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Schottky barrier formation and the initial metal–atom bonding state: InP(110)–Al vs GaAs(110)–Al

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We investigated the adatom states for different Al coverages of InP(110) by synchrotron-radiation photoemission, including ultralow coverages below 0.2 monolayer. The adatom states below 0.1 monolayer and above ~3 monolayer appear similar to the corresponding Al–adatom states on GaAs(110). In particular, the results for both systems appear consistent with the formation of Al clusters at 0.1–2 monolayer coverage, and the Fermi-level pinning occurs when the cluster formation starts. However, the similarity between the two systems is limited at intermediate (0.1–2 monolayer) coverages. At those coverages we observe a new bonded state for Al on InP, which is not observed on GaAs. Our results emphasize, in general, the need to extend the experiments to ultralow coverages when studying the Schottky barrier formation process.

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Recent experiments[1] emphasized the crucial importance of the ultralow metal coverage (<0.2 monolayer) chemisorption stage in the Schottky barrier formation process on III–V substrates. In fact, this crucial role had been suggested for several years by the experimentally observed, extremely fast shift of the interface Fermi-level position E_F during the early stages of metal coverage of III–V substrates.[2] However, only recently the direct study of an ultralow coverage chemisorption stage was reported.[1] The experiment was performed by synchrotron-radiation photoemission on Al adatoms on cleaved GaAs. Its results revealed the existence of different Al bonding species below and above 0.1 monolayer coverage. This discovery was in agreement with the prediction[3] that in this range of coverages the Al adatoms start to form clusters which are weakly interacting with the substrates, and therefore are not isolated anymore as in an epitaxial chemisorption model. The formation of clusters can provide a natural source of energy to overcome the activation barriers in a number of crucially important processes,[3] e.g., the Al–Ga exchange reactions and the formation of Fermi-level pinning surface defects.

In general, the above experiments demonstrated the importance of studying ultralow metal coverages to obtain a complete picture of the Schottky barrier formation for III–V semiconductors. Along this line, we recently extended the study of ultralow metal coverages to another interface of fundamental importance, Al on cleaved InP(110). We present here synchrotron-radiation photoemission results on this system, starting at Al coverages as low as 1/40 monolayer. The results show that InP(110)–Al shares many properties with GaAs(110)–Al. For example, our result as well as those of other authors[4] on InP(110)–Al are consistent with the formation of Al clusters at intermediate coverages. Furthermore, they reveal the occurrence at intermediate and high coverages of an exchange reaction which displaces substrate cation atoms, similar to the Al–Ga exchange reaction observed for GaAs(110)–Al.[1,5,6] There is, however, a clear difference in the evolution of the Al adsorption state for the two systems. At intermediate coverages (0.1–1 monolayer) we observe a new bonded Al adsorption state on InP(110), not found on GaAs(110).[1] This is revealed by the fact that the Al $2p$ binding energy passes through a maximum at coverage of 0.1–1 monolayer for InP (110)–Al (indicative of bonding to an electronegative species), while the binding energy as a function of coverage for GaAs(110)–Al decreases monotonically throughout (indicative of the increase in cluster size). This is consistent with the fact that Al–P bonding is far more stable than Al–As bonding.[3] The existence of this new bonded state does not seem to influence the fundamental features of the Schottky barrier formation process, which appears primarily related to the formation of Al clusters.

The experimental procedure followed for InP(110)–Al was similar to that described in Ref. 1 for GaAs(110)–Al. The InP crystals were n-type, Sn-doped, with $n = 1\times10^{18}$ cm^{-3}. A crucial factor in the ultralow coverage experiments was the quality of the cleaved surface, which was required to be free of Fermi-level pinning by cleavage-induced defect states. The signal to noise necessary to detect the Al $2p$ peak at ultralow coverages was achieved with signal averaging over 30–60 min. This required extreme care in avoiding contamination, e.g., by keeping the pressure as much as possible in the low 10^{-11} Torr range and limiting the rise to less than 2.5×10^{-10} Torr during the Al depositions. The results presented here are representative of several different runs on high quality cleaved substrates.

The evolution of the Al–adatom state on InP(110) is illustrated by the Al $2p$ spectra of Fig. 1. The final, strong Al $2p$ peak observed at high coverages corresponds to the formation of a metallic–Al overlayer (the horizontal scale in Fig. 1 is referred to this peak). At ultralow coverages (1/20 monolayer or less) the binding energy of the peak is larger by ~1 eV than for metallic Al. This binding energy is similar to that

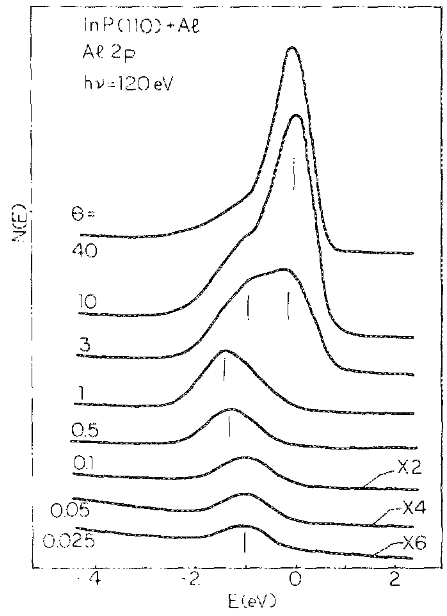

FIG. 1. Evolution of the Al 2*p* core-level peak for increasing Al coverage of a cleaved InP(110) surface. The photon energy, 120 eV, was selected to minimize the photoelectron escape depth, therefore enhancing surface sensitivity. The corresponding equivalent overlayer thickness θ is shown at the left-hand side of each spectrum. The spectra were shifted in energy to account for the band-bending-change effects, so that the observed shifts are over and above the band bending. The horizontal scale is referred to the clean-surface position of the Al 2*p* peak.

observed for ultralow coverage Al on GaAs(110).[1] We see from Fig. 1 that at coverages of 0.1–1 monolayer the Al 2*p* binding energy *increases* by 0.35–0.4 eV. This is in sharp contrast with the 0.3–0.5 eV *decrease* in the binding energy of Al 2*p* on GaAs(110), observed in this range of coverages.[1] Notice that the 1 monolayer peak of Fig. 1 is very asymmetric, and appears to contain an unresolved second component at lower binding energies. Above 1 monolayer coverage the evolution of Al 2*p* on InP(110) becomes again similar to that on GaAs(110).[1,5,6] At 3-monolayer coverage we start seeing the metallic–Al peak, together with another feature corresponding to the low binding energy component of the 1-monolayer peak.

We conclude that the evolution of the Al 2*p* peak on InP(110) is similar to that on GaAs(110) both below 0.1 monolayer coverage and above 1 monolayer coverage, but different for the intermediate range between 0.1 and 1 monolayer. Therefore, the interpretation of the results is similar for the two systems except at intermediate coverages. The ultralow coverage Al 2*p* peak can be attributed for both systems to isolated Al adatoms or small Al clusters.[1,3] For GaAs(110)–Al, the subsequent decrease in binding energy is explained by the formation of weakly interacting Al clusters whose size increases with coverage.[1,3] At high coverages, Al 2*p* on GaAs(110) further shifts towards lower binding energies, and it reaches eventually its metal–Al position. This further decrease in binding energy is explained[3] by the evolution from Al clusters to a thick, metallic Al overlayer. A similar evolution occurs in InP(110)–Al. In fact, the formation of Al clusters in this system is supported by recent results of McKinley *et al.*[4] Furthemore, it is the most reasonable explanation for the high binding energy Al 2*p* component observed in Fig. 1 for coverages of 3 monolayer or more, and for the corresponding, unresolved low binding energy component of the 1 monolayer spectrum.

The above analysis explains the evolution with coverage of Al 2*p* on InP(110), except for the high binding energy peak observed at intermediate coverages (0.1–1 monolayer). This peak reveals a new bonded Al adsorption state peculiar to the InP(110) substrate. From our results, however, this new state does *not* appear to have much influence on the Schottky-barrier formation process. In fact, the establishment of the Schottky barrier appears very similar for InP(110)–Al and for GaAs(110)–Al. For the latter system Zunger[3] proposed that the formation of Al clusters weakly interacting with the substrate releases enough energy to activate the formation of Fermi-level pinning defects as suggested by Spicer and co-workers.[7,8] This picture is consistent with the results of Ref. 1—the shift of E_F saturates, giving the Schottky barrier height, *at about the same coverage for which clusters start to be formed.* The corresponding results for Al on InP(110) are shown in Fig. 2. The final distance between E_F and the bottom of the conduction band E_c corresponds to the Schottky barrier height. From our experiments we obtain a value of 0.3–0.4 eV, in agreement with Refs. 7 and 9. We see from Fig. 2 that most of the Fermi-level shift occurs at ultralow coverages, and it appears to saturate at coverages of 0.1–0.2 monolayer. This is the same coverage at which Al clusters start forming on GaAs(110).[1,3] Therefore, a relation between the formation of weakly interacting clusters and the Fermi-level pinning appears to exist both for InP(110)–Al and for GaAs(110)–Al.

Another similarity between GaAs(110)–Al and InP(110)–Al is the occurrence of an Al– substrate cation exchange reaction starting at coverages of a few tenths of a monolayer.[5,6] The free In produced by this reaction is clearly revealed by the low binding energy component of the In 4*d* peaks of Fig. 3. The exchange reaction is even more energetically favorable for InP(110)–Al than for GaAs(110)–Al. In fact, the cohesive energy[10] of the bulk Al–P bond (2.13 eV) is

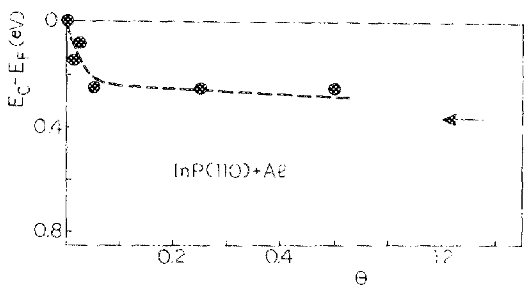

FIG. 2. Shift of the Fermi level at the interface between InP(110) and Al during the early stage of Al coverage. The shift of the Fermi level with respect to the conduction band edge was deduced from the shifts of the In 4*d* and P 2*p* peaks in spectra taken with a constant E_F. The horizontal arrow marks the final position of E_F at large coverages, corresponding to the Schottky-barrier height.

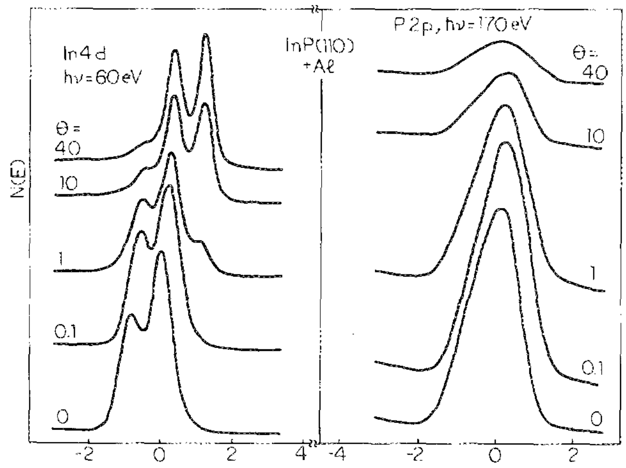

FIG. 3. Evolution of the In 4*d* and P 2*p* peaks for increasing Al coverage of InP(110). The horizontal scales are referred to the high coverage positions of the In $4d_{5/2}$ peak and of the P 2*p* peak. The spectra were *not* corrected for band-bending-change effects, and the low coverage shifts reflect the shifts in the gap of the Fermi level as shown in Fig. 2. The appearance of a free-In, low binding energy component given by the exchange reaction is very clear in the In 4*d* spectra above 0.1 monolayer coverage.

0.39 eV bigger than that of the bulk In–P bond, while the cohesive energy of the bulk Al–As bond (1.89 eV) is only 0.26 eV bigger than that of the Ga–As bond. The corresponding difference in heat of formation[10] is 21.3 ± 0.27 kcal/mole between InP and AlP, and only 9.8 ± 1.8 eV between GaAs and AlAs. Annealing experiments on GaAs(110)–Al by Kahn *et al.*[11,12] emphasized that, although energetically favorable, the exchange reaction can only start after enough energy is provided to overcome its activation barrier. Once again, the formation of Al cluster is a natural source for this energy, and the correlation between the starting coverages for island formation and for the exchange reaction in GaAs(110)–Al supports this hypothesis.[1] A similar correlation exists between the coverages at which the Fermi-level shift saturates and the exchange reaction starts for InP(110)–Al.

In summary, synchrotron radiation photoemission experiments at ultralow coverages of Al on InP and GaAs have revealed a number of novel features of these adsorption processes, some of which are extremely important in the Schottky-barrier formation. From these results, from results obtained at higher coverages, and from the experiments of other authors[4] we conclude that the following features are common to both systems. First, the adsorption process is not layer by layer, nor is it epitaxial even below 1/2 monolayer, but it involves the formation of Al clusters starting at coverages of 0.1–0.2 monolayer. Second, the state of Al at ultralow coverage appears similar for both systems, since the corresponding Al 2*p* levels are close in energy. Third, the formation of clusters appears related to the pinning of the Fermi level and therefore to the Schottky-barrier formation. This is consistent with the hypothesis[3] that the formation of clusters releases the energy necessary for the creation of E_F pinning localized states. Fourth, the cluster-formation stage is accompanied by an exchange reaction which frees surface-cation atoms. In fact, the free-cation atoms are clearly revealed by the corresponding core-level spectra, and a recent morphology study by angle-resolved photoemission[13] more specifically demonstrated that the Al clusters on GaAs(110) contain free Ga atoms. The formation of clusters is a possible source of energy to overcome the activation barrier for the exchange reaction.[1] Fifth, the Al clusters evolve at large coverages becoming a metallic–Al overlayer.

We have seen that the most important difference between GaAs(110)–Al and InP(110)–Al is the presence of a new bonded state for Al adatoms on InP(110) at coverages of 0.1–0.5 monolayer—while the Al adatoms on GaAs(110) simply evolve from their rather weakly bound ultralow coverage state to the formation of clusters. A possible explanation of this difference is the already mentioned large cohesive energy of the Al–P bond,[10] which makes energetically favorable the formation of some substrate–adatom bonds. We emphasize that the experimental results are not sufficient to identify the nature of this new bonded state, although the authors of Ref. 4 seem to favor the twofold adsorption site bridging As and Ga as proposed by Ihm and Joannopoulos for GaAs(110)–Al.[14]

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