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The adsorption of Bi and Sb on clean cleaved InP(110) surfaces has been studied with soft x-ray photoemission spectroscopy at the BESSY synchrotron radiation source in Berlin. Bi and Sb were deposited onto ultrahigh vacuum cleaved InP(110) surfaces at substrate temperatures of 300 K [room temperature (RT)] and 120 K [low temperature (LT)]. In this paper we focus on the evolution of the overlayer emission intensities as a function of coverage. Spectra of the Bi 5*d* and Sb 4*d* core level emission lines were taken from the submonolayer regime up to coverages of approximately 60 and 20 monolayers (ML) of Bi and Sb, respectively. The spectra were then deconvoluted using a core level fitting routine. In all cases, good agreement between the experimental and fitted curves was achieved by introducing two chemically shifted components of the Bi 5*d* and Sb 4*d* core level emission which are interpreted in terms of Bi(Sb)–substrate and Bi(Sb)–Bi(Sb) bonds. However, for RT deposition, the evolution of the Bi 5*d* and Sb 4*d* spectra is significantly different in the coverage range below 2 ML. In the Bi case the adatom–substrate component grows first, and only after about 0.5 ML is the Bi–Bi component observed. The two components have equal intensity at about 2 ML. In contrast, the two components in the Sb 4*d* spectra grow with equal intensity until 1 ML. The spectra for higher coverages for both systems are dominated by the component assigned to adatom–adatom bonds and the overlayer is found to be semimetallic. The LT spectra do not have the easily resolvable features seen in the RT spectra which may indicate that the growth is much more disordered. However, the overlayers at LT are more laminar. In addition, we present the band bending versus coverage behavior for the Bi/*p*-InP(110) interface, which is compared to that of Sb/*p*-InP(110).

I. INTRODUCTION

The adsorption of bismuth on GaAs[1–4] has attracted interest recently. This interest stemmed from many previous studies[5–12] of the formation of interfaces between antimony and III–V semiconductors. Antimony was thought to be unique among the metals in that the first overlayer grows in an ordered way on GaAs(110). However, photoemission data and low-energy electron diffraction (LEED) results[1,3] show that the same is the case for 1 ML of bismuth on GaAs(110). The Bi/III–V interfaces thus are likely to be another group of model systems which may allow the geometric structure to be correlated with the electronic properties of the interface.

In this paper we present synchrotron radiation excited soft x-ray photoemission spectroscopy (SXPS) results from Sb and Bi overlayers on InP(110). The overlayer spectra (Sb 4*d* and Bi 5*d*) carry information about the chemistry of the interface. However, it is well known that the Sb/InP(110) interface is unreactive[10,11] and we have recently shown that the same is true for Bi/InP(110).[13] Fortunately, the development of the overlayer spectra also carries information about the growth of the Sb or Bi on the semiconductor surface which has fundamental implications for the electronic structure of the interface and the height of the Schottky barrier in particular. As a method of varying the growth mode we have studied the formation of both of these interfaces as a function of temperature. We show for both interfaces that at room temperature (RT), a first layer is quickly formed and that subsequent deposition leads to strong clustering of the Sb or Bi. The growth mode is therefore close to being Stransky–Krastanov. In contrast, at [low temperature (LT), 120 K] our results indicate that the growth mode, again for both Sb and Bi on InP(110), is more laminar but very disordered. We have also measured the band bending formation of the Bi/*p*-InP(110) as a function of temperature and have noticed surface photovoltage effects (SPV). When corrected for SPV the band bending is

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dramatically dependent on the formation temperature and, therefore, on the growth mode of the interface. We also discuss the differences between the two interfaces and consider the implications for the Schottky barriers (SB) formed.

II. EXPERIMENTAL DETAILS

The SXPS experiments were performed at the TGM 2 beamline of the electron storage ring in Berlin (BESSY). The overlayer (Sb 4*d* and Bi 5*d*) core level emission spectra were taken at normal emission using a Vacuum Generators ADES 400 angle resolving spectrometer. The analyzer had an angular acceptance of approximately 4°. The combined resolution (light and electrons) was 0.2 eV at the photon energies used, 55 and 45 eV. The resolution was measured from the Fermi edge of a clean gold foil in electrical contact with the sample which was also used as a reference for the Fermi level.

Clean InP(110) surfaces were prepared by cleaving aligned prenotched crystals supplied by MCP Ltd. [*p*-type (Zn) 1.6×10^{18} cm^{-3}] at pressures better than 1×10^{-10} mbar. Antimony was evaporated from a Knudsen-cell-like oven, while a commercial Knudsen cell (W.A. Technology Ltd.) was used for the bismuth evaporation. The pressure during evaporation was kept below 2×10^{-10} mbar. The sources were located at a distance of 30 cm from the sample surface to minimize radiative heating effects. The evaporation rates were measured using quartz crystal balances mounted close to the sources and these were calibrated for a large thickness against a similar balance mounted at the sample position. A nominal thickness scale in monolayers (ML) which assumes layer-by-layer growth and unity sticking coefficient both on samples and balances was established (Sb: 1 ML = 2.52 Å; Bi: 1 ML = 2.91 Å). For both sources, stable evaporation rates between 0.02–0.2 ML min^{-1} were achieved.

III. RESULTS AND DISCUSSION

In Figs. 1–4 we present the overlayer core levels (Sb 4*d* and Bi 5*d*) for Sb/InP(110) and Bi/InP(110). After normalization to the photon flux, all spectra have been analyzed with a core level fitting program which can deconvolute the spectra into as many as four spin–orbit split doublets. However, all the spectra presented here could be fitted reasonably with two or (for the highest coverages) one doublet(s). Each doublet is allowed to have an independent value for such parameters as the Doniach–Sunjic (DS) asymmetry and the Gaussian broadening.

A. Sb room temperature deposition

The Sb 4*d* spectra taken at RT in Fig. 1 show clearly the symmetric growth of two features in the submonolayer spectra. At coverages <0.5 ML the two components of the fit have a relatively large Gaussian broadening (~ 0.5 eV). This reflects the inability to resolve the two features which are clearly seen at larger coverages. This broadening is caused by a range of binding energies which is in turn indicative of a range of adsorption sites for the Sb adatoms.

At coverages >0.5 ML the situation is quite different. The two clearly defined peaks shifted by 480 meV indicate two different adsorption sites for the Sb. We suggest that the high binding energy (BE) one is due to Sb bound to the substrate and the lower BE one due to Sb bound only to other Sb adatoms. The reasons for this argument were already discussed elsewhere.[10,12] There it was pointed out that Sb–In bonds are more likely to be formed than Sb–P ones because the latter are not found in nature. The assumption of preferential bonding of the Sb adatoms to In substrate atoms may also help to explain the unexpected Schottky barrier heights observed for Sb on InP[14] at large coverages, i.e., <0.3 and >1.1 eV for *n*- and *p*-type InP, respectively. It should also be mentioned that the preferential bonding to the In atoms does not necessarily contradict a zig–zag chain arrangement of the Sb atoms in the first monolayer. An alternative zig–zag chain model which only consists of Sb–Ga and Sb–Sb bonds was first proposed for 1 ML of Sb on GaAs(110) by Skeath *et al.*[6] Since it was not favored by the experimental evidence and calculations, it was ruled out. However, more recent self-consistent calculations have shown that such a model is, in fact, possible for many Sb/III–V systems[15] and that such a

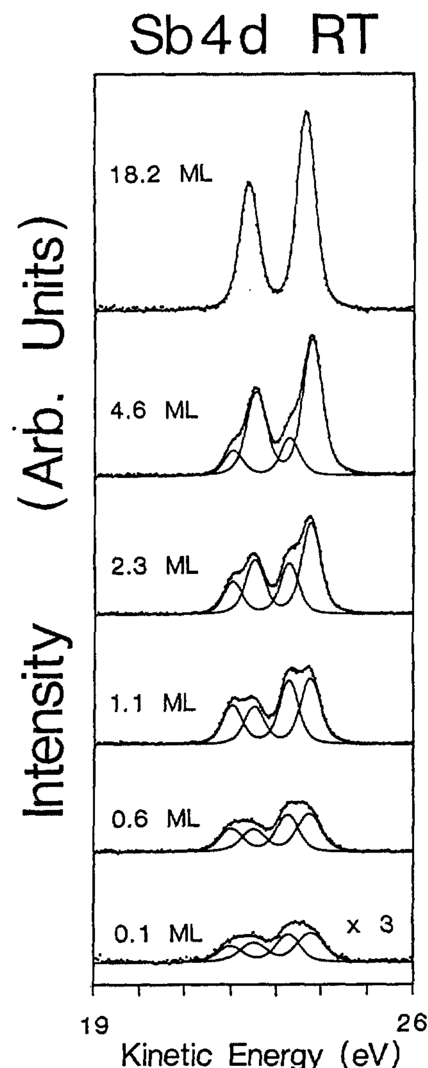

FIG. 1. Sb 4*d* core level emission spectra for various Sb coverages deposited onto InP(110) at RT. Photon energy = 55 eV.

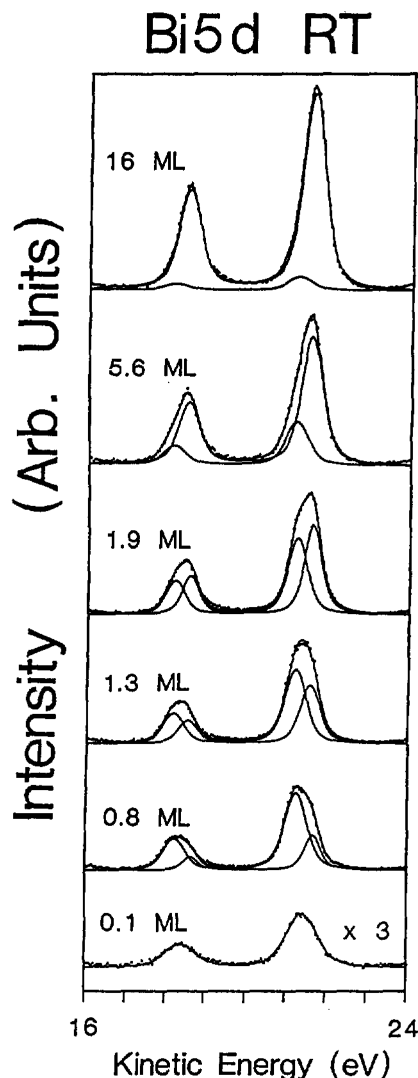

FIG. 2. Bi 5*d* core level emission spectra for various Bi coverages deposited onto InP(110) at RT. Photon energy = 45 eV.

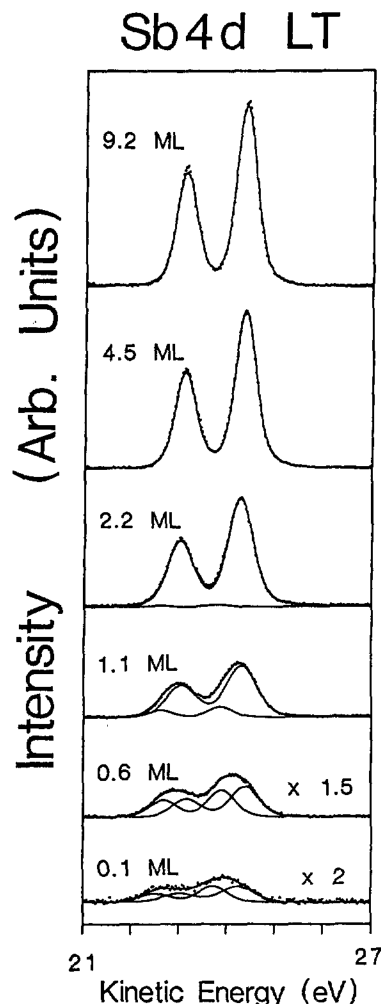

FIG. 3. Sb 4*d* core level emission spectra for various Sb coverages deposited onto InP(110) at LT. Photon energy = 55 eV.

model is also consistent with the STM results. In the case of Sb on InP(110), a reevaluation of this model involving detailed calculations would also be useful. So far, the experimental data are not yet conclusive. For instance, the bonding of Sb to P and thus the same zig–zag arrangement as for Sb on GaAs cannot entirely be ruled out. The evolution of the Sb 4*d* emission does appear very similar for Sb adsorbed on GaAs(110)[7] and InP(110). However, in other aspects, the ordered first ML of Sb is quite different on both substrates as shown, for example, in another paper at this conference by Esser *et al.*[16] dealing with the thermal stability of Sb overlayers on GaAs(110) and InP(110).

On deposition of more than 1 ML, the Sb–Sb peak grows and the Sb–substrate peak decreases in intensity as the first layer is covered. This is also shown in Fig.5 where the relative intensity of the high BE peak (Sb–substrate) is plotted as a function of Sb coverage. After the increase up to about 1 ML, the intensity of this Sb–substrate peak decreases exponentially. From the slope of the attenuation, a value for the apparent electron escape depth can be derived. The large value of 7.5 ML indicates strong clustering beyond 1 ML coverage. In the spectra above 6 ML, the Sb–Sb component does not require a significant DS asymmetry ($a < 0.0004$) indicating that the overlayer does not yet become metallic at these coverages. This is consistent with the Raman data[17] revealing that the Sb overlayer at these coverages is amorphous and thus probably semiconducting. A transition to the crystalline, semi-metallic phase occurs between 10 and 20 ML.

B. Bi room temperature deposition

At very low coverages (< 0.1 ML) the development of the Bi 5*d* core levels for Bi/InP(110) in Fig. 2 is very similar to that of the Sb 4*d* described above; the spectra are broad and symmetric indicating that initially the Bi adatoms are in a range of sites. The high coverage spectra (> 5 ML) are also dominated by a component due to Bi bound only to other Bi adatoms. At coverages exceeding 20 ML the presence of a DS asymmetry clearly reveals the semimetallic nature of the Bi. However, the spectra for coverages between 0.5 and 5 ML are significantly different from those for Sb/InP(110). This can already be judged from the raw data.

Below 1 ML, the spectra are asymmetric with the spectral

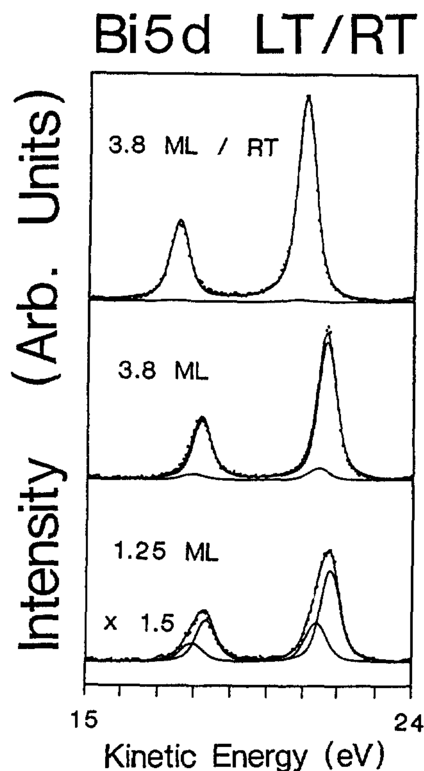

FIG. 4. Selected Bi 5*d* core level spectra for the LT deposition onto InP(110) and the warming up to RT. Photon energy = 45 eV.

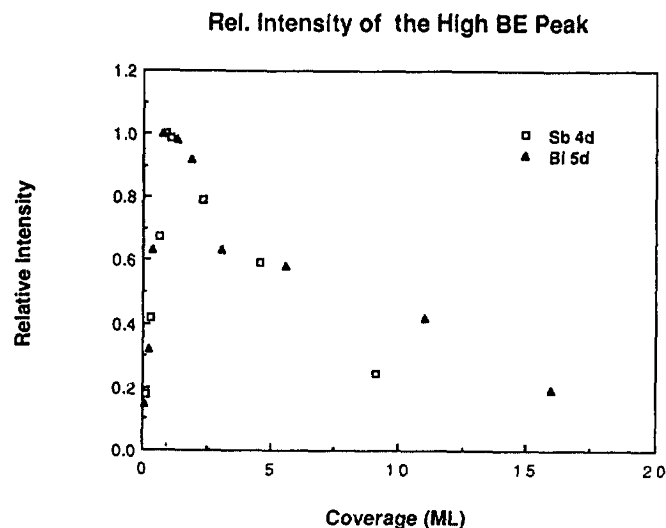

FIG. 5. Relative intensity of the high BE component which is obtained from the curve fitting procedure and assigned to the adatom–substrate bond as a function of coverage. Maximum intensity = 1. Sb: open squares, Bi: full triangles.

weight to the high BE side. As more bismuth is deposited, the spectral weight shifts to the low BE side with the spectra being almost symmetric but broad around 1.5 ML. This situation is in a clear contrast to Bi/GaAs(110)[1,3] and Sb/InP(110) described above. The difference is even more evident in the evolution of the pair of spin–orbit split doublets fitted to the data. In the cases of Bi/GaAs,[1] Sb/GaAs,[7] and Sb/InP, both the low and high BE components are found to grow together until 1 ML. In the Bi/InP spectra presented the high BE component, again assigned to Bi–substrate bonds, is stronger than the low BE one (shifted by 0.4 eV) up to approximately 1.5 ML. The high BE one reaches its maximum intensity around 0.8 ML. At that coverage the amount displayed by the high BE component is equivalent to approximately 0.5 ML, i.e., the amount needed to cover one of the substrate species. Therefore, it seems reasonable to assume that Bi is preferentially bonded to only one of the substrate species. Unlike the Sb/InP system for which one can only speculate about the possibility of preferential bonding, the evolution of the Bi 5*d* emission is a good indication for the preferential bonding. On simple chemical arguments that Bi does not form bonds to P the In atom is a more likely choice for a single adsorption site, as we have suggested for Sb/InP.[10,12]

The relative intensity of the Bi-substrate peak is also plotted in Fig. 5 as a function of Bi coverage. After reaching its maximum, the decrease of the intensity may be divided into two steps. First, a fast decrease until about 2.5 ML followed by a decrease with a lower slope than that of Sb. The former is indicative of a more laminar growth up to 2.5 ML. It was also argued for Bi on GaAs that Bi grows in a layer-by-layer fashion up to about 2.5 ML before the onset of island growth.[1] Thereafter, the degree of clustering is larger than is observed for Sb/InP(110). Here, the apparent escape depth is 11 ML. The same behavior was found in the In 4*d* intensity attenuation curves for Sb and Bi coverage. The stronger ability of clustering for Bi simply reflects a higher mobility on the InP surface at RT.

C. Sb and Bi low temperature deposition

The LT results for Sb are presented in Fig. 3. The core levels at low coverages are broader than those at RT, requiring the relatively high value of the Gaussian broadening (0.5 eV) in the fits. Again, this broadening is explained by a range of binding sites for the Sb adatoms leading to a range of binding energies. At higher coverages the core levels are different from those at RT in that the broadening remains large throughout the coverage range. At coverages > 1 ML the low BE component increases and at higher coverages dominates the spectra. This component is again attributed to Sb bound only to other Sb atoms.

The Bi core levels at low coverages show a similar evolution to the Sb 4*d* levels in Fig. 3 and can be fitted in the same way with two broad peaks representing a range of binding energies. At the somewhat higher coverages, the high BE peak also loses intensity relative to its low BE partner as the Bi–Bi component grows. When the Bi overlayer of 3.8 ML was warmed to RT the fitted high BE component was found to decrease to a negligible intensity.

It must be clearly stated that the LT core levels (both Sb and Bi) are not suitable candidates for the fitting procedure as they do not show distinct features in the same way as the RT ones do. We have also achieved reasonable fits of the low coverage spectra with only one very broad component (0.7 eV) to represent the range of binding energies. With this analysis the asymmetry in the spectra > 1 ML must then be

taken care of by the introduction of a new component to higher BE. A third possibility would be one with only one doublet throughout the coverage range but with a relatively large DS factor at the higher coverages. This proved not to yield reasonable fits in either the Sb or the Bi case.

In both cases the growth of the overlayer at LT is found to be very laminar as judged by the In 4*d* intensity attenuation.[10,13] At LT electron escape depths of 1.5 and 1 ML are evaluated for Sb and Bi, respectively. These values are in good agreement with the empirical data by Seah and Dench.[18]

D. Band bending at the Bi/InP(110) interface

In a previous study[13] it was shown that there are no chemical shifts in the In 4*d* spectra when Bi is deposited and that the interface thus is abrupt. The rigid shifts in the In 4*d* core level spectra can be attributed to the band bending at the interface. Furthermore, the strong clustering of Bi at RT allows the substrate core level emission and thus the band bending to be monitored up to nominal deposition thicknesses of several tens of ML. The position of the interface Fermi level in the band gap is shown in Fig.6. It is apparent from the RT data that the band bending does not reach its final value at 1 ML coverage since a decrease of about 100 meV is found for coverages > 1 ML. The final position of the Fermi level [0.8 eV above valence-band maximum (VBM)] is only approached for coverages beyond the onset of metallicity (> 20 ML). This behavior is in good agreement with the band bending derived from electric field induced Raman scattering (EFIRS).[19] However, the position of the maximum band bending in the low coverage range is slightly shifted and the minimum beyond is more pronounced in the EFIRS data. A possible reason for the latter could be the fact that the photoemission data represent an average over almost the entire sample area, whereas the Raman information is only collected within an area of less than 100 μm in diameter. The variation of band bending below 20 ML is likely to be induced by imperfections in the overlayer (< 1 ML) and partial healing of those (> 1 ML). The Schottky barrier of 0.8 eV at the highest coverages is in good agreement with the EFIRS data as well as electrical measurements of thick Bi contacts to InP(110)[19] (*I–V*: 0.83 eV and *C–V*: 0.85 eV). In addition, the Schottky barrier height for Bi on *n*-type InP was measured to be 0.48 eV by *I–V*.[19] When this is considered with the theoretical pinning level of 0.76 eV calculated by Tersoff,[20] it seems that a metal induced gap state (MIGS) model can explain the *final* pinning position of the Fermi level. This is in contrast to the Sb case for which a modified MIGS model which takes the exact bonding at the interface into account may be more appropriate.

An interesting effect occurs at the LT deposition of Bi. There is emission of photoelectrons above the reference Fermi level as measured from a gold foil in electrical contact with the sample. This was also observed previously by Alonso *et al.*[21] and they explained this phenomenon as being due to a surface photovoltage (SPV) effect. Hence the interface Fermi level position has to be corrected for SPV. As can be seen in Fig. 6, the values after SPV correction give rise to Schottky barriers larger than 1 eV. These surprisingly high barriers are no longer in accordance with the MIGS model. It is also worth mentioning that the same barrier is found after warming up to RT, where the SPV effect is negligible. The reason for this behavior is not clear, but one may again speculate that the detailed nature of the bonding being somewhat different for LT deposition has a large effect on the formation of the Schottky barrier. This is an important result as it implies that the method of interface preparation plays a crucial role in determining the final SB height. The possibility arises that by choosing the formation temperature carefully, the SB at the interface when warmed to RT may be tuned to a desired height. This possibility requires further study.

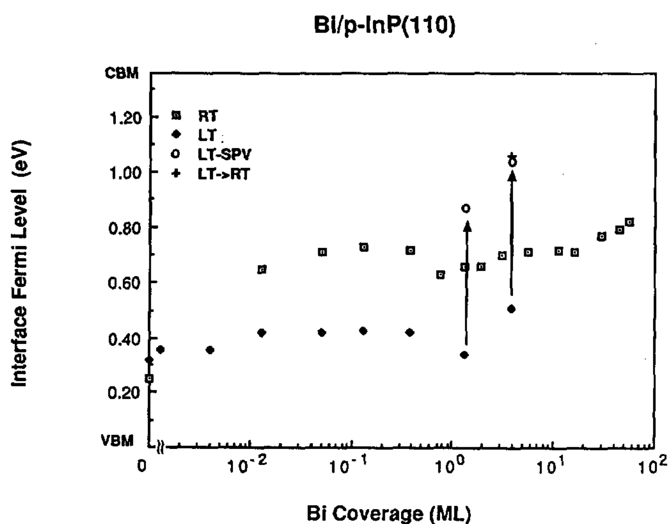

FIG. 6. Position of the interface Fermi level in the band gap as a function of coverage for RT and LT deposition of Bi onto *p*-type InP. Also indicated are the SPV corrections of the LT data and the position at RT after a LT deposition.

IV. SUMMARY

The evolution of the Sb 4*d* and Bi 5*d* core level emission intensities reveals a pronounced difference for the adsorption of Sb and Bi onto clean cleaved InP(110) at RT. Two spin–orbit splitted doublets are sufficient to curve fit the experimental data. The high BE component may be assigned to the adatom–substrate bond and the low BE one to the adatom–adatom bond. While this assignment is not conclusive for the Sb case, the Bi 5*d* spectra can be easily interpreted in this sense. Then the Bi is likely to be bonded preferentially to one substrate species which is presumably In. For Sb, the evolution of the Sb 4*d* emission is very similar to that of Sb on GaAs where the two components obtained from curve fitting were interpreted in terms of Sb–Ga and Sb–As bonds. However, there seems to be enough indirect evidence to question whether the same is the case for Sb on InP. There is a need for a theoretical reevaluation of alternative models for the bonding of the group V elements to InP(110), such as that proposed by Skeath *et al.*[6]

The RT evolution of the band bending at the Bi/*p*-InP interface demonstrates that the final pinning position is not

reached at 1 ML coverage but that as much as 60 ML are needed before the Schottky barrier formation is completed. The RT data are consistent with a MIGS model.

The LT data are characteristic of a more disordered but also more laminar adsorption. In terms of band bending, the LT experiments have revealed that SPV effects occur at the Bi/InP interface and have to be taken into account for the evaluation of the correct band bending. The final coverage SB height even after warming up to RT is found to be different from that formed at RT. The barrier height cannot be explained by a simple MIGS model. The exact nature of the bonding at the interface is likely to have this pronounced effect on the barrier height.

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