Subangstrom depositions of Cr cause an overall broadening of the P $2p$ emission and the attenuation of the surface component. Consistent implementation of the fitting routine and the excellent statistics of the spectra made it possible to conclude that this broadening was caused by the formation of two distinct reaction products in the low coverage regime. The first is represented by a spin-orbit doublet shifted $0.3 \pm 0.02$ eV to lower binding energy. This component contributes 20% of the total P $2p$ emission when 0.1 Å of

Cr is deposited, although quantitative assessments for coverages below 1 Å suffered because of the near degeneracy in energy with the surface shifted component. The second reacted component appeared at 0.47 eV higher binding energy. It was apparent after the deposition of 0.7 Å of Cr and it quickly dominated the total emission spectrum. Analogous results were obtained for Ti/InP(110) where it was found that the first reaction peak appeared at 0.48 eV lower binding energy and the second was degenerate with the bulk emission.

This detailed P $2p$ line-shape analysis for Cr/InP(110) and Ti/InP indicates that two distinct chemical environments are induced by the deposition of the metal atoms. The coverage range over which the first appears suggests that it represents the transition region from the substrate to the more stable phosphide. (The intensity of this component was a maximum when 1 Å of Cr was deposited, as will be discussed in subsequent paragraphs.) We speculate that true interface states localized at the boundary should also appear, states which are not related to the
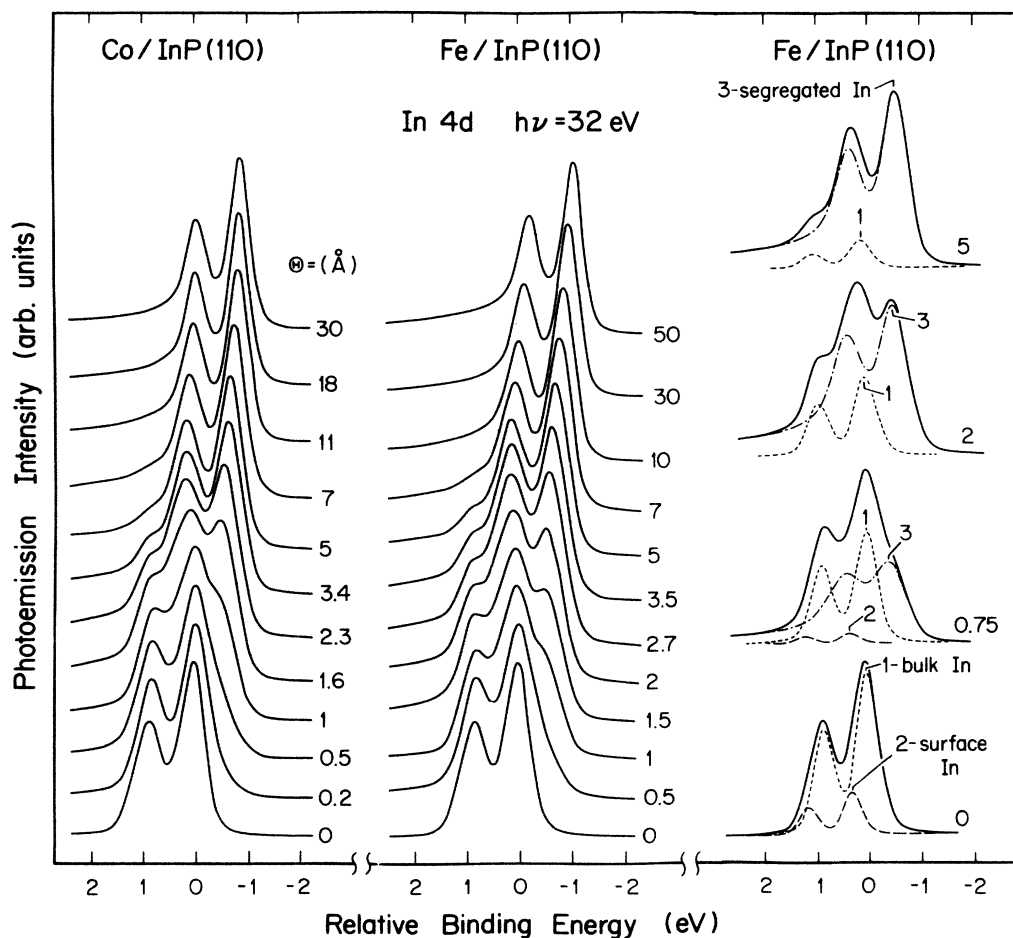


FIG. 3. Bulk-sensitive In $4d$ photoemission spectra as a function of Co and Fe coverage. The spectra have been background subtracted, normalized, and corrected for band bending. In $4d$ decompositions for the clean surface, shown at the bottom right, were used to extract the surface-to-bulk intensity ratio and the effective photoelectron probe depth. The third component exhibits clear symmetry and a continuous shift to lower binding energy, indicating metalliclike environments for the In atoms and progressive solution in the metal overlayer. The surface shifted component (2) is at fixed energy, 0.32 eV, with respect to the substrate (1).

formation of macroscopic compounds. A similar transition region or precursor was observed by del Giudice et al.[21] for Ti/Si. This precursor may be related to Ti or Cr atoms which have substituted In atoms at near-surface In sites. Intriguingly, their presence does not produce a unique effect on the Schottky barrier, as shown in Fig. 1. Comparison with the results for Fe and Co shows that the first-formed component for Ti and Cr is shifted to lower binding energy while the final compound in all cases appears at higher binding energy. For the Co and Fe, there was no evidence for the transition region.

To gain quantitative information about the different chemical environments for In and P at these interfaces, we have used these line-shape decompositions to obtain the integrated intensities for each component, $I_i$, as a function of coverage $\Theta$, normalized to the total emission for the clean surface, $\ln[I_i(\Theta)/I(0)]$. In Fig. 6 we display the P $2p$ attenuation curves for Cr/InP(110) and Fe/InP(110). Figure 7 shows the In $4d$ attenuation curves for Ti and Fe overlayers. Figure 8 summarizes the results for all four systems for easy comparison. In all cases, there is strong In segregation, P trapping at the interface, and no evidence for island formation. The disap-

pearance of P with coverage and the amount of In segregated in the case of Ti is evidence of the high reactivity of this metal. The shallow slope for the In attenution curves at high coverages correlates with the low solubility of In in these metals.

The P $2p$ emission exhibits two different trends for these interfaces, consistent with the absence of the transition region for Fe and Co. Nonetheless, all of the results show that there is strong reaction of metal adatoms with substrate anions and the development of reacted components, starting from the earliest stages of interface formation. For Cr and Ti overlayers, the results of the upper portion of Fig. 6 show that the first component rises to relative maximum at 1 Å deposition but is rapidly attenuated with a $1/e$ decay length of less than 3 Å. Its decay is accompanied by the growth of the second component. The second component reaches a maximum at 5 Å and is then attenuated ($1/e$ length $\sim 4$ Å). When 15 Å of Cr have been deposited, the total P signal is reduced to less than $e^{-3}$ or 5% of its starting value, indicating that P is trapped near the buried interface.[1] Analogous trapping is observed for Fe and Co overlayers, but line-shape analysis does not show the ultrathin transition region.
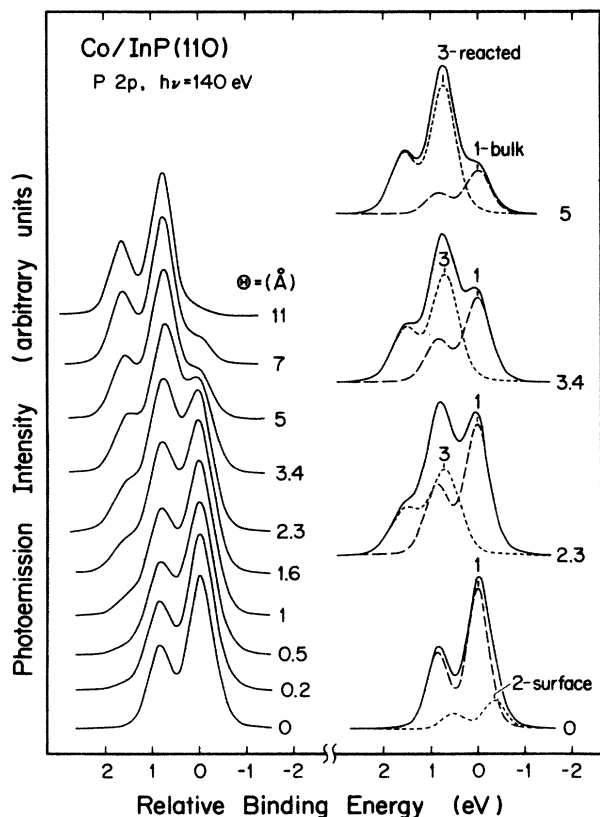


FIG. 4. P $2p$ core-level spectra for Co/InP(110) at $h\nu = 140$ eV. Depositions reveal a surface component (2) which is shifted 0.29 eV to lower binding energy relative to the substrate (1). The reaction product (3) has a well-defined binding-energy shift of 0.73 eV and corresponds to a Co-P compound which forms at the interface and expels In atoms to the free surface.
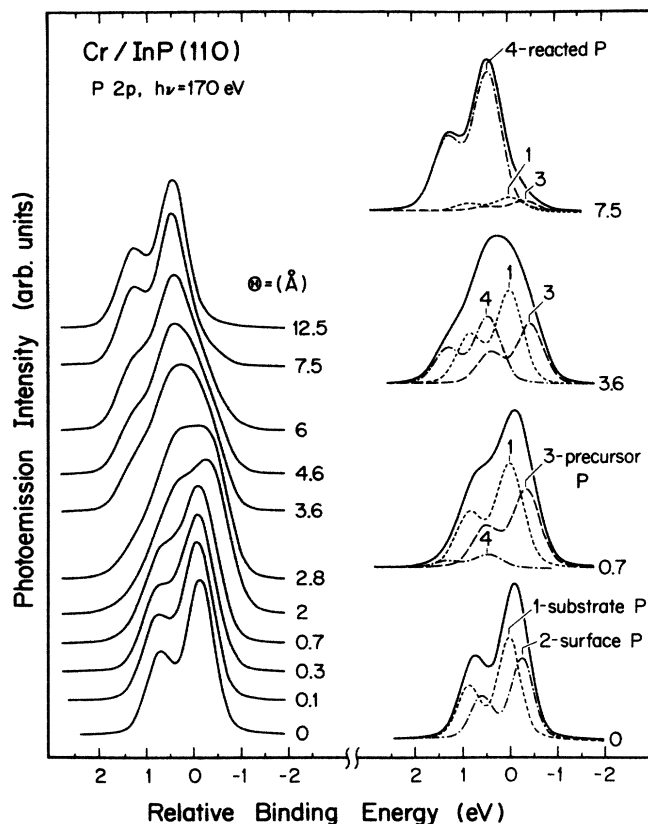


FIG. 5. P $2p$ energy distribution curves taken at 170 eV photon energy for Cr/InP(110). The final component, labeled 4, appears at higher binding energy and is attributed to the formation of a stable metal phosphide, as for all of the systems studied here. For the early transition metals Ti and Cr, a component (3) is observed which may be related to Ti or Cr atoms that occupy In atom sites at the $M$/InP interface. It is not observed for Fe or Co overlayers.
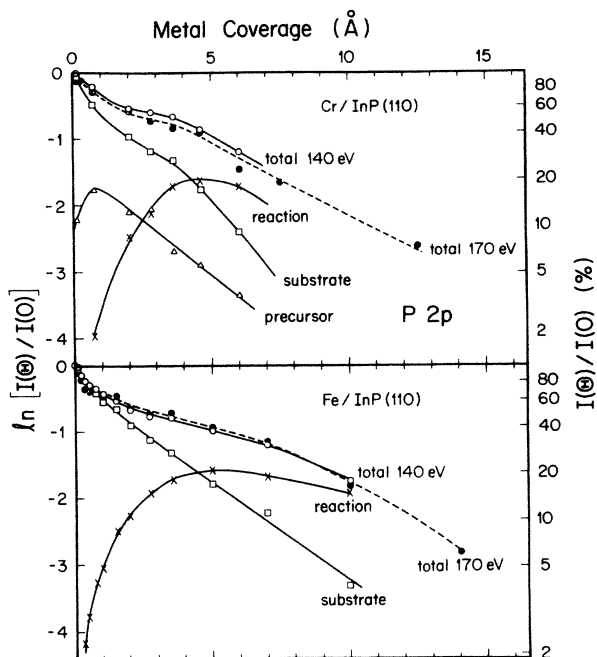
FIG. 6. Top panel: P 2*p* core-level attenuation curves for Cr/InP(110) at *hν*=140 and 170 eV. The total bulk-sensitive attenuation at *hν*=140 eV is decomposed to show the behavior of the substrate, the transition region, and the phosphide reaction product. Bottom panel: same as above, but for Fe/InP(110). The *total* attenuation curves for Fe and Cr are similar, but decompositions show an obvious difference related to the precursor reaction for Ti and Cr.

Instead, the phosphide phase grows, reaches a maximum at 5 Å deposition, and decays as the metallic overlayer forms.

The initial growth of the phosphide overlayer causes the emission intensity of In 4*d* to decrease with increasing metal coverage, as can be seen in Fig. 7. However, the In 4*d* emission starts to *increase* after the deposition of 1.6 Å of Co, 2.7 Å of Fe, 4 Å of Cr, or 7 Å of Ti. This onset of segregation reveals the expulsion of In atoms from the complex, intermixed region where phosphide nuclei are forming and coalescing.[18] Once reactions become diffusion limited, continued adatom deposition leads to the formation of metal layers. Indium atoms can be trapped in this layer as a supersaturated solution, which is an energetically unfavorable configuration, or they can continue to segregate. From the results of Figs. 7 and 8, we see that the In content of the probed region remains high, with a maximum in the In emission that varies from interface to interface.

The intriguing process of segregation has been addressed recently by Lin *et al.*[4] They found that the cohesive energies and the atomic sizes of the substrate species with respect to those of the overlayer materials are dominant factors in determining segregation. Their analysis predicted, and our results confirm, that In is highly prone to segregate on these metals.[22] We have also compared our results for growing *M*/InP interfaces
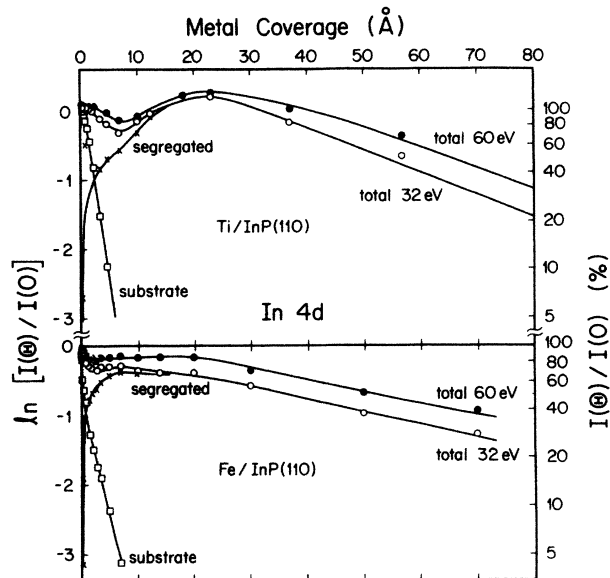
FIG. 7. In 4*d* attenuation curves for Ti/InP(110) and Fe/InP(110). Both bulk and surface core-level intensities first decrease but reach a minimum and increase in intensity. This interesting behavior is explained in terms of the onset of In surface segregation, as discussed in the text. Because of the stronger reactivity of Ti with P of the substrate, the effect is more pronounced for Ti/InP than for other *M*/InP interfaces.

with the results of sputter profiling experiments for 100-Å Co/InP(110) and 75-Å Cr/InP(110).[23] These sputtering profiles for Co showed a region near the buried interface which is In deficient (the region where Co-P formation dominates). The presence of In in the metal layer outside this region suggests that not all of the In atoms li-
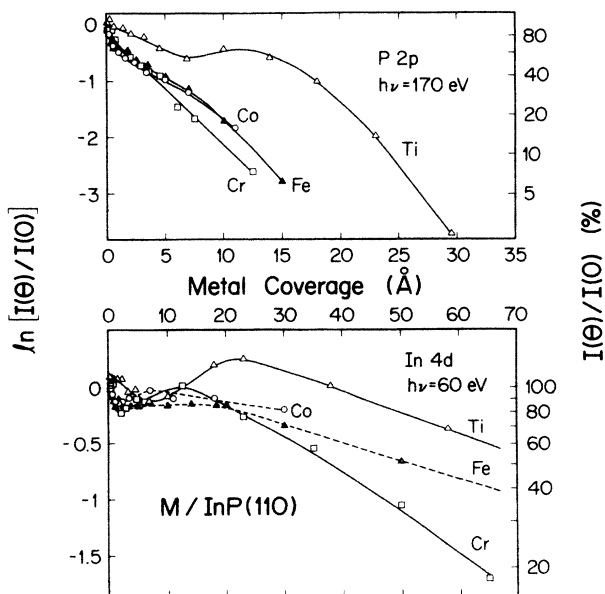


FIG. 8. The total In 4*d* and P 2*p* surface-sensitive core-level attenuation curves summarizing results for Ti, Cr, Fe, and Co.
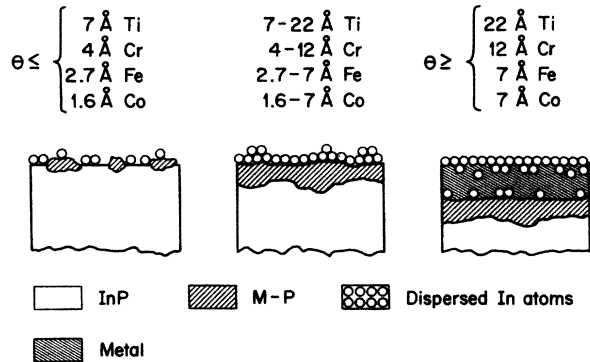
FIG. 9. Schematic of $M$/InP(110) interface development, as dicussed in the text, showing the existence of reacted regions contacting the substrate, metallic overlayers at intermediate coverage, but In segregation at high coverage, partially cooling the surface in a dispersed manner.

berated by substrate disruption are segregated to the surface but that some are captured in the interface region. For the more reactive metals, the expulsion of In is more pronounced and there is a greater In accumulation in the metal layer adjacent to the Cr-P region.[23]

The morphologies sketched in Fig. 9 are consistent with the results presented here for the evolving Ti/InP(110), Cr/InP(110), Fe/InP(110), and Co/InP(110) interfaces. For depositions below $\sim 7$ Å for Ti, $\sim 4$ Å for Cr, $\sim 2.7$ Å for Fe, and $\sim 1.6$ Å for Co, there is substrate disruption which leads to metal-phosphide formation and the release of In atoms. Further metal deposition to $\sim 22$ Å for Ti, $\sim 12$ Å for Cr, and $\sim 7$ Å for Fe and Co produces a metal-phosphide layer which covers the substrate and ejects most of the trapped In to the surface region. Reaction ceases at room temperature as the phosphide region is covered. Much of the segregated In continues to segregate. As expected from bulk thermodynamics, metal-phosphide formation is very favorable. Although the four systems show similar morphologies, Schottky-barrier heights present very different values and were not correlated with differences in P compound formation.

## ACKNOWLEDGMENTS

[1]L. J. Brillson, Surf. Sci. Rep. 2, 123 (1982), presented a detailed review of the literature.

[2]See, for example, Y. Shapira, L. J. Brillson, A. D. Katanani, and G. Margaritondo, Phys. Rev. B 30, 4580 (1984); F. Schäffer, W. Drube, G. Hughes, R. Ludeke, D. Rieger, and F. J. Himpsel, J. Vac. Sci. Technol. A 5, 1528 (1987); R. H. Williams, A. B. McLean, D. A. Evans, and W. G. Herrenden-Harker, J. Vac. Sci. Technol. B 4, 966 (1986).

[3]J. H. Weaver, in Analysis and Characterization of Thin Films, edited by K. N. Tu and R. Rosenberg (Academic, New York, in press); Phys. Today 39 (1), 24 (1986).

[4]Z. Lin, F. Xu, and J. H. Weaver, Phys. Rev. B 36, 5777 (1987).

[5]T. Miller and T. C. Chiang, Phys. Rev. B 29, 7034 (1983); K. Stiles, A. Kahn, D. G. Kilday, and G. Margaritondo, J. Vac. Sci. Technol. A 5, 1527 (1987).

[6]T. Kendelewicz, W. G. Petro, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. B 2, 453 (1984).

[7]T. Kendelewicz, M. D. Williams, W. G. Petro, I. Lindau, and W. E. Spicer, Phys. Rev. B 31, 6503 (1985).

[8]T. Kendelewicz, R. S. List, M. D.Williams, K. A. Bertness, I. Lindau, and W. E. Spicer, Phys. Rev. B 34, 558 (1986).

[9]S. A. Chambers, F. Xu, H. W. Chen, I. M. Vitomirov, S. B. Anderson, and J. H. Weaver, Phys. Rev. B 34, 6605 (1986); F. Xu, J. J. Joyce, M. W. Ruckman, H.-W. Chen, F. Boscherini, D. M. Hill, S. A. Chambers, and J. H. Weaver, ibid. 35, 2375 (1987), and references therein.

[10]M. P. Seah and W. A. Dench, Surf. Interface Anal. 1, 2 (1979).

[11]G. K. Wertheim and S. B. Dicenzo, J. Electron Spectrosc. Relat. Phenom. 37, 57 (1985).

[12]S. Doniach and M. Šunjíc, J. Phys. C 3, 285 (1970).

[13]J. J. Joyce, Ph.D. thesis, University of Wisconsin, 1987 (un- published).

[14]D. E. Eastman, T. C. Chiang, P. Heimann, and F. J. Himpsel, Phys. Rev. Lett. 45, 656 (1980).

[15]C. Priester, G. Allan, and M. Lannoo, Phys. Rev. Lett. 58, 1989 (1986).

[16]W. Mönch, Solid State Commun. 58, 215 (1986).

[17]R. S. List, T. Kendelewicz, M. D. Williams, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. A 3, 1002 (1985).

[18]F. Xu, C. M. Aldao, I. M. Vitomirov, Z. Lin, and J. H. Weaver, Phys. Rev. B 36, 3485 (1987).

[19]All of the Co phosphides are thermodynamically more stable than InP, which is reflected in their experimentally obtained heats of formation, namely $-205$, $-188$, and $-126$ kJ/mol for $CoP_3$, $Co_2P$, and CoP, compared to $-88$ kJ/mol for InP (see NBS Tables of Chemical Thermodynamical Properties [J. Phys. Chem. Ref. Data 11, Suppl. 2 (1982)]); O. Kubachewski and C. B. Alcook, Metallurgical Thermochemistry (Pergamon, Oxford, 1979). The constant binding energy of the reacted P $2p$ spin-orbit doublet indicates that a single, well-established compound is being formed.

[20]See, for example, Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, edited by D. H. Ring and D. P. Woodruff (Elsevier, New York, 1981), p. 171.

[21]M. del Giudice, J. J. Joyce, M. W. Ruckman, and J. H. Weaver, Phys. Rev. B 35, 6213 (1987).

[22]F. Boscherini, Y. Shapira, C. Capasso, C. M. Aldao, and J. H. Weaver, J. Vac. Sci. Technol. B 5, 1003 (1987); F. Boscherini, Y. Shapira, C. Capasso, C. M. Aldao, M. del Giudice, and J. H. Weaver, Phys. Rev. B 35, 9580 (1987).

[23]D. M. Hill, F. Xu, Z. Lin, and J. H. Weaver, Phys. Rev. B (to be published).