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Experimental study of the GaP-Si interface

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The interface formation between cleaved GaP(110) substrates and Si overlayers was studied with synchrotron-radiation photoemission techniques. The experimental information included measurements of the valence- and conduction-band discontinuities and of the substrate band bending. In particular, we searched for possible overlayer-ordering effects on the discontinuities in annealed interfaces. No annealing-induced discontinuity changes were found within the experimental uncertainty of 0.1 eV. On the contrary, the substrate band bending was drastically changed by the annealing process.

I. INTRODUCTION

The advent of surface-sensitive experimental techniques has enhanced, in recent years, the fundamental and practical interest in heterojunction interfaces.[1] Research performed at Xerox,[2–5] Frascati,[6,7] Berkeley,[8,9] Rockwell International,[10–14] Duisburg,[5,15,16] and in Wisconsin[6,7,17–19] clearly demonstrated, for example, that photoemission methods can be used to provide *local* measurements of the valence-band discontinuity ΔE_v. This is an interface parameter of crucial importance in determining the physical properties of heterojunction devices.[20] Extensive photoemission measurements of ΔE_v performed in recent years[2–19] provided for the first time a solid basis of data to test discontinuity theories.[21–24] The result of these tests was that no current theory is able to predict the discontinuities with an accuracy acceptable for device research (<0.05 eV). Likewise, surface-sensitive experiments on the band bending[16,19] provided the data basis for the theoretical treatment of the interface Fermi-level pinning.[25] Once again, the theoretical accuracy is far from being acceptable in predicting the pinning position—which is linked to the heterojunction built-in potential, another crucial parameter in heterojunction physics.[20]

There is at present a clear need for more sophisticated theoretical descriptions of the heterojunction interface properties.[26,27] These descriptions must include local effects influencing the heterojunction parameters, which are ignored by most current theories.[21–24] Unfortunately, there are many local factors which *a priori* could be important—interface ordering, substrate orientation, local roughness, microscopic diffusion, different kinds of defects, etc. A theoretical treatment of all these effects would be prohibitively complicated and expensive. Therefore, it is necessary to perform experiments which sort out the most important among the above local factors.

Even from an experimental point of view, however, an indiscriminate study of all local effects cannot be performed for a large number of interfaces. Systematic photoemission measurements of ΔE_v for amorphous Si and Ge overlayers on group IV, III-V, and II-VI semiconductors required almost three years of experiments.[18,19] Clearly, more detailed studies must be concentrated to a small number of particularly important interfaces. These are determined by the good lattice and/or chemical matching of the component semiconductors, and by their potential applications in heterojunction technology. Examples are GaAs-Ge, ZnSe-Ge, GaAs-$\mathrm{Ga_{1-x}Al_xAs}$, CdS-InP, and GaP-Si.

While many studies have been dedicated to the GaAs-Ge system, very few experiments have dealt with the other interfaces in the above list. Our present study is dedicated to the GaP-Si system. The heterojunction GaP-Si is important because of its small lattice mismatch and potential use, e.g., in integrated optics or in heterojunction transistors.[28–33] Preliminary experiments[34] were successful in increasing the reliability of the photoemission-band—discontinuity measurements by reducing the uncertainty in estimating band-bending changes during the interface formation. This was achieved by estimating independently both ΔE_v and the conduction-band discontinuity ΔE_c with different photoemission techniques. We present here the results of an extensive study of the establishment of the GaP-Si interface parameters during the interface-formation process. In particular, we investigated the effects of the interface ordering, one of the possible local factors in determining the heterojunction parameter.[11,35] This goal was achieved by studying as-grown and annealed interfaces both with photoemission and with low-energy electron diffraction (LEED). The results clearly demonstrated that ordering effects do not change the band discontinuities, within the experimental uncertainty of 0.1 eV, but they do influence the Fermi-level pinning and therefore the built-in potential. This explains, in particular, why discontinuity models not including microscopic interface effects[22,23] have been reasonably successful in estimating ΔE_v. The accuracy given by these calculations[22,23] is certainly not satisfactory for practical applications. However, it is good enough to conclude that those simple theoretical models give a good first-order understanding of the nature of the heterojunction discontinuities.

In Sec. II we describe our experimental procedure. In Sec. III we discuss the experimental spectra and their relevance to the band discontinuities and to the interface Fermi-level pinning. The main conclusions will be summarized in Sec. IV.

II. EXPERIMENTAL PROCEDURE

These experiments were performed both at the synchrotron-radiation facility of the Frascati National Laboratory, Frascati, Italy, and at the University of Wisconsin Synchrotron Radiation Center, Stoughton. Photoemission experiments were performed with monochromatized radiation emitted by the storage rings ADONE (Italy) and Tantalus (Wisconsin), at photon energies in the range 10—100 eV. Clean GaP substrates with (110) orientation were obtained by *in situ* cleaving *n*-type ($n=2.3\times10^{17}$ cm^{-3}) single crystals. Angle-integrated photoemission spectra were taken on the clean substrate and then on the same substrate covered by a Si film of increasing thickness. The Si source was a home-made, miniaturized electron-bombardment source mounted on a 2.75-in. Conflat flange. The tip of a Si single crystal was bombarded by electrons emitted by a loop W filament and accelerated to 3500 eV. A W-foil sheet focused the electrons on the target and at the same time shielded the substrate from the source filament. The typical deposition rate was a few tenths of an angstrom per minute. The equivalent overlayer thickness was measured by a water-cooled quartz microbalance.

The annealing studies were performed by electron bombarding the back of the substrate. The substrate temperature was measured with a Chromel-Alumel thermocouple touching the substrate surface. The annealing temperatures and times were in the ranges 200—450 °C and 0.5—20 min. The effects of the annealing were routinely tested by observing the LEED signal of the interface. The experiments were performed under ultrahigh-vacuum conditions, at pressures in the 10^{-11}-Torr range (rising to no more than 8×10^{-10} Torr during Si deposition and annealing). The cleanliness of the interface was probed with the photoemission spectra themselves, and the interaction time with the LEED electron beam was minimized. The photoemission spectra were taken with double-pass cylindrical mirror analyzers under computer control. The overall energy resolution determined by the photon monochromators and by the analyzers was 0.25—0.45 eV (full width at half maximum of the equivalent Gaussian response function).

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Measurements of ΔE_v

The photoemission approach to measure the valence-band discontinuity[1] can be understood by using the interface band diagram of Fig. 1. The conventional photoemission spectra or energy-distribution curves (EDC's) approximately reproduce the features of the density of occupied states, shifted by $h\nu$, the photon energy. When no Si is present, the upper edge of the clean GaP substrate corresponds to the top of the GaP valence band, E_v^{GaP}. The distance in energy between E_v^{GaP} and E_F, the Fermi level, can be estimated by linear extrapolation of the GaP EDC edge and by linear interpolation of the EDC edge for a thick, freshly evaporated metal film (Au in our case). This distance can be expected, in general, to change during the GaP-Si interface formation, since E_F is pinned at a different position in the substrate gap by new, localized electronic states. After Si deposition and as long as the overlayer is reasonably thin, the EDC'S reflect the electronic states of both Si and GaP. In a few heterojunction interfaces, e.g., ZnSe-Ge, the discontinuity ΔE_v is so large that two different edges can be seen in the EDC's corresponding to the valance bands of the two components.[19,35] In those few cases, ΔE_v can be measured directly from the distance in energy of the two edges.[19] Unfortunately, in GaP-Si ΔE_v does not give two separated edges. Therefore, estimating ΔE_v from the EDC's becomes slightly more complicated.

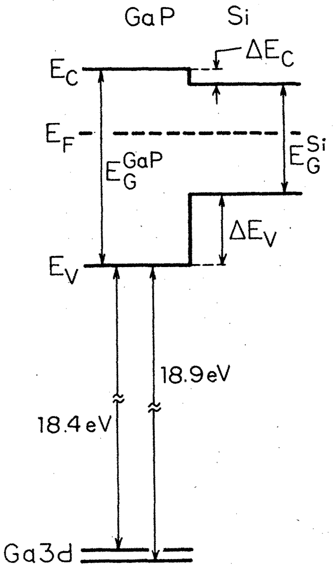

FIG. 1. Energy-band diagram for the GaP-Si heterojunction interface. The region shown here is sufficiently close to the interface to neglect the band bendings. Also shown is the bulk distance in energy between the Ga $3d$ doublet and the top of the GaP valence band, deduced from photoemission data.

It is, of course, possible to measure the position of E_v^{GaP} as explained above, and that of E_v^{Si} *after* the interface formation, by linear extrapolation of the EDC edge for Si-covered GaP. However, the distance between these two energy positions is *not*, in general, equivalent to ΔE_v, since the substrate band bending, and therefore the distance $E_F-E_v^{\text{GaP}}$, can change during the interface formation.[1] This possible change must be estimated to correct $E_v^{\text{Si}}-E_v^{\text{GaP}}$ and obtain ΔE_v. The band-bending changes are often estimated by observing the shift in energy of core-level photoemission peaks.[19] This is a delicate point, since the core levels are affected by local chemical shifts in addition to the band bending. The deconvolution of the two effects is by no means trivial, and affects the reliability of the measurement of ΔE_v. In many cases,[19] a correlation was observed between the substrate-cation core-level shifts and the band-bending changes. As we shall see, however, this rule is broken in the case of GaP-Si.

For our present experiment we solved the problem of estimating band-bending changes by carefully selecting $h\nu$ in order to enhance the *substrate* valence-band features in the Si-covered GaP EDC's. For example, the $h\nu = 17$ eV EDC's of Fig. 2 clearly exhibit the clean GaP peaks ~4.5 and 7–8.5 eV below E_F, even after Si coverage. We see from these spectra that the clean GaP features do not change their positions during the interface formation. Therefore, we conclude that the substrate band bending is *not* changed in this case by the Si adatoms. This breaks the rule[19] that the band-bending changes are reflected by the substrate-cation core-level shifts. In fact, the data of Fig. 3 (taken from Ref. 19) show that the Ga 3*d* peak shifts in energy during the interface formation—while the P 2*p* peak does not.

The invariance of the substrate band bending implies that ΔE_v is in this case simply given by $E_v^{\mathrm{Si}} - E_v^{\mathrm{GaP}}$, without further correction. One interesting point observed in Fig. 2 is that the EDC edge keeps shifting up to Si coverages of the order of 10 Å. Therefore, ΔE_v is not completely established until those coverages (while a few angstroms were sufficient for most other interfaces[19]). The final value of ΔE_v deduced from the data of Fig. 2 is 0.8 eV. The experimental uncertainty primarily arises from the linear extrapolation of the spectral edges, and we estimate it to be ±0.1 eV (a better accuracy would require full theoretical calculations of the near-edge density of states[12]). The value $\Delta E_v = 0.8$ eV is 0.15 eV smaller than that given in Ref. 19, where the band-bending changes were estimated from the cation core-level shift. This also implies a small revision of the empirical valence-band edge of GaP in the Katnani-Margaritondo table,[18] from −0.96 to −0.88 eV. The experimental value $\Delta E_v = 0.8$ eV is close to the theoretical prediction by Frensley and Kroemer,[22] $\Delta E_c = 0.96$ eV, while Harrison's prediction,[23] 0.5 eV, and that of the electron-affinity rule,[21] 0.33 eV, are less accurate.

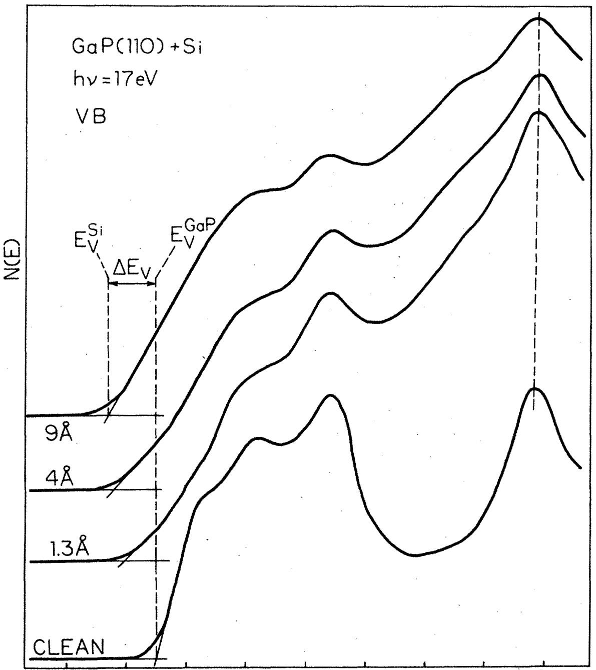

FIG. 2. Valence-band photoemission spectra taken at a photon energy of 17 eV on clean, cleaved GaP, and then on Si-covered GaP. The energy-position invariance of the GaP valence-band features at 4–4.5 and 7.6–8.2 eV below E_F demonstrates that the GaP band bending does not change during the formation of this interface. Therefore, the valence-band discontinuity ΔE_v is directly given by the distance in energy between the spectral edges of the clean and Si-covered GaP surfaces. We estimate $\Delta E_v = 0.8$ eV.

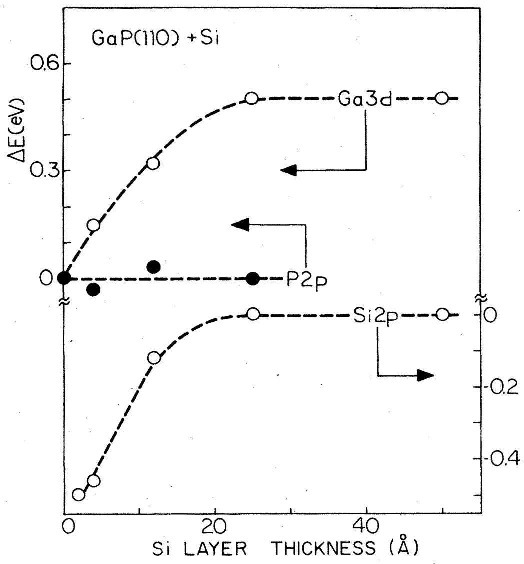

FIG. 3. Shifts in energy of the Ga 3*d*, P 2*p*, and Si 2*p* core levels during the formation of the GaP-Si interface. The experimental points were taken from Ref. 19. The positions shown here are deduced from the median energy of each peak. However, we shall see in the discussion of Fig. 5 that the Ga 3*d* peak actually consists of two different components. The Ga 3*d* shift shown here is determined by the behavior of both components, which depend on both band-bending and chemical-shift changes. The energy scale for Ga 3*d* and P 2*p* is referred to the clean-surface position of these peaks, and that for Si 2*p* to its thick-overlayer position.

The reliability of our estimates of ΔE_v was enhanced by the parallel measurements of ΔE_v *and* ΔE_c described in Ref. 34. ΔE_c was deduced from the evolution of the Ga 3*d* and Si 2*p* local optical-absorption edges measured with the partial-yield photoemission technique during the interface-formation process. The measured values of ΔE_v and ΔE_c were cross tested by verifying that their sum coincided within the experimental uncertainty, with the difference between the optical gaps of the two semiconductors.

The fact that the EDC-edge shift in Fig. 2 does not saturate until rather high Si coverages could be attributed to a still-evolving overlayer valence-band density of states. However, many previous experiments[1,19] have demonstrated that the essential valence-band features, including the edge, are established at smaller coverages (this general result is reasonable if one considers the small number of atoms required to reproduce the essential valence-band features in cluster calculations). One more likely explanation for the above effect is the establishment of interface dipoles due to diffusion processes or to surface chemical reactions or to both. The shift of the Ga 3*d* level found in Fig. 3, which we have seen not be correlated with the band-bending changes, gives additional evidence for the occurrence of processes of this kind.

B. Annealing effects

Experiments performed on the GaAs-Ge system had suggested that the valence-band discontinuity could be strongly affected by the ordering of the overlayer.[5] This is not a general property of all heterojunctions. In fact, *direct* measurements of ΔE_v for the ZnSe-Ge system[35] did not show any measurable change during annealing processes which restored a 1×1 LEED pattern. Therefore it appears necessary to test each one of the most important heterojunction interfaces and assess the magnitude of the annealing effects, if any. In our present study we found no detectable change in ΔE_v, but we did observe a dramatic change in the substrate band bending upon annealing.

The annealing-induced changes in band bending are evident from a parallel analysis of Figs. 4 and 5. Figure 4 shows the valence-band spectra of clean GaP and of as-grown and annealed GaP covered by 4 Å of Si, in the region 3.5–10 eV below E_F. In this region two GaP valence-band peaks are clearly visible. The deposition of 4 Å of Si on the room-temperature substrate did not change the position in energy of these features. Therefore, there was no change in band bending, as we already deduced from the spectra of Fig. 2. The Si overlayer completely removed the LEED pattern, due to its amorphous character. A 5-min annealing at 350 °C restored a LEED pattern, but the intensity of its spots was much weaker than for the clean substrate. Annealings at lower temperatures did not restore any LEED pattern. Annealings at higher temperatures, up to 450 °C, gave the same pattern as the 350 °C annealing. The strength of the Si signal at the valence-band edge also suggested some Si depletion upon annealing. This depletion, however, was much less pronounced than the strong Ge depletion induced by annealing of the ZnSe-Ge system.[35] Annealings for times longer than 5 min did not change these experimental results.

It is evident from Fig. 4 that the 350 °C annealing changes the position of the GaP valence-band features by 0.1(2) eV. The cause of this shift is a change in the substrate band bending, as confirmed by the spectra of Fig. 5. Shown in Fig. 5 are the Ga 3*d* spectra of the clean substrate and of the as-grown and annealed GaP-Si interface. The Si deposition causes a shift of the Ga 3*d* peak, as already shown in Fig. 3. We have seen that this shift is not due to a change in band bending, but to a change in the local chemical environment of the Ga atoms. The line shape of the middle spectrum in Fig. 5 suggests that there are two Ga 3*d* components for the as-grown GaP-Si interface. The position of one of these components coincides with that of the clean GaP Ga 3*d* peak. Therefore, this component can be attributed to Ga atoms in a chemical environment similar to that of the GaP surface, and its position is consistent with the already deduced band-bending invariance during Si deposition. After annealing there is no longer any clear evidence for a second component, and the Ga 3*d* position is shifted by 0.1(2) eV with respect to the clean surface. This shift is the same as that observed in Fig. 4 for the GaP valence-band features. This indicates that the shift between the clean-surface and

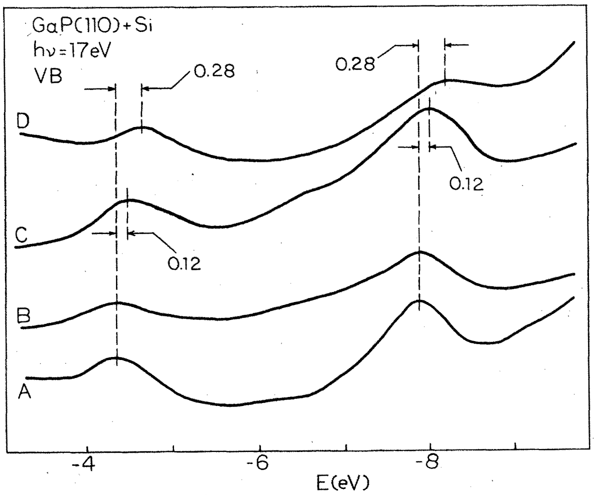

FIG. 4. GaP bulklike valence-band photoemission features. *A*, clean GaP; *B*, GaP with 4 Å of Si, deposited with the substrate at room temperature, as-grown; *C*, same as *B*, after 5 min annealing at 350 °C; *D*, GaP with 4 Å of Si, deposited with the substrate at 250 °C, as grown.

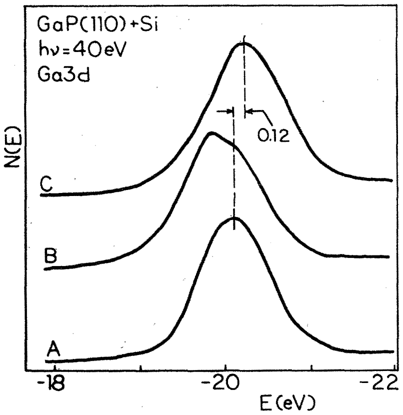

FIG. 5. Ga 3*d* spectra. *A*, clean GaP; *B*, GaP with 4 Å of Si, deposited with the substrate at room temperature, as-grown; *C*, same as *B*, after 5 min annealing at 350 °C. Curve *B* shows evidence of a fine structure consisting of two components whose possible nature is discussed in the text.

annealed-interface positions of the Ga $3d$ spectrum is due to a change in band bending, while the as-grown interface spectrum is also affected by a change in the chemical environment of part of the Ga atoms.

From the above results the following picture emerges as far as the interface Fermi-level pinning is concerned. On the clean GaP surface, E_F is pinned (1.5 ± 0.1) eV above E_v^{GaP}. Partial-yield spectra[36] (see discussion below) revealed a band of unoccupied surface states extending in the gap of GaP, as theoretically predicted by Calandra *et al.*[37] The bottom edge of this surface-state band, deduced from partial-yield spectra after correction for surface core-level shifts and for core excitonic effects,[38] is 1.4—1.6 eV above E_v^{GaP}, i.e., it is correlated with the above pinning position of the Fermi level. The same correlation is found with the theoretical surface-state—band edge,[37] predicted to be 1.53 eV above E_v^{GaP}. Therefore we concur with the conclusion by Norman *et al.*[39] that the surface-state band is responsible for the Fermi-level pinning on clean GaP.

The invariance of the band bending upon Si coverage also implies the invariance of the Fermi-level—pinning position. This could be interpreted either as an invariance of the pinning mechanism or as a coincidence of the results of two different pinning mechanisms. The first hypothesis is ruled out by the partial-yield spectra (see below), which show that the surface-state band of clean GaP is removed by the Si adatoms. The second hypothesis requires new, Si-induced localized states to pin the Fermi level. For III-V substrates these states are generally identified with native defect states,[1] extending to heterojunction interfaces the Spicer's defect model for metal-semiconductor interfaces.[40] For example, Allen and Dow[25] theoretically predicted the surface-antisite-defect pinning levels for n-type GaP to be 1.4 eV (P on Ga site) and 1.25 eV (Ga on P site) above E_v^{GaP}. The first value is close to our experimental pinning position. The antisite-defect hypothesis would also explain the qualitative differences between the heterojunction-interface pinning positions for GaAs and GaP substrates.[41]

The annealing-induced changes in band bending, observed in Figs. 4 and 5, require yet another change in the E_F-pinning mechanism. Notice that the difference in energy between the pinning positions for the as-grown and annealed interfaces, 0, 1(2) eV, is close to the difference in energy[25] between the above two surface-antisite-defect levels, 0.15 eV.

The possible changes in ΔE_v due to annealing have been explored by analyzing the near-edge EDC's. Figure 6 shows a series of these curves, taken on as-grown and annealed interfaces. These curves have been shifted in energy to compensate for the changes in band bending due to annealing, so that the GaP peak on the right-hand side is in the same position for different spectra. The values of ΔE_v estimated from these curves are 0.6(6) eV for the as-grown surface (the Si coverage is still below the saturation value for ΔE_v), and 0.6(0) and 0.6(2) eV for the interfaces annealed at 350 and 450 °C, respectively. All these values coincide within the experimental uncertainty of 0.1 eV. The same conclusion is valid for all our annealing studies.

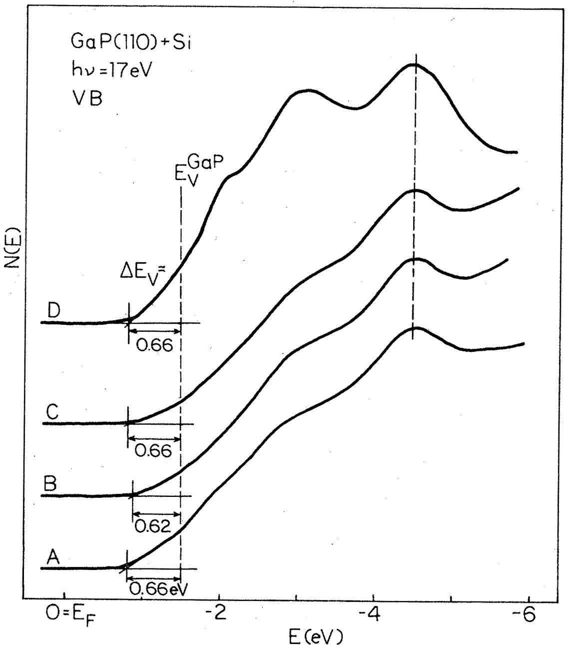

FIG. 6. Valence-band spectra taken on GaP with 4 Å of Si. *A*, Si deposited on room-temperature GaP, as-grown interface; *B*, same as *A*, after 5 min annealing at 350 °C; *C*, same as *B*, after further annealing, 5 min at 450 °C; *D*, Si deposited on GaP kept at 250 °C, as-grown interface. The dashed line on the left-hand side shows the position of the valence-band edge of clean GaP, deduced from Fig. 2. Curves *B*, *C*, and *D* were shifted in energy to compensate the band-bending changes with respect to the clean GaP surface, as emphasized by the alignment of the bulk-GaP feature at 4—4.5 eV below E_F. Also shown are the valence-band discontinuities deduced from each curve. All these values coincide with each other within the experimental uncertainty.

The above results qualitatively coincide with those we obtained for interfaces prepared by depositing Si on a hot GaP substrate. When the substrate was dept at 250 °C during deposition, the resulting interface exhibited LEED features roughly equivalent to those obtained after deposition on a room-temperature substrate and annealing at 350 °C or more. Figure 6 shows that the resulting ΔE_v, 0.6(6) eV, again coincides with the value obtained upon deposition on a room-temperature substrate. Instead, the Fermi-level—pinning position is different. In fact, the position is different even from that obtained after deposition on a room-temperature substrate and annealing. This is shown by the results of Fig. 4. The pinning position of E_F for the hot-substrate Si deposition is 1.7(8) eV above E_v^{GaP}. This result could again be explained in the framework of the defect model,[40] with an interplay of different kinds of defects.

The fact that the E_F-pinning position changes depending on the details of the interface-preparation process has interesting implications in the general problem of interface barriers for both heterojunctions and Schottky diodes. Systematic studies by Brillson and co-workers[42] have revealed the dependence of the interface barriers on the chemical properties of the interface. This result has been sometimes considered in contrast to the defect model.[40] Results by Williams and co-workers[43] on InP-metal interfaces suggested a way to reconcile the two points of view, assuming that there is a relation between chemical properties and the kinds of defects formed during overlayer deposition. Our present results generally support that idea. In fact, we see that E_F is pinned in positions which could be explained by surface defect levels. In addition, the pinning involves a small density of localized states not directly visible in our photoemission spectra, as in the defect model. However, we obtain different pinning positions depending on the interface preparation. Once again, therefore, the specific kind of defects responsible for the Fermi-level pinning appears to depend on the local chemical processes.[1]

IV. CONCLUSIONS

We studied the formation of the GaP(110)-Si interface with different photoemission techniques and with LEED. The main results of our investigation are the following. The band discontinuities reach their saturation value only after Si coverages of the GaP substrate of about 10 Å. The saturation value of ΔE_v is 0.8 eV. The value of ΔE_v is not changed by annealing processes which give a partial reordering of the Si overlayer.

We confirm that for the clean GaP surface the Fermi level is pinned by a surface-state band extending into the forbidden gap,[39] and the pinning position is 1.5 eV above the top of the GaP valence band, E_v^{GaP}. The pinning position stays the same when Si is deposited on room-temperature GaP. However, the clean-surface states are removed, and therefore the pinning mechanism must change. Upon annealing, the pinning position shifts away from the valence-band edge by 0.1(2) eV. The pinning positions for as-grown and annealed interfaces are consistent with the theoretical Fermi-level—pinning energy levels produced by different kinds of surface antisite defects.[25]

Qualitatively similar conclusions can be drawn from data taken on Si overlayers deposited on hot GaP substrates. From all these results we conclude that the details of the interface-preparation process do not detectably influence the band discontinuities, which, together with the built-in potential, are the most important heterojunction parameters.[20] This is reasonable since the systematic work by Katnani and Margaritondo[18,19] demonstrated that the first-order contributions to these parameters are essentially bulklike—but we emphasize that local effects cannot be ruled out, in general, on the basis of our present data, which only concern the effects of annealing in a particular heterojunction.

The interface-preparation process does influence the Fermi-level—pinning position, and therefore the interface barriers, i.e., the built-in potential.[1,40,42] This result has interesting fundamental implications on the relative role of interface chemistry and of native defects in establishing the built-in potential. Furthermore, it has practical interest since it introduces a degree of freedom in preparing heterojunction devices with the desired characteristics.

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