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Dependence of core-level photoemission spectra on overlayer growth mode: Al on InP(110)

A. B. McLean*
Department of Physics, University College, P. O. Box 78, Cathays Park, Cardiff, CF1 1XL, United Kingdom

I. T. McGovern
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, West Germany
and Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland

C. Stephens
Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland

W. G. Wilke, H. Haak, and K. Horn
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, West Germany

W. Braun
Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY),
Lentzeallee 100, D-1000 Berlin 33, Germany

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The adsorption of Al overlayers on the clean, cleaved InP(110) surface has been studied, with the InP substrates at room and low (~120 K) temperatures, using synchrotron radiation excited soft-x-ray photoemission spectroscopy. This interface exhibits a well-documented exchange reaction at room temperature, and a visual comparison of the spectra taken at 300 and 120 K suggests that this reaction is inhibited at 120 K. However, there are also significant changes in the interface growth mode as the temperature is lowered. The reacted indium feature exhibits a coverage-dependent binding energy, so that its spectral weight is obscured by overlap with the bulk indium feature. Moreover, escape-depth considerations invalidate a simple comparison of reactivity at the two temperatures.

During the last three years several experimental groups have studied the formation of the Al/GaAs(110) interface, with the semiconductor substrate at low temperature (~100 K).[1-5] The general aim of these studies has been an understanding of the mechanism, or mechanisms, controlling the Schottky-barrier height. At room temperature (RT) the aluminum forms clusters whereas at low temperature (LT) this effect is reduced and the overlayer is more laminar.[1-3] Furthermore, a kinetically limited exchange reaction occurs at this interface.[6] In Zunger's model[7] the energy to initiate this reaction is supplied by the exothermic formation of the aluminum clusters. Therefore, it is expected that the reaction will be similarly reduced at low temperature and such an effect has been deduced from photoemission data.[2,4,5] If the degree of interface reactivity is important in Schottky-barrier formation, the correct estimation of reactivity as a function of temperature is desirable.

The room-temperature behavior of the Al/InP(110) interface has been similarly described in terms of adlayer clustering and exchange reaction.[8] In the present study the formation of this interface at 300 and 120 K is compared. A cursory examination of the core-level photoemission spectra supports the view that the aluminum-indium exchange reaction is reduced at low temperature. However, cooling the substrate also alters the interface growth mode. Both the aluminum adatoms and the exchange-reacted indium atoms have reduced mobility. The adlayer is more laminar and photoemission features show coverage-dependent binding-energy shifts: This results in two competing effects: The reacted indium feature is obscured in the LT spectrum and the intensity of this feature overestimates the reactivity relative to that at RT. A similar difficulty may exist at other exchange-reacted interfaces. Estimation of the temperature dependence of interface reactivity from core-level photoemission spectra requires a knowledge of the changing interface morphology.

The soft-x-ray photoemission spectroscopy (SXPS) experiments were performed at TGM3 of the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY). The combined energy resolution of the monochromator and the ADES 400 analyzer, at the time of measurement, was approximately 0.3 eV at a photon energy of 40 eV, and 0.5 eV at a photon energy of 100 eV. The angular acceptance of the ADES analyzer was approximately 4°.

The surfaces were prepared by cleaving aligned and prenotched bars of highly doped, p-type indium phosphide ($N_d \simeq 1\times 10^{17}$ cm^{-3}; MCP UK Ltd), in a preparation chamber, using the double-wedge and double-notch technique at a base pressure of 1×10^{-10} mbar. The quality of the surfaces was ascertained by examining the reflected zero-order light from the surface; a flat surface with a low step density produced a well-collimated reflection. Five cleavage surfaces were obtained from a single bar of indium phosphide, and the results presented below are a composite from these surfaces. For the low-temperature measurements the sample holder was cooled with liquid nitrogen, and the sample temperature was measured using a thermocouple in direct contact with the sample.

The aluminum overlayers were evaporated from a single-core, chemically cleaned, and outgassed tungsten filament which was mounted in a liquid-nitrogen- cooled jacket (Vacuum Generators). During aluminum deposition the system pressure rose to between 2 and 4×10^{-10} mbar. The flux of the evaporator was continuously monitored by a quartz-crystal oscillator placed close to the source. The equivalent thickness of the aluminum overlayer was calculated assuming that the sticking coefficient of aluminum on both the quartz crystal and the InP(110) surface was unity, and that the resultant overlayers were laminar. The calibration of the source was crosschecked by placing a second thickness monitor at the sample position.

In Fig. 1(a) the room temperature In 4d core-level emission is presented for the clean surface and also for the clean surface plus various thicknesses of aluminum. The incident photon energy was 40 eV, and the curves have been shifted to account for band bending and extraneous experimental shifts. The spectra have been normalized to photon flux and are further offset for clarity. The low-temperature In 4d emission is presented in Fig. 1(b). The room-temperature Al 2p core-level emission corresponding to the various thicknesses deposited onto a clean InP(110) surface are presented in Fig. 2(a). The incident photon energy was 100 eV. The spectra have also been normalized to photon flux. The low-temperature core-level emission is presented in Fig. 2(b). The spectra in Figs. 1 and 2 are for different starting surfaces. However, the same trends and spectral line shapes are observed for the five surfaces studied. The In 4d spectra in Fig. 1 are normalized to approximately the same ordinate scale, as are the Al 2p spectra in Fig. 2. Note the different intensity scale factors for each of the low-temperature Al 2p spectra.

We begin by discussing the In 4d core-level emission at 300 K. As aluminum is deposited, a low-binding-energy component is observed in the In 4d emission and this is discernible at our lowest coverage of 0.6 ML. As the overlayer is built up the magnitude of this component grows substantially. This component originates from "free" or "phase-segregated" indium released by the cation-exchange reaction. The magnitude of this component may be used as a measure of the interfacial reactivity.

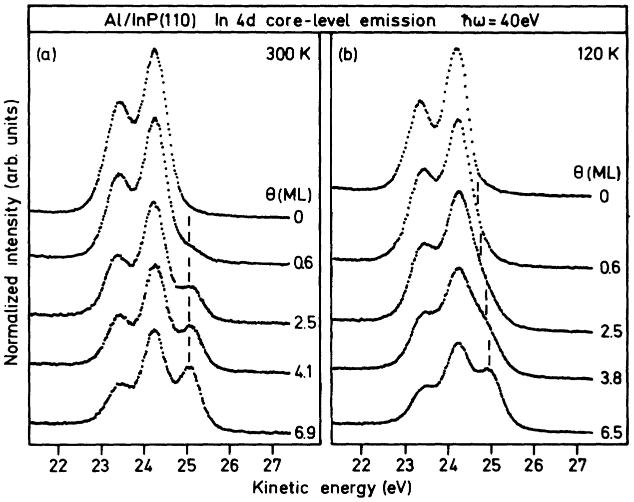

FIG. 1. Photoelectron spectra in the region of the In 4d core level for Al/InP(110) with $\hbar\omega = 40$ eV at (a) 300 K and (b) 120 K. Al coverages are shown for each spectrum in monolayers (ML).

In the corresponding spectra at low temperature, this low-binding-energy component is not as readily discernible at the lower coverages. This suggests that the exchange reaction is initially suppressed at low temperature in agreement with the accepted view of cluster-initiated reaction at this interface. However, in the higher coverage regime the reacted component is as large as in the room-temperature spectra, as was noted in earlier work.[9]

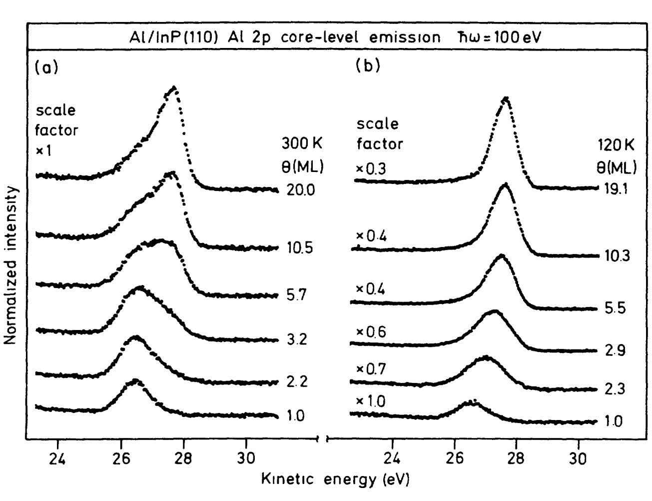

FIG. 2. Photoelectron spectra in the region of the Al 2p core-level emission for Al/InP(110), with $\hbar\omega = 100$ eV at (a) 300 K and (b) 120 K. Al coverages are given in monolayers.

Moreover, the reacted component moves gradually towards lower binding energy, in contrast to its approximately constant binding energy observed at room temperature. This behavior has a natural explanation. At low temperature the mobility of the indium atoms is significantly reduced, and the aggregation of indium will be inhibited. The In 4*d* binding energy reflects the indium cluster size and the higher binding energy at 120 K indicates that the clusters are smaller than at 300 K. Any comparison that is made between room-temperature and low-temperature reactivities must take these changes into account.

We now discuss the Al 2*p* core-level emission presented in Fig. 2. At room temperature, and in the coverage range we have studied, these spectra comprise two visible features. The higher binding feature which dominates at lower coverages has been attributed to aluminum in the surface layer. This component may therefore be regarded as a complementary measure of reactivity. The lower-binding-energy component which dominates the high-coverage regime is emission from metallic aluminum.

Cooling the substrate dramatically alters the Al 2*p* emission. The spectra seem to comprise a single component whose spectral weight moves gradually to lower binding energy as the overlayer is built up. In Fig. 2, the low-temperature signal at the lowest coverage is only 0.65 times that of the room-temperature intensity; we assign this to the error in coverage determination which is large at these small coverages. In the low-temperature spectra [Fig. 2(b)] the reacted peak is only clearly visible at low coverages. It is hidden in the tail of the metallic Al emission at higher coverages, and does not appear as a distinct shoulder as it does in the room-temperature spectra. This is because the metallic Al peak exhibits the same gradual shift with coverage as observed in the In 4*d* spectra at low temperature. Additionally, the metallic Al peak at low temperature shows a much more rapid increase with coverage than at room temperature; the intensity of the highest-coverage spectrum in Fig. 2(b) is 2.7 times that of the corresponding spectrum in Fig. 2(a). This indicates a significant (and expected[1]) change in the growth mode. The aggregation of aluminum is similarly inhibited by reduced mobility, and the resultant adlayer is considerably more laminar. As SXPS only samples the topmost four layers, the relative strength of the metallic components is greatly enhanced at low temperature.

The same two themes are apparent in both the In 4*d* and Al 2*p* core-level emission spectra. A direct comparison of room-temperature and low-temperature spectra suggests that the reactivity is reduced in the latter, but this simple comparison may be invalidated by the alteration in the interface growth mode. We have applied deconvolution techniques[10] to these spectra. The In 4*d* spectra can be deconvolved into bulk, surface, and reacted components throughout the coverage range. A sample fit of the room-temperature coverage of 6.9 ML is shown in Fig. 3(a). The resultant coverage-dependent binding energy of the reacted component is shown in Fig. 3(b). At the lower coverages at low temperature, there is significant overlap in binding energy of the reacted and bulk components. It is this overlap that can result in an underestimation of the intensity of the reacted component. A better estimation of the reacted to bulk intensity ratio is obtained from the core-level deconvolution and this is shown as a function of aluminum coverage in Fig. 3(c). We have also applied the deconvolution techniques to the Al 2*p* spectra. However, the absence of distinct shoulders in the low-temperature spectra restricts the effectiveness of this method.

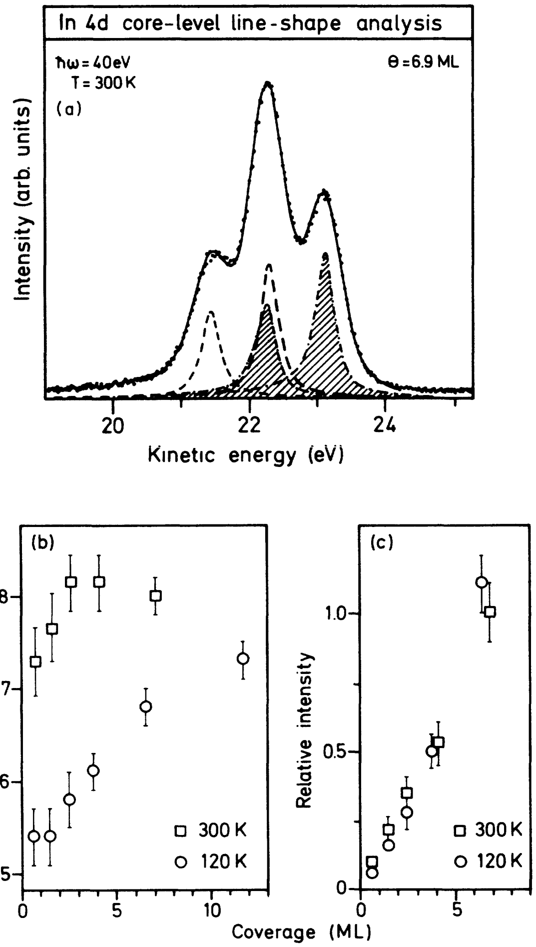

FIG. 3. (a) The results of fitting two Gaussian broadened Lorentzian doublets (solid line) to the measured In 4*d* core-level spectrum (points) with an Al overlayer thickness of 6.9 ML. The Lorentzian doublets corresponding to the bulk (dashed line) and reacted (hatched curves) components are also shown. At this coverage the surface component is negligible. (b) The energy position of the reacted component relative to the bulk component at 300 K (squares) and 120 K (circles) for several Al coverages. (c) The intensity ratio of the reacted to the bulk component at 300 K (squares) and 120 K (circles).

The escape-depth considerations must also apply to the In 4*d* spectra. This means that the comparison of reacted to bulk ratios (although correctly assessed) does not show the relative reactivity at the two temperatures. At RT the free indium is in island form, whereas at LT the structure is more laminar. A direct comparison as in Fig. 3(c) will overestimate the latter reactivity. That these ratios are approximately the same at the two temperatures implies some reduction in reactivity at the lower temperature, but to a degree that cannot be readily quantified. A further complication may be the surface segregation properties of free indium.

In conclusion, lowering the temperature results in reduced mobility that alters the photoemission spectra in two ways: a binding-energy effect which is recoverable by deconvolution and an escape-depth effect. The latter effect limits the correct estimation of reactivity change with temperature. A similar situation may exist on other exchange-reacted interfaces. However, as gallium has a higher tendency to cluster than indium,[7] the effects may be less marked in gallium compounds.

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[*] Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598.

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