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Direct evidence of the onset of In surface segregation for Co/InP(110)

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We present the first clear experimental evidence of the existence of an onset for the phenomenon of cation surface segregation at evolving metal-semiconductor interfaces. High-resolution soft-x-ray photoemission results for Co/InP(110) show that the total In 4*d* intensity decreases in the ultrathin Co overlayer region (≤ 1.6 Å), *increases* steadily until a nominal deposition of ~ 7 Å, and attenuates slightly thereafter. Detailed In 4*d* core-level line-shape analysis reveals that a chemically shifted peak appears in the earliest stage of interface formation and grows in relative intensity. Studies of In/InP(110) and In/Co interfaces show that this new feature corresponds to dispersed In atoms segregated on the surface and that three-dimensional In clusters do not form. Together, these results show that there is a critical coverage which triggers In surface segregation and also show how the atom distribution evolves as the overlayer thickens.

Chemical reactions, Schottky barrier formation, growth morphologies, and interdiffusion during *M*/InP(110) interface formation (where *M* is a metal) have attracted a great deal of attention.[1-5] The interest is stimulated by both possible technological applications in electronic devices and the need to develop general models for interface properties. Comparison of experimental results for *M*/InP systems with those for analogous *M*/GaAs and *M*/InSb systems is leading to a more complete understanding of the physical mechanisms of interface formation for compound semiconductors, and comparison with *M*/Si and *M*/Ge reveals the preferential chemistry of metal-anion reactions.[1-5] Despite this progress, however, the detailed interactions which occur at very low coverage when a disrupted, intermixed layer is growing are still poorly understood.

In this Rapid Communication, we address the phenomenon associated with the onset of surface segregation and the physical or morphological configuration of the interface when it occurs. The results of our photoemission study of Co/InP(110) interfaces show clear evidence of the existence of an onset for cation surface segregation. These results are discussed within the framework of Co-P compound formation and an atomic redistribution process for dissociated In at the interface. Sputter profiles provide complementary information about the distribution of atoms for the fully reacted layer after a thick metal overlayer has been deposited.

Soft-x-ray photoemission experiments were performed at the Aladdin storage ring at the Wisconsin Synchrotron Radiation Center using the Grasshopper Mark V beamline. These measurements emphasized core-level line-shape changes and core-level intensity variations as a function of the amount of Co deposited. Maximum surface sensitivity was achieved by suitable choices of photon energies, and maximum chemical information was obtained by operating with high resolution (photons plus electrons ~ 0.2 eV for In and ~ 0.4 eV for P). Samples of InP (*n* type, Sn doped at 4×10^{17} cm^{-3}) were cleaved *in situ* at an operating pressure of 5×10^{-11} Torr to produce high-quality, mirrorlike (110) surfaces free of Fermi-level pinning. Co was evaporated from resistively heated W boats situated ~ 30 cm away from the samples. The deposition rates were monitored by a calibrated quartz oscillator. In all cases, the samples were exposed to the Co source only after the evaporation rate was fully stabilized, and timed evaporations were used to ensure the reproducibily of the coverage. The term "nominal coverage" will be used here to indicate that the Co layer does not grow in a simple layer-by-layer fashion but rather induces disruption and intermixing. Indeed, low-energy electron-diffraction studies confirmed that the overlayer does not grow in an ordered, epitaxial way at room temperature.[6]

In the lower portion of Fig. 1 we show representative core-level energy distribution curves (EDC's) for the evolving Co/InP(110) interface. Spectra on the left show the In 4*d* emission for the clean surface, for a low coverage regime at 1.6 Å, and for a high coverage of 30 Å. Analogous results are shown on the right for P. All spectra are background subtracted, with band bending removed, and normalized to the same height to emphasize chemical effects. Detailed core-level line-shape analysis demonstrates that the P 2*p* and In 4*d* peaks develop a shoulder at higher and lower binding energy, respectively, at very low Co coverage (≤ 1 Å).[6] The new feature in the P 2*p* EDC's has a well-defined binding energy and falls 0.73 eV deeper than that of the substrate. Its position remains constant for all Co coverages and it can be associated with a Co-P compound. Inspection of the bulk heats of formation of possible Co-P compounds shows that they are more stable than InP.[7] We conclude that Co disrupts the substrate and reacts with P to form the nuclei of a distinct compound, even at very low coverage. From the In 4*d* EDC's, we see that the new feature grows and shifts continuously to lower binding energy with coverage. At 1.6 Å Co, its intensity exceeds that of the substrate and it dominates the spectra thereafter. With increasing deposition, the Doniach-Sunjic line-shape asymmetry, an index of the effects of metallic screening[8] for this shifted peak, increases gradually and saturates to a value of 0.18 at a

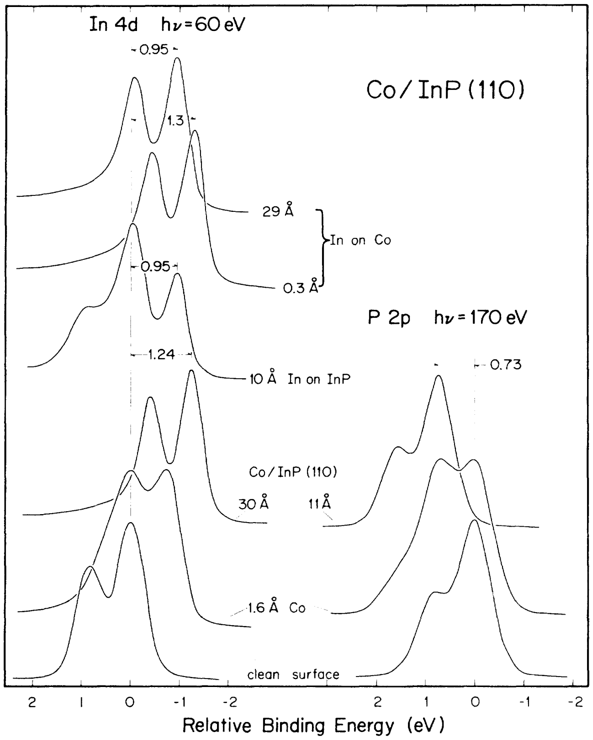

FIG. 1. In $4d$ and P $2p$ core-level EDC's for Co/InP(110) for the clean surface, for a low coverage during intermixing, and for a higher coverage as the reaction products and segregation dominate. Also shown are the shifting In $4d$ EDC's for In overlayers grown on pure Co and on InP(110). Band bending has been removed from the spectra to emphasize chemical changes. From the In results at the left we conclude that In dissociates during Co/InP interface formation and segregates to the surface as a dispersed layer. From the P results, we see a distinct Co-P compound shifted 0.73 eV relative P in InP.

coverage of ~7 Å. [The results of these analyses will be presented elsewhere in a more comprehensive study of reactive metal overlayers on InP(110).[6]]

In order to obtain energy and line-shape references for the In $4d$ emission for Co/InP(110), we also investigated In/InP(110) and In/Co interfaces, as summarized by the three EDC's in the upper portion of Fig. 1. The In $4d$ core-level EDC's of In grown on pure Co show a continuous shift in peak position toward higher binding energy with a total shift of 0.35 eV from 0.3- to 29-Å In thickness. This corresponds to a change in In morphology from dispersed In atoms to bulk In metal. In the same coverage range, we see a gradual change in spin-orbit splitting from 0.86 to 0.89 eV, indicating the slightly delocalized character of the shallow $4d$ levels. Also shown in Fig. 1 are In $4d$ EDC's for a 10-Å overlayer of In on InP(110) for comparison to the configuration of 30 Å Co/InP and pure In on Co. As can be seen, the chemical shift for In for 30 Å Co/InP is much greater than would be expected if these atoms were aggregating in the form of three-dimensional (3D) In clusters. Instead, they appear in a state very similar to dispersed In atoms and Co. We conclude that In does not cluster when it is segregated on the substrate after dissociation from the substrate by Co reacting with P.

The normalized attenuation and growth curves of In $4d$, P $2p$, and Co $3p$ total core emission intensities make it possible to assess the morphology of the evolving layer and examine the distribution of the various species. In Fig. 2, we show these normalized intensities in the form $\ln[I(\theta)/I(0)]$ for In and P and $\ln[I(\theta)/I(30\ \text{Å})]$ for Co where $I(\theta)$ is the emission at coverage θ and $I(0)$ is the integrated emission for the clean surface. These results were obtained with photon energies of 60 and 32 eV for In, 170 and 140 eV for P, and 100 eV for Co to enhance the surface and bulk sensitivity of the measurements (mean free paths, λ, of ~4–5 and ~12 Å with 95% of the signal coming from within 3λ of the surface[9]). To obtain these intensity variations, corrections were made for the incident photon beam intensities and secondary electron backgrounds. From Fig. 2, we see that the P $2p$ intensity decreases rapidly with coverage while that for In $4d$ decreases much less at low coverages, reaches a minimum of 1.6 Å, then increases until a nominal deposition of 7 Å. Above that, the In intensity decreases very slowly: At 30 Å nominal Co coverage, the surface-sensitive In $4d$ intensity is still ~80% of the value observed for the cleaved surface. Complementary information obtained from the change in intensity of the Co $3p$

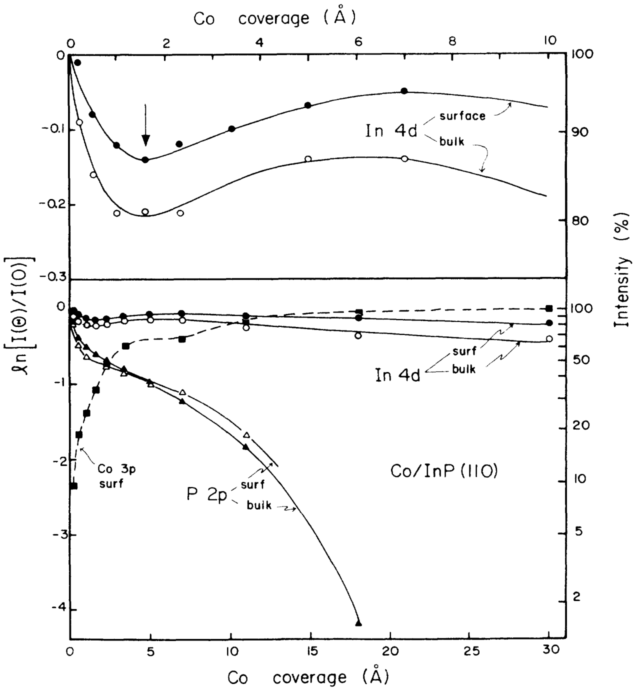

FIG. 2. Attenuation curves for In $4d$, P $2p$, and Co $3p$ intensities, $\ln[I(\theta)/I(0)]$ for In and P and $\ln[I(\theta)/I(30)]$ for Co. The upper panel shows the attenuation curves for low metal coverages to demonstrate the initial drop, bottoming out, and increase in the In $4d$ emission. These results reveal the onset of surface segregation.

emission indicates a rapid increase in emission, a shoulder below 7 Å, and a gradual rise thereafter. Although we show that the intensity saturates at 30 Å, this normalization is arbitrary since the probed region is clearly not pure Co. Indeed, the rate at which In 4*d* emission intensity is lost indicates that a very thick coverage would be needed to extinguish it entirely.

To emphasize the dramatic changes in In 4*d* emission at the *beginning* of the interface formation, we amplify the low coverage portion of its attenuation curve in the upper panel of Fig. 2. The increase in In 4*d* intensity at 1.6 Å Co coverage (see arrow) is both unexpected and interesting since the rapid decrease of the P 2*p* signal excludes any correlation to Co cluster formation. To our knowledge, such a phenomenon in *M*/InP systems has never before been reported.

From the above, a physical picture of interface formation can be drawn. At the lowest coverage, Co adatoms disrupt the InP substrate and produce a highly heterogeneous surface region, even at room temperature. Cobalt reacts preferentially with phosphorus to nucleate Co-P and release In. Initially, the dissociated In atoms are mixed with the Co-P nuclei along the interface and the emission from both In and P decreases. With increasing Co deposition, however, the Co-P nuclei grow both laterally and vertically, and the amount of liberated In increases. When the nominal coverage reaches ~1.6 Å, there is a transition from dispersed small Co-P nuclei to larger or coalesced nuclei. When this occurs, In atoms are expelled toward the free surface because of the gain in energy due to compound accretion. This is reflected by increased In emission. Such segregation continues until the nominal Co coverage of ~7 Å, at which point the adatoms are no longer able to diffuse through the overlayer to reach the substrate and reactive intermixing is kinetically limited. The resulting Co accumulation on the surface is seen through increased Co 3*p* emission. The very slow attenuation of In 4*d* signal at higher coverages indicates that a large number of segregated In atoms "float" on the overlayer. Physically, this reflects the limited solubility of In in Co. Throughout the range where intermixing occurs, phosphorus is chemically trapped near the interface,[1,10] and the rapid reduction in P 2*p* emission indicates that the overlayer is nearly homogeneous along the surface.

It should be noted that the relative increase of the surface-sensitive In 4*d* intensity does not reflect the real increase in In concentration on and near the free surface since emission from deeper regions is simultaneously reduced. Indeed, the two processes of In surface segregation and metal covering up compete with each other. Only when a large amount of In moves toward the surface is it possible to observe a rise in the total intensity; otherwise a plateau region or a relatively small reduction in slope in the attenuation curve can be observed. For our case here, the accretion of the Co-P nuclei provides a strong driving force for such segregation.

Recent studies of Co/GaAs(110) and (100) interfaces formed at room temperature have demonstrated that Ga atoms are trapped in the near interface region while some As atoms can segregate to the vacuum surface.[11] The quite different distributions of anions and cations for Co/GaAs and Co/InP are very interesting. Inspection of the heats of formation of the most stable bulk Co-P and Co-As compounds[7] (−204.7 kJ/mol for CoP_3 and −144 kJ/mol for Co_2As_3) suggests that the difference may be due to the details of anion trapping.[1] In a recent analysis of surface segregation in approximately fifty *M*/(III-V semiconductor) systems, we found that the cohesive energy and the relative atomic sizes of the substrate and overlayer materials were the most important factors in determining semiconductor atom surface segregation.[10] The larger atomic size of In vs Ga and As vs P and the smaller cohesive energy of In vs Ga and As vs P also favor relatively larger In and As segregation.

As a further test of the strong tendency for surface segregation of In, we performed sputter profiling experiments for a 100-Å Co/InP(110) interface. The results showed strong surface segregation of In and the incorporation of In in the Co overlayer. This incorporation is consistent with the gradual decay of the In 4*d* emission in Fig. 2 for $\theta \geq 7$ Å. At the same time, there was no evidence for P either at the surface or in the Co overlayer until the Co-P region was reached.[12]

The Co/InP(110) interface was recently investigated by Kendelewicz *et al.*[13] Their attenuation curve for the total In 4*d* intensity showed a plateau in the region of Co coverage between 1–10 Å, but the energy resolution of their core-level spectra, the limited number of overlayer thickness investigated, and the modest statistics did not provide resolution of the details shown in Fig. 2. However, as discussed above, the plateau is an indication of the movement of In atoms toward the surface, and their findings are essentially in agreement with our more detailed results.

In conclusion, we have reported the first clear experimental evidence of the existence of the onset of the surface segregation process, observing In segregation for Co/InP(110). These results have lead to a general picture of interface formation at room temperature. Recent systematic studies show that such an onset for the surface segregation process exists in many other *M*/(III-V compound semiconductor) systems as well.[12] This finding is of fundamental importance in understanding the physical mechanism responsible for the formation of intermixed interfaces.

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