Independence of Fermi-Level Position and Valence-Band Edge Discontinuity at GaAs-Ge(100) Interfaces

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The valence-band discontinuity, ΔE_V, and the Fermi-level position, E_F, at GaAs-Ge(100) heterojunctions are investigated by synchrotron radiation photoemission for variations in GaAs surface As and ambient As_4 during molecular-beam epitaxial growth. E_F can be varied by 0.35 eV at the interface, and its position is uncorrelated with the constant 0.46 ± 0.05 eV measured for ΔE_V. These results are not consistent with a defect model for heterojunction barrier heights.

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The interface between two different, lattice-matched semiconductors is one of the most interesting systems in solid-state physics.[1] Such heterojunctions are electrically characterized by two parameters: The band-edge discontinuity which is a result of the band-structure change across the interface, and the band bending which is a measure of the Fermi-level location in the gaps on both sides of the interface. Only recently has real progress been made in understanding the key mechanisms that determine these two parameters.[2-5] This report establishes for the first time that band discontinuities have nothing to do with Fermi-level pinning. Previous results for semiconductor overlayers deposited onto cleaved surfaces seemed to point in the opposite direction.[3] We show that a theoretical description of the band-structure discontinuities between different semiconductors is unrelated to localized states or to charge redistribution introduced at the boundary during the interface formation. The band-electronic-state changes across interfaces are not only important in heterojunction physics. They are related to the general problem of the absolute energy position of the electronic structure of semiconductors across interfaces with all classes of solids.[2]

Recently, experimental studies have successfully related the interface barrier height to native surface defects created on the substrate side during the interface formation.[3,4] This approach is an extension of the defect model proposed by Spicer *et al.*, to explain the barrier height at metal and oxide-semiconductor interfaces.[6] It is important to understand the validity of such a defect model and its implication on the band discontinuity at heterojunction interfaces. Pinning of the Fermi level on both sides of the interface requires a correlation between the E_F final position and the band discontinuity as a result of the "detailed balance" condition that E_F is continuous across the junction at equilibrium. Furthermore, for such defect levels to be effective in this pinning, their energetic positions in the band gaps would have to line up across the interface.

In this paper, we present the first systematic, correlated measurement of E_F and ΔE_V at a heterojunction interface. The intimate boundary between isoelectronic GaAs and Ge semiconductors is studied as a prototype of epitaxial, structurally continuous system. By testing both the final positions and their evolution with heterojunction growth, we show that a defect model is not applicable to GaAs-Ge(100) heterojunction band offsets. The E_F final position *is not correlated* with ΔE_V. We show that the initial and final E_F move in the upper half of the GaAs band gap. An explanation of those results in terms of the defect model would invoke defect levels at different positions in the gap. Also, it would require an *ad hoc* redistribution of the charge density on both sides of the interface to maintain the same ΔE_V at the interface. Neither seems likely, and we conclude that defects do not play an important role in determining barrier heights.[7]

The experiments were performed on the 4° beam line at the Stanford Synchrotron Radiation Laboratory. The samples were grown *in situ* by molecular-beam epitaxy (MBE). The details of the GaAs(100) surface preparation procedure is described elsewhere.[8] Auger-electron spectroscopy and low-energy electron diffraction were employed to check for contaminations and for the ordering of the surface layer. Energy distribution curves for the valence band and As($3d$), and Ge($3d$) cores were taken with a double-pass cylindrical-mirror analyzer. The photon energy was chosen to optimize the surface sensitivity. The overall energy resolution is 0.15 eV. As($3d$) and Ga($3d$) line shapes and peak intensities were used to determine

clean surface chemistry and stoichiometry. The ΔE_V and E_F were obtained with use of two methods.[3,9] For thick Ge overlayers on nearly a dozen GaAs(100) surfaces of different starting stoichiometry, the same result is obtained for ΔE_V within ± 0.05 eV. This is taken as a measure of our experimental uncertainty and reproducibility.

The GaAs(100) surface exhibits a variety of surface reconstructions, among them $c(4\times4)$, $c(2\times8)$, $c(8\times2)$, and (4×6). These surface reconstructions have been related to the surface stoichiometry.[10,11] The exact stoichiometry corresponding to each reconstruction is controversial; however, it is possible to order these reconstructions in terms of the corresponding surface coverage of As. Using the $3d$ core intensities, measured for these samples, we find unambiguously that the surface As in our characterized GaAs(100) surfaces decreases, going from $c(4\times4)$ to $c(2\times8)$ to $c(8\times2)$ to (4×6). Following standard convention, the low-energy electron-diffraction pattern designations are used as a shorthand notation for the *relative* amount of starting surface As concentration.

Figure 1 shows the evolution of E_F during the interface formation between GaAs (100) or (110) surfaces and epitaxial, lattice-matched Ge. The very important observation from this figure is the different starting and ending positions of E_F for the different starting surface reconstructions of GaAs(100). We find that this change in E_F position correlates with the excess of starting GaAs surface As.[12] Notice that the initial position of E_F varies by over 0.3 eV, going from at least a monolayer of surface As for the $c(4\times4)$, to a half monolayer on the $c(8\times2)$, to at least a $\frac{3}{4}$ monolayer of Ga on the 4×6 starting GaAs(100) surface.[13] Importantly, we observe that this trend is maintained as the interface of GaAs-Ge(100) forms. As seen in Fig. 1 at saturation (i.e., ~ 8 Å Ge overlayer thickness), the junction is more n type as the As coverage of the starting surface increases. This suggests that As can act as a donor in doping the thin Ge layer.

For all the interfaces, we measured the same $\Delta E_V \pm 0.05$ eV independent of the final E_F positions in Fig. 1. Figure 2 schematically summarizes the results of Fig. 1 in terms of the energy bands and the Fermi-level position at the (100) interfaces we studied. The experiments clearly demonstrate two points: First, the observed differences between the various surface reconstructions do not influence the band discontinuity; however, they influence the barrier heights on both sides of the interface. The rearrangement of the charge distribution on both

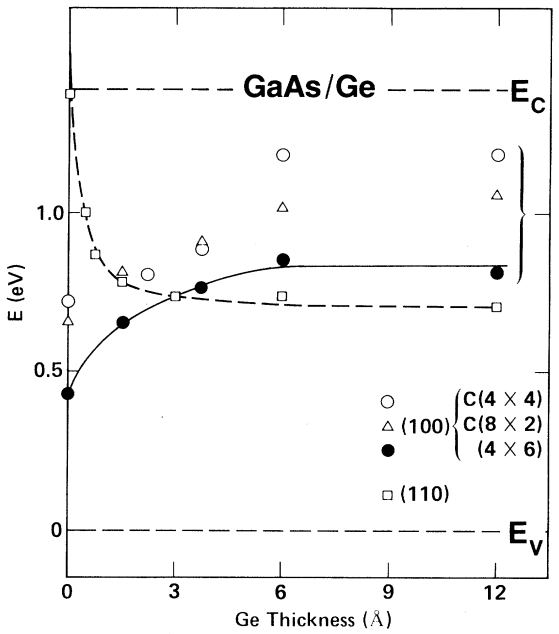

FIG. 1. The evolution of the Fermi-level position during the interface formation, as measured by the Ga($3d$) photoelectron energy on the substrate side of the heterojunction. The initial and final positions of E_F vary among the different MBE-grown GaAs(100) subsurfaces. The final E_F position moves towards the conduction-band edge by over 0.30 eV on going from the Ga-rich (4×6) surface to the As-rich $c(4\times4)$ surface. Note that the E_F at the cleaved GaAs(110)-Ge interface differs from the MBE GaAs(100)-Ge interface in the following ways: First, it exhibits a faster evolution from the free-surface value. Second, its final position is at the same position proposed for defects induced by oxygen and metal deposition.

sides of the interface does not create a measurable dipole layer at the interface.[5,7] Further, doping does not influence the potential step at the abrupt, epitaxial interface (i.e., ΔE_V).[2] Second, ΔE_V and E_F are two uncorrelated parameters for a heterojunction which implies that the origins of the valence-band discontinuity and of the Fermi-level final position are different for semiconductor/semiconductor interfaces.

The above observations raised the question about the role of mobile As in determining the valence-band discontinuity[14] and the Fermi-level position.[12] To study the extent of the role of As during the interface formation, we performed experiments which intentionally introduced As during epitaxial growth of the Ge overlayer. Figure 3 shows the evolution of E_F during the interface formation between GaAs(100) subsurfaces and co-MBE deposition of

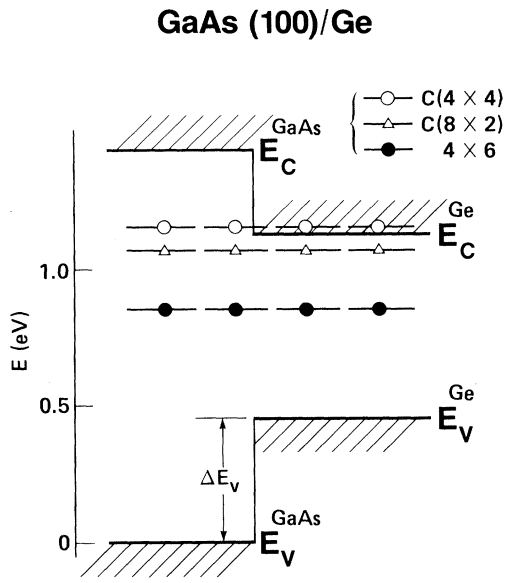

FIG. 2. Schematic of the energy bands and the Fermi-level position at the interface on a 10-Å scale. The valence-band discontinuity is the same at the interface between the various surface reconstructions of GaAs(100) surface and Ge. However, the Fermi-level position at the interface depends on the surface stoichiometry. This observation clearly demonstrates the independence of the Fermi level and the valence-band discontinuity.

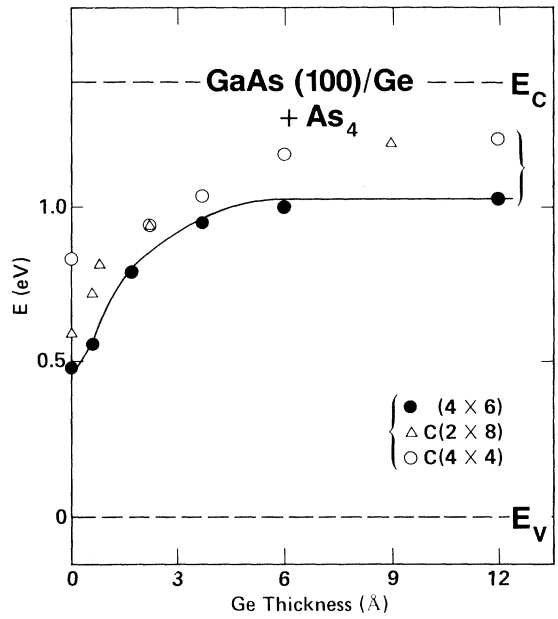

FIG. 3. The evolution of the Fermi level during the interface formation between the various surface reconstructions of GaAs(100) and Ge. The difference between this figure and Fig. 1 is that we deposited Ge while the shutter for the As source was open. This figure when compared with Fig. 1 shows that the presence of As influences the final E_F position. E_F for the Ga-rich, (4×6) surfaces moved toward the conduction band by over 0.10 eV. E_F for the As-rich, $c(4\times4)$ only slightly moved toward the conduction band because E_F is already close to the top of the conduction band of Ge when no As is introduced. It is important to mention that we measured the same ΔE_V for these interfaces. This demonstrates that the excess of As, while it influences the final E_F position, does not influence ΔE_V.

Ge and As_4. Notice that the initial E_F positions for the clean surfaces reproduce those presented in Fig. 1. The effect of the coevaporated As is more noticeable for the As-deficient starting surface, i.e. (4×6). Notice that the final E_F position moved toward the conduction-band edge by over 0.1 eV when As is introduced; compare Figs. 1 and 3. The As-induced change for the As-rich starting surface, $c(4\times4)$, is smaller because that starting surface is already saturated with As, and the Fermi level is already nearly degenerate with the Ge conduction band without additional As in the ambient. The final E_F position for a starting surface in between the above two surfaces, namely $c(2\times8)$, is consistent with what we expect from the observed trend discussed above. Again, we measured the same valence-band discontinuity for the GaAs-Ge interfaces prepared in this way as for those grown with Ge alone. The role of As as a dopant to change E_F without affecting ΔE_V is supported by these experiments.

The question remains as to whether deposition-induced defect states influence the Fermi-level position at the GaAs side of the interface or whether an As doping of Ge alone accounts for the change in E_F. It is clear from Figs. 1 and 3 that the Fermi-level final position is not due to *deposition-induced defects*; the evolution is slower than the one observed for metal-semiconductor interfaces and the final position cannot be explained by a single defect. Further, E_F changes occur in the upper half of the GaAs band gap. This demonstrates that the deposition-induced defects do not occur in sufficient density to pin the Fermi level. It would seem that a >0.3 eV ΔE_F for a change of less than a monolayer of As at the starting substrate surface favors a simple donor in Ge being responsible. The independence of ΔE_V and E_F demonstrate that the conduction and valence bands on both sides of the interface move freely to maintain the same ΔE_V. This observation supports the above conclusion.

The interesting question arises as to why the E_F position for cleaved GaAs(110) appears to evolve

so differently from GaAs(100) and apparently "pin" independent of overlayer material. As seen in Fig. 1, the starting E_F position for the cleaved GaAs(110) is indicative of a flat-band condition, i.e., no cleavage steps. Notice the difference in the evolution and in the final position of E_F for the two surfaces' crystallographic orientations. This behavior difference between cleaved (110) heterojunction's and MBE (100) interface formation may just reflect the same differences seen in (110) heterojunctions between the cleaved GaAs substrates[3,4] and the MBE-prepared GaAs(110) starting surfaces.[15] This difference might indicate that there are two different mechanisms responsible for the final E_F positions.

In summary, we find that the Fermi-level position moves in the upper half of the band gap by 0.35 eV as the surface coverage of As increases at the lattice-matched interface between MBE-grown GaAs(100) and Ge. Further, the valence-band discontinuity and the Fermi-level position are *uncorrelated.* Both observations cannot convincingly rule out the presence of defects; however, they demonstrate that such defects do not occur in sufficient densities to play a primary role in semiconductor heterojunctions.[7] The understanding of heterojunctions must focus on the detailed atomic structure at the interface in order to provide a model for the potential barrier that occurs between different semiconductors.

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