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Temperature dependence of the heterojunction band offset: Si on InP(110)

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We present a photoemission study of the initial growth stages of amorphous Si on the InP(110) cleaved surface, performed at 120 K and compared with the room-temperature (RT) results. Deposition at low temperature gives a larger valence-band discontinuity with respect to RT and high-temperature (280 °C) growth. This effect is explained by the smaller outdiffusion of In atoms in the silicon overlayer.

I. INTRODUCTION

We analyzed in detail the early stages of growth of silicon at low temperature (120 K) and at room temperature (RT) on the InP(110) cleaved surface. Photoemisison core-level analysis of low-temperature growth reveals a milder In interdiffusion than for growth at RT or higher temperatures.[1-3] We unexpectedly found a valence-band discontinuity at 120 K, $\Delta E_v = 0.9$ eV, higher than at RT, $\Delta E_v = 0.7$ eV,[2] which is still higher than the 0.46-eV value obtained[3] on similar systems grown at 280 °C. Other quoted values[3,15] for RT ΔE_v are 0.56 and 0.57 eV. These differences indicate that a number of local factors—interface chemistry, microdiffusion, and probably the quality of the substrate—influence the heterojunction band lineup, the charge transfer, and the interface electrostatic dipoles.

In recent years, the study of electronic properties of heterojunctions has greatly expanded due to the important potential applications of such systems to device engineering and, in particular, to optoelectronic devices. However, the phenomena which govern the junction properties are not yet completely understood.

In particular, the theoretical evaluation of band discontinuities is the objective of a large number of models.[4-14] Many experiments have been performed with different techniques to provide the necessary data background to test the models.[13,15] Recently, the possibility of tuning the band discontinuities by means of a thin intralayer deposited at the interface has been investigated both experimentally[16-22] and theoretically.[23,24]

The main difficulties in understanding the laws of heterojunction band discontinuities originate from the physical and chemical processes which can occur during growth and lead to a real interface situation that is different from the ideal abrupt junction. In particular, the substrate temperature can strongly influence the morphology and chemistry of the interface.

II. DESCRIPTION OF EXPERIMENTAL APPROACH

We deposited Si overlayers on cleaved (110) surfaces of p-InP ($p = 1 \times 10^{18}$ cm^{-3}) at 120 K and at RT. Core levels and valence bands were analyzed as functions of the Si layer thickness and by photoemission spectroscopy using synchrotron radiation. The experiment was performed at the Mark V beam line of the Synchrotron Radiation Center storage ring in Stoughton, which is equipped with a Grasshopper monochromator. Emitted electrons were analyzed by means of a cylindrical mirror analyzer and the overall resolution was 0.2–0.3 eV.

We evaporated Si by joule heating. The InP substrate was kept at 120 K using a closed-circuit helium refrigerator. The nominal overlayer thickness was measured with a quartz microbalance. The core-level data were analyzed with computer least-squares fits. Each In 4d core-level peak was decomposed in bulk, surface, and outdiffused components.[25] We used the convolution of a Gaussian and a Lorentzian line shape for each component.

III. DISCUSSION OF THE RESULTS

The figures show valence band, In 4d, and Si 2p core-level spectra as a function of Si thickness. Figure 1 shows the valence-band edges and Fig. 2 the overall evolution of the In 4d peak for Si thickness ranging from 1 to 20 Å. In Fig. 3, we see the best fits of the In 4d core levels shown in Fig. 2.[26]

The In 4d core emission is the convolution of at least three components: surface, bulk, and outdiffused. The In 4d bulk components stay at a constant kinetic energy during the entire growth process (see Figs. 2 and 3) indicating the absence of any band bending changes. This means that the energy separation of the valence-band edges of Fig. 1 that correspond to 0- and 20-Å coverages coincide with ΔE_v.

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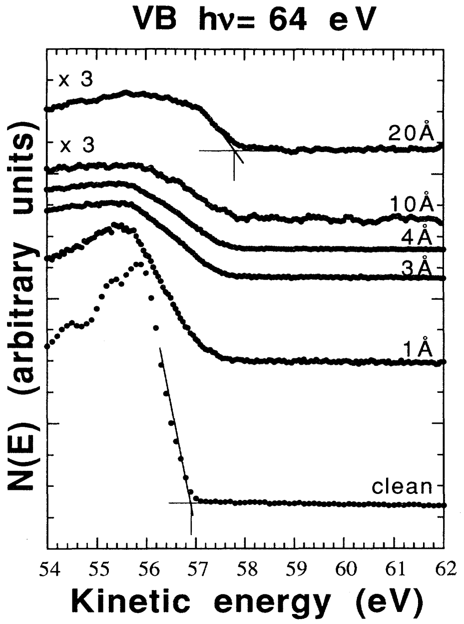

FIG. 1. Valence band of the Si/InP(110) junction for different Si coverages. The evolution of the valence-band edge reveals the creation of a valence-band discontinuity of 0.9 eV. Deposition temperature was $T=120$ K.

We estimate, therefore, a band offset of $\Delta E_v = 0.9$ eV for low-temperature deposition. The values obtained at RT and 280 °C are $\Delta E_v = 0.7$ eV (Ref. 2) and $\Delta E_v = 0.46$ eV (Ref. 3). The RT value $\Delta E_v = 0.5$ eV of Ref. 3 is also very different from the low-temperature value. This is the experimental evidence that the growth temperature changes the band discontinuity of the Si/InP system. Note that no change in ΔE_v was observed by annealing, after deposition, the Ge/ZnSe(110) heterojunction.[27]

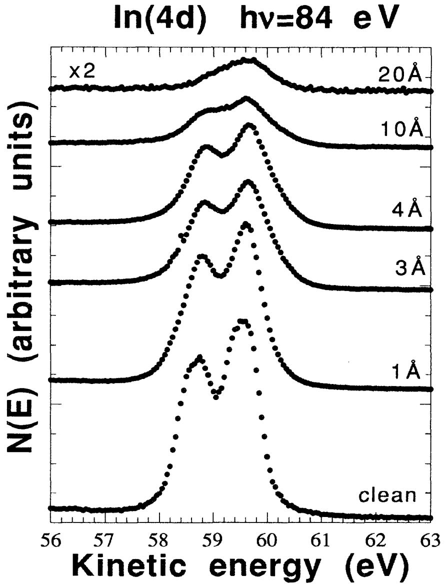

FIG. 2. Evolution of the In 4*d* core levels as a function of the Si overlayer thickness. Deposition temperature was $T=120$ K.

In Fig. 2, the peaks normalized to the incoming photon flux show a decreasing intensity as a function of Si coverage. Silicon grows as an amorphous phase on the InP bulk, as observed by low-energy electron-diffraction analysis, and is *p*-like due to defects at the interface.[28] The spectra of Fig. 3 have been normalized to a constant height to better emphasize line-shape and intensity changes. We do not report the best fits of the two spectra

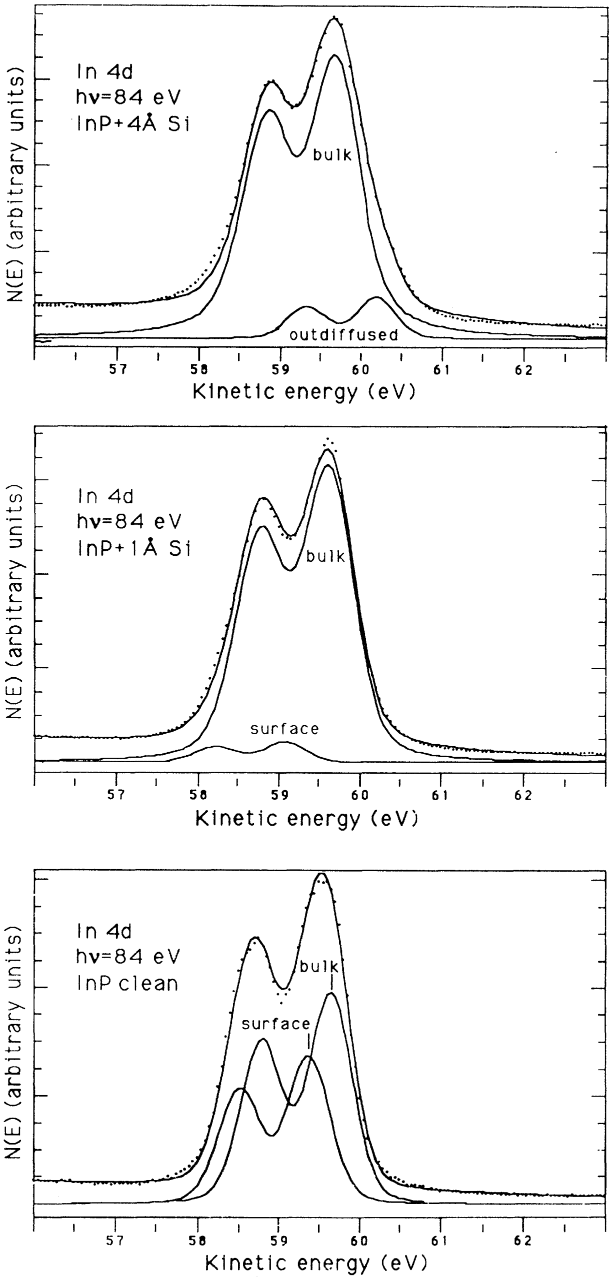

FIG. 3. Deconvolution of the In 4*d* core-level peaks for the clean InP(110) surface (bottom), and for coverages of 1 Å (center) and 4 Å of Si (top). The experimental data correspond to the three spectra of Fig. 2.

of Fig. 2 above 4 Å of Si deposition since they are similar to the last one.

The cleaved InP spectrum is well explained by the superposition of two spin-orbit doublets, one from the surface atoms and the other from the bulk, in agreement with theoretical predictions as well as with previous experiments.[29] The surface peak is at higher binding energy (about 0.3 eV) than the bulk peak. The spectrum corresponding to the deposition of 1 Å of Si is again explained by two rather than three components, with a reduced intensity for the surface contribution. An attempt to fit the 1-Å–Si spectrum with three doublets was not successful.

When the Si thickness reaches 4 Å, the situation appears quite different. The surface peak is no longer present, but there are still two components. One is the bulk component with high intensity at the same binding energy of the previous spectrum. The smaller component is due to In atoms outdiffused into the silicon overlayer. The spectra taken at coverages higher than 4 Å show a similar outdiffused component confirming that the In outdiffused atoms remain on top of the overlayer. The intensity ratio of these two components shows that the In diffusion in the overlayer is very low at this temperature, and the bulk component remains the dominant feature.

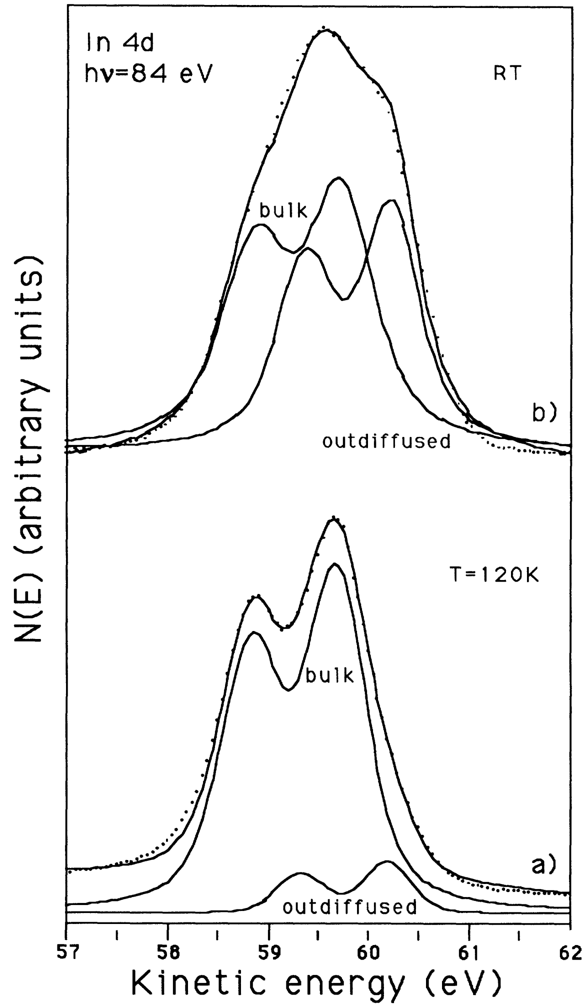

FIG. 4. Comparison between the deconvolution of the In 4*d* core level of the 4-Å Si/InP system at 120 K (a), and of the 10-Å Si/InP system at room temperature (b).

In Fig. 4, we compare the deconvolution fits of In 4*d* after the deposition of 10-Å Si on the InP bulk at 120 K [Fig. 4(a)], and at RT [Fig. 4(b)]. In the RT case, the outdiffused component is nearly of the same intensity as the bulk one. The intensity ratio between the bulk and the outdiffused peaks in Figs. 4(a) and 4(b) changes from 6.4 at 120 K to 1.1 at RT.

It is indeed clear from Fig. 5 that some In-Si interaction occurs at the interface. The Si 2*p* core levels become sharper as the overlayer thickness increases. The presence of an increasing overlayer component explains the shift of the Si 2*p* level.

The P 2*p* core levels (not reported in the figures) do not show any reacted component nor appreciable broadening, and present an attenuation rate consistent with a layer-by-layer growth of the silicon overlayer. Our results are consistent with those obtained for the Ge/InP(110) interface.[1]

We conclude that the outdiffusion of In atoms is stronger for interfaces prepared at RT or higher temperature than at low temperature. The higher the temperature, the richer in phosphorus is the interface.

When the In atoms segregate to the overlayer surface, the real interface is better schematized by a Si/InP interface with a phosphorus intralayer. This temperature-induced intralayer strongly modifies the charge transfer at the interface with respect to the ideal abrupt case. We explain the valence-band discontinuity variation as being due to the additional electrostatic dipole induced by the phosphorus atoms left at the interface when indium is re-

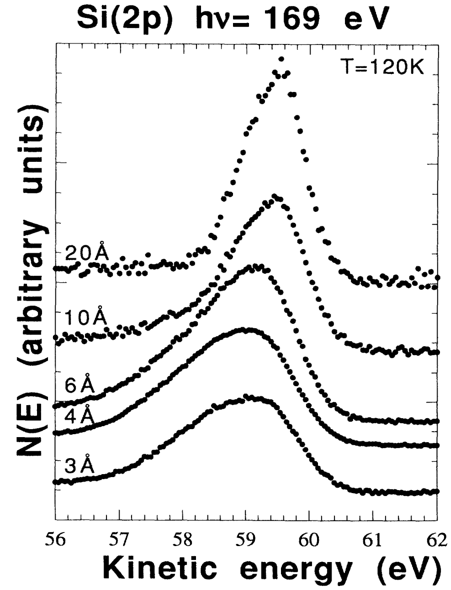

FIG. 5. Si 2*p* core levels taken for increasing thicknesses of the Si overlayer. Note that on going from the lowest coverage to the highest, the peak becomes sharper.

moved. The P-induced dipole was evaluated following a simple calculation model proposed in Ref. 16.

The model, based on simple electronegativity arguments, schematizes the heterojunction as a sequence of planes of spheres representing the InP, Si, and P species. The abrupt InP-Si system represents the low-temperature interface, and the InP-P-Si the RT interface. The phosphorus intralayer could be a fraction of a monolayer or more than one monolayer, depending on the temperature.

The P-induced dipole contribution is evaluated by comparing the charge transfer at the interface with and without the phosphorus intralayer. In the electronegativity approach,[30,31] the charge transfer between two different species, which react to form a stable compound, occurs until the two species reach a common electronegativity value. The charge transfer is evaluated with the expression (see Ref. 16)

$$\rho=(S_A-S_B)/\Delta S_A ,$$

where we use the Sanderson electronegativity values $S_{A,B}$, and $\Delta S_A=2.08S_A^{1/2}$ is a normalization factor (see Table I for the $S_{A,B}$ and ΔS_A values relative to this work and Refs. 30 and 31 for a complete tabulation).

For the abrupt case, the spheres located in the planes at the interface have a surface density of $\sigma_{\mathrm{InP}}=7.3\times10^{18}$ spheres/m^2 for InP and $\sigma_{\mathrm{Si}}=1.36\times10^{19}$ spheres/m^2 for amorphous silicon.[32] The two planes at the interface are separated by a distance equal to the sum of the two covalent radii $d=3.2$ Å. The resulting total dipole voltage drop in the abrupt InP-Si junction is 0.25 eV.

To evaluate the P-induced dipole contribution we hypothesize two possible interface configurations.

(i) The phosphorus atoms remaining at the interface rearrange to saturate the Si dangling bonds due to the different surface densities of the InP and Si planes. We will consider the extreme case of complete saturation of Si dangling bonds. The density of Si dangling bonds is of the order of $\sigma_{\mathrm{db}}=6.25\times10^{18}$ m^{-2}. The electronic charge transfer occurs from Si atoms to P atoms and the additional dipole, which decreases the value of ΔE_v, is 0.17 eV.

(ii) The second configuration is based on the hypothesis that when In atoms leave the interface, the final configuration is InP-P-Si (one plane of InP spheres, one of P, and one of Si). The P plane replaces the InP plane at the interface. Following the Sanderson criterion the junction can be further schematized as a series of planes with the (InP-P) average electronegativity followed by planes of Si spheres. We consider this system as an abrupt junction where the average electronegativity value of the first side of the interface (InP-P) is 3.27 [using Eq. (1) of Ref. 16].

TABLE I. Parameters for the electronegativity model (from Refs. 22 and 23). S is the Sanderson electronegativity and ΔS is the normalization factor corresponding to the electronegativity variation due to a unit electronic charge transfer.

Species	S	ΔS
P	3.43	3.85
In	2.84	3.51
Si	2.84	3.51
InP	3.12	3.67

In this case, the charge-transfer difference between the abrupt InP-Si and InP-P-Si produces an additional dipole, that again decreases ΔE_v. The (InP-P) system has higher electronegativity than InP and the calculated voltage drop at the (InP-P)-Si is 0.38 eV with a difference of 0.13 eV compared to the abrupt InP-Si case.

Both of the adopted configurations result, therefore, in an additional electrostatic dipole that decreases ΔE_v in agreement with the experimental findings. This model gives surprisingly good results but has of course severe limitations and is not intended to describe in detail the interface structure. The main limitations arise from the hypothesized temperature-induced dynamical process rearranging the interface, and from neglecting other interface dipole terms such as those caused by defects or microdiffusion processes. The model demonstrates, nevertheless, that at least one kind of possible interface dipole change produces effects of the same magnitude and sign as those experimentally observed.

IV. CONCLUSIONS

We analyzed the outdiffused In atoms during the formation of the Si/InP(110) interface at 120 K and RT, and their effects on the band lineup. We deduced from the fitting of the In 4*d* core levels that the outdiffusion of the indium atoms is reduced at low temperature. The band offset increases from 0.7 to 0.9 eV on going from RT to 120 K. This is explained by simple electronegativity arguments: when the In atoms outdiffuse to the overlayer surface, P atoms left at the interface induce an additional electrostatic dipole decreasing ΔE_v.

ACKNOWLEDGMENTS

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[32] These values can be simply evaluated by

$$N_{A,B}=\rho_{A,B}N_{\mathrm{Av}}/MW_{A,B}$$

and

$$\sigma_{A,B}=(N_{A,B})^{2/3}\ ,$$

where $N_{A,B}$ is the number of spheres of the two species in a cubic meter, $\rho_{A,B}$ is the density in g/m^3, N_{Av} is the Avogadro number, $MW_{A,B}$ is the molecular weight, and $\sigma_{A,B}$ is the surface density.