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Parallel measurements of both heterojunction band discontinuities by synchrotron-radiation photoemission

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Both the conduction-band discontinuity, ΔE_c, and the valence-band discontinuity, ΔE_v, at the interface between a cleaved GaP substrate and a Si overlayer were measured in parallel with photoemission techniques. ΔE_v was measured in the conventional energy distribution curve mode, while ΔE_c was measured in the partial-yield mode. The results open the way to more reliable estimates of the discontinuities for compound-semiconductor heterojunctions.

Several authors[1-16] have recently used photoemission methods to perform *local* measurements of the valence-band discontinuity, ΔE_v, at semiconductor heterojunction interfaces. ΔE_v was estimated either directly, from the double edge of conventional valence-band photoelectron energy distribution curves (EDC's) taken on the surface of one semiconductor covered by a thin layer of the other semiconductor,[5,6] or indirectly, from the valence-band edges of the clean substrate and of a thick overlayer of the second semiconductor.[5,6] This indirect method required a correction for the change in the substrate band-bending during interface formation. In turn, the correction was deduced from the energy shift of the substrate core levels. This is a delicate point, since the core-level shifts are affected both by the band-bending changes and by chemical-shift changes due to the formation of interface bonds.[4-6] The deconvolution of these two factors is not trivial, and it introduces an element of uncertainty in the final result.[5] On the other hand, photoemission is the only local way to measure heterojunction discontinuities,[1-16] and therefore it plays a central role in the research on these crucial parameters.

The development of an alternate local method to estimate heterojunction discontinuities is, therefore, important and timely. We show here that the partial-yield mode of synchrotron-radiation photoemission[17] (PY) can be used to measure the conduction-band discontinuity, ΔE_c, with an approach similar to that used to measure ΔE_v in the conventional EDC mode.[1-16] The estimated accuracy, including possible excitonic effects,[18] is of the same order of magnitude as that achieved in most photoemission measurements of ΔE_v, ± 0.1 eV.[5,6] Therefore, this approach can be used to check the photoemission measurements of ΔE_v and reveal at least the large errors which could arise from the band-bending-change correction discussed above.[5]

It is well known[19] that photoemission in the EDC mode consists of measuring the number of collected photoelectrons from a surface as a function of their energy, at constant photon energy $h\nu$. Figure 1 shows the corresponding spectra taken on a clean, freshly cleaved GaP(110) surface in the energy region of the valence-band edge, E_v, and then on the same surface covered by 4 Å of Si deposited *in situ* by electron bombardment. The entire experiment was performed under ultrahigh vacuum conditions (pressures in the 10^{-11} Torr range, rising to less than 8×10^{-10} Torr during Si deposition). The photons were emitted by the storage rings ADONE at the Frascati National Laboratory and Tantalus at the University of Wisconsin Synchrotron Radiation Center. In both laboratories, the photoelectron analysis was performed by double-pass cylindrical-mirror instruments under computer control.

The establishment of ΔE_v is evident in the spectra of Fig. 1. We see new states created above the GaP valence-band edge. The substrate band-bending does not appear to be affected by the overlayer in this case, as shown by the constant position in energy of the GaP valence-band feature at $\simeq -3.16$ eV.[20] Therefore, ΔE_v is given by the difference

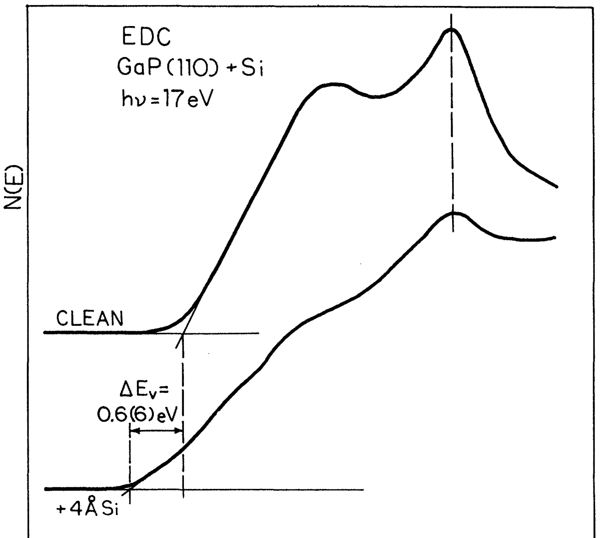

FIG. 1. Energy distribution curves taken at a photon energy of 17 eV on cleaved, clean, and Si-covered GaP. The estimated valence-band discontinuity from these curves is 0.6(6) ±0.1 eV as discussed in the text.

of the edge positions for the two spectra. After estimating the edge positions by linear extrapolation, we obtain $\Delta E_v = 0.6(6) \pm 0.1$ eV. This value is $\simeq 0.1$–0.15 eV smaller than the final ΔE_v obtained with a thick (> 15 Å) Si overlayer.[20] Several previous experiments have shown that the fundamental overlayer valence-band features, including the edge, are already established for thicknesses of the order of a few angstroms.[5,6] Therefore, the residual, weak dependence of ΔE_v on the thickness is not likely to be due to a still evolving valence-band spectrum. A probable cause is a change in the interface dipoles due to diffusion and/or substitutional reactions. In the present experiment, the use of a Si overlayer thinner than that required for saturation of ΔE_v was necessary to perform parallel ΔE_c measurements in the PY mode.

Photoemission in the PY mode is performed by measuring the yield of secondary photoelectrons at a given kinetic energy E_k, as a function of the photon energy.[17] Therefore, it requires a tunable photon source—synchrotron radiation. It has been demonstrated[17] that these spectra reflect the optical absorption coefficient, measured with a high-surface sensitivity which can be tuned by changing E_k. Figure 2 shows PY spectra taken both on clean and Si-covered GaP, with $E_k = 1$ or 4 eV. These spectra were taken in the photon energy region of the Ga 3*d* edge, which is still visible for Si coverages of a few angstroms. The 4-eV spectrum is more surface sensitive than the 1-eV spectra, due to the shorter photoelectron mean free path.[19] In fact, the top spectrum of Fig. 2 exhibits below-edge features due to optical transitions from Ga 3*d* to *surface* states in the GaP gap.[21,22] The corresponding features are almost completely absent in the $E_k = 1$ eV clean GaP spectrum, except for a residual shoulder immediately below the edge. The portion of the intrinsic Ga 3*d* absorption edge in clean GaP was deduced in two ways: from the 1-eV spectrum, by linear extrapolation; from the 4-eV spectrum, after correction for the Fano-like surface-state contribution, as discussed in Ref. 23 (the corrected curve is the dashed line in Fig. 2). Both estimates give the same value, $h\nu = 20.6$ eV. After Si coverage, the conduction-band edge is shifted to lower photon energies. This is revealed by the different positions in Fig. 2 of the nearly linear, above-edge portions of the two bottom spectra. The estimated magnitude of the shift is $\simeq 0.4$ eV. We propose that this shift is due to transitions between overlapping Ga 3*d* wave functions and bulklike states of the overlayer, and that its value corresponds to ΔE_c. This interpretation is supported by the following internal-consistency test.

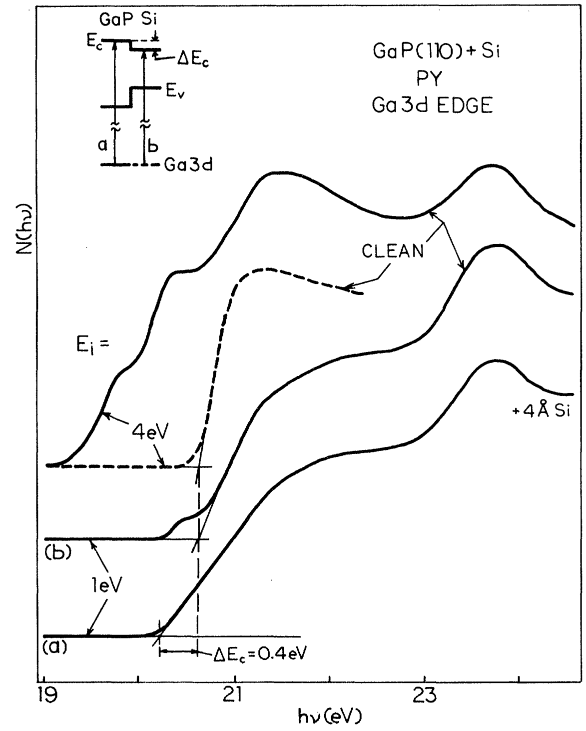

FIG. 2. Partial-yield spectra for clean and Si-covered GaP, showing the Ga 3*d* optical absorption edge. The PY curve taken at a kinetic energy $E_k = 4$ eV is more surface sensitive than those taken at $E_k = 1$ eV, and it exhibits optical transitions to surface states. The dashed line shows the same spectrum after correction for those surface contributions. We argue in the text that the Si-induced shift in the $E_k = 1$ eV PY spectral edge reflects the conduction-band discontinuity.

The sum of the two heterojunction discontinuities must be equal to the gap difference between the two semiconductors.[5] If we take the sum of the above estimates of ΔE_v and ΔE_c and subtract it from the optical room-temperature gap of GaP, 2.24 eV, the result is 1.18 eV (estimated accuracy: ± 0.15 eV). This value coincides within the experimental accuracy with the optical gap of amorphous Si prepared in a similar way, 1.26 eV.[24]

The positive result of the test implies that all the "spurious" factors in the discontinuity measurements cannot be of magnitude larger than the experimental uncertainty. Possible "spurious" factors for ΔE_c are (i) the presence of core-excitonic shifts[18] in the Ga 3*d* edge (a comparison of the Ga 3*d* EDC binding energy and of the above clean-GaP Ga 3*d* edge gives a core-excitonic shift of 0.4 eV for this edge[20]) and (ii) optical transitions involving Ga atoms in a different chemical environment than for clean GaP. The negligible role of these factors is reasonable, since (i) core-excitonic effects for the clean and Si-covered GaP surfaces tend to cancel each other while estimating the Si-induced edge shift, and (ii) in surface-sensitive EDC's taken in the Ga 3*d* region,[20] the only Ga 3*d* peak chemically shifted with respect to clean GaP is that of free Ga, and we estimate that its intensity corresponds to a negligible contribution to the 1-eV PY curves. Our interpretation of the Si-induced Ga 3*d* edge shift is also supported by the PY Si 2*p* edge which shifts to higher photon energies when E_k is changed from 4 to 1 eV, decreasing the surface sensitivity. This is explained by an increase in the relative contribution of transitions to GaP conduction-band-edge states overlapping the Si 2*p* wave functions, confirming that the overlayer-substrate wave function overlap is sufficient to give reasonably large transition probabilities. Furthermore, the observed Si 2*p* edge shift indicates that the GaP surface states are removed by the Si adatoms, since they would have otherwise given a shift in the opposite direction. Therefore, they cannot be involved in the Si-induced shift of the Ga 3*d* edge.[25]

The magnitude of the above "spurious" factors in the PY ΔE_c measurements must be tested for each heterojunction system. Therefore, these measurements have *per se* a reliability limit. We have seen that reliability limits also exist for the EDC measurements of ΔE_v.[5,6] However, we have shown here for the first time that *both* kinds of measurements can be performed in parallel. Their results can be cross checked, increasing the overall reliability and in particular ruling out trivial errors. We emphasize that the goal of eliminating gross errors can be achieved even using nonsaturation coverages as we were forced to do here. In fact, sources of big errors, e.g., large core level chemical shifts affecting the EDC estimate of ΔE_v,[5,6] strongly affect presaturation coverages as well as saturation coverages.

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[1] P. Perfetti, D. Denley, K. A. Mills, and D. A. Shirley, Appl. Phys. Lett. 33, 66 (1978).

[2] D. Denley, K. A. Mills, P. Perfetti, and D. A. Shirley, J. Vac. Sci. Technol. 16, 1501 (1979).

[3] P. Perfetti, N. G. Stoffel, A. D. Katnani, G. Margaritondo, C. Quaresima, F. Patella, A. Savoia, C. M. Bertoni, C. Calandra, and F. Manghi, Phys. Rev. B 24, 6174 (1981); G. Margaritondo, N. G. Stoffel, A. D. Katnani, H. S. Edelman, and C. M. Bertoni, J. Vac. Sci. Technol. 18, 290 (1981); G. Margaritondo, N. G. Stoffel, A. D. Katnani, and F. Patella, Solid State Commun. 36, 215 (1980).

[4] G. Margaritondo, A. D. Katnani, N. G. Stoffel, R. R. Daniels, and Te-Xiu Zhao, Solid State Commun. 43, 163 (1982).

[5] A. D. Katnani and G. Margaritondo, J. Appl. Phys. 54, 2522 (1983).

[6] G. Margaritondo, Solid-State Electron. 26, 499 (1983).

[7] S. P. Kowalczyk, W. J. Schlaffer, E. A. Kraut, and R. W. Grant, J. Vac. Sci. Technol. 20, 705 (1981).

[8] S. P. Kowalczyk, E. A. Kraut, J. R. Waldrop, and R. W. Grant, J. Vac. Sci. Technol. 21, 482 (1982).

[9] E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, Phys. Rev. Lett. 44, 1620 (1980).

[10] J. R. Waldrop and R. W. Grant, Phys. Rev. Lett. 26, 1686 (1978).

[11] R. W. Grant, J. R. Waldrop, and E. A. Kraut, Phys. Rev. Lett. 40, 656 (1979); J. R. Waldrop, S. P. Kowalczyk, R. W. Grant, E. A. Kraut, and D. L. Miller, J. Vac. Sci. Technol. 19, 573 (1981).

[12] R. S. Bauer and J. C. McMenamin, J. Vac. Sci. Technol. 15, 1444 (1978).

[13] P. Zurcher and R. S. Bauer, J. Vac. Sci. Technol. A 1, 695 (1983).

[14] R. S. Bauer and J. C. Mikkelsen, Jr., J. Vac. Sci. Technol. 21, 491 (1982).

[15] W. Mönch, R. S. Bauer, H. Gant, and H. Murschall, J. Vac. Sci. Technol. 21, 498 (1982).

[16] W. Mönch and H. Gant, J. Vac. Sci. Technol. 17, 1094 (1980); W. Mönch and H. Gant, Phys. Rev. Lett. 48, 512 (1982).

[17] W. Gudat and C. Kunz, Phys. Rev. Lett. 29, 169 (1972).

[18] G. Margaritondo, A. Francios, N. G. Stoffel, and H. S. Edelman, Solid State Commun. 36, 297 (1980), and references therein.

[19] G. Margaritondo and J. E. Rowe, J. Vac. Sci. Technol. 17, 561 (1980).

[20] P. Perfetti, F. Patella, F. Sette, C. Quaresima, C. Capasso, A. Savoia, and G. Margaritondo (unpublished).

[21] F. Manghi, C. M. Bertoni, C. Calandra, and E. Molinari, Phys. Rev. B 24, 6029 (1981).

[22] D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 34, 1624 (1975).

[23] F. Sette, P. Perfetti, F. Patella, C. Quaresima, C. Capasso, M. Capozi, and A. Savoia (unpublished).

[24] M. H. Brodsky, R. S. Title, K. Weiser, and G. D. Pettit, Phys. Rev. B 1, 2632 (1970).

[25] The observed Si 2*p* edge shift between the $E_k=4$ and 1-eV PY curves is 0.25–0.3 eV. Therefore, under the assumption that transitions to GaP conduction band states give a strong contribution to the $E_k=1$ eV PY curve, one could even claim a quantitative agreement with our measured $\Delta E_c = 0.4 \pm 0.1$ eV. This would also support our conclusion that excitonic effects cancel each other when measuring edge shifts. However, an accurate estimate of ΔE_c from the Si 2*p* edge shift to *higher* photon energies requires a good knowledge of the relative contributions to the local absorption coefficient, i.e., of the interface wave functions. Since these are not available, we cannot exclude the possibility of the above quantitative agreement being fortuitous.