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Dopant concentration dependences and symmetric Fermi-level movement for metal/n-type and p-type GaAs(110) interfaces formed at 60 K

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The coverage-dependent Fermi-level movement for Ag, Co, and Ti interfaces formed at 60 K on n-type and p-type GaAs is shown to be symmetric but dependent on the bulk dopant concentration. Photoemission results show that E_F remains close to the band edges until ~ 1 monolayer for doping of 1×10^{17} cm^{-3} while E_F movement is induced by far fewer adatoms for doping of 2×10^{18} cm^{-3} with overshooting for p-type GaAs. Remarkable surface chemical and structural insensitivity is reflected by similar band-bending trends for adatoms which exhibit very different reactivities and amounts of substrate disruption. We conclude that E_F movement is controlled by the coupling between adatom-induced states and those of the substrate at low temperature, with strong dependence on the bulk doping of the semiconductor.

Important studies of metal-semiconductor interface formation have shown that Fermi-level evolution for metal overlayers on GaAs is strongly temperature dependent. Results to date have shown that E_F remains close to the conduction-band minimum (CBM) for low-temperature (60–200 K) atom deposition on n-type GaAs, but that it moves rapidly toward midgap for p-type GaAs, often overshooting its final position before stabilization.[1,2] These results have been interpreted in terms of isolated adatoms acting as donors, and recent calculations have correlated the magnitude of the overshoot with the adatom ionization potential.[3]

This paper demonstrates that these low-temperature studies present only part of a very interesting story. By changing the dopant concentration and type, we show that Fermi-level movement is actually symmetric for n- and p-type samples of comparable concentration. In the coverage region below 1–2 monolayers (ML), there are relatively small adatom-induced effects for low dopant concentrations but significant changes related to the enhanced adatom-semiconductor coupling at high dopant levels. This behavior is observed for unreactive (Ag), weakly reactive (Co), and highly reactive (Ti) adatoms, and there is analogous behavior for InP(110). Surface disruption and bulk defects play a secondary role in controlling band bending.

High-resolution synchrotron-radiation photoemission experiments were done at the Wisconsin Synchrotron Radiation Center using the Minnesota extended-range grasshopper monochromator and beamline. The details of the experimental system have been given elsewhere.[4] Briefly, single crystals of GaAs(110) were cleaved at 60 K at an operating pressure of $\sim 5\times10^{-11}$ Torr. To eliminate spurious effects due to partially pinned clean surfaces, only those cleaves with E_F within 60 meV of the CBM, or valence-band maximum (VBM) were used. The bulk samples were grown by the horizontal Bridgeman technique, and were obtained from Crystal Specialties and from Metal Specialties (MCP Electronics, Ltd.). The n-type (p-type) samples were Si (Zn) doped, and the doping concentrations were 2×10^{18} cm^{-3} [high doping (HD)] and 1×10^{17} cm^{-3} [low doping (LD)]. Manufacturers' specifications indicate etch-pit densities of $(5\text{–}19)\times10^{3}$ cm^{-2}, with no correlation between dislocation and doping concentrations. The measurements were conducted at 60 K, and sets of spectra were obtained under identical conditions for n-type and p-type samples with both LD and HD concentrations.

Adatom deposition was done from hot sources, with sample exposure to the vapor flux for time intervals following stabilization of the deposition rate at 1 Å/min or less. During deposition, the pressure was below 4×10^{-10} Torr for Ag and Co and below 2×10^{-10} Torr for Ti. Complete sets of Ga $3d$ and As $3d$ core-level spectra were acquired at each coverage with photon energies selected to give different surface sensitivities (mean-free paths λ of ~ 3.5 and ~ 7 Å). Valence-band spectra were used to investigate surface quality and the onset of metallicity.[1,2,5] Line-shape analysis of core-level emission using a nonlinear least-squares-fitting routine made it possible to separate the substrate components from adatom-induced components and to measure changes in band bending with precision of 30 meV.[4] Chemically-shifted components were more readily identified with the surface-sensitive spectra, and analysis of bulk- and surface-sensitive spectra enhanced the reliability in determining band-bending changes. For cleaved n-type and p-type GaAs surfaces at 60 K, the Ga $3d$ (and As $3d$) core-level energies were separated by ≥ 1.42 eV, indicating unpinned initial conditions (bandgap 1.52 eV at 60 K). The amount of material deposited is given as ML equivalents, referenced to the GaAs(110) surface density, 8.6×10^{14} atoms/cm^2, with 1.51 Å/ML for Ag, 0.97 for Co, and 1.56 for Ti.

Previous studies have shown that Ti disrupts ~ 6 Å of the GaAs(110) substrate at 300 K, that Ti–As bonding configurations form, that the intermixed region close to the buried interface is Ga deficient, and that there is As atom segregation to the free surface.[6] Detailed temperature-dependent studies have shown that the same amount of disruption occurs at 60 and 300 K, but that ki-

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netic processes involved with redistribution of the released semiconductor atoms are greatly reduced at 60 K.[7] The present studies show that adatom-induced chemical changes were indistinguishable for n-type and p-type samples, regardless of dopant concentration, as expected.

In Fig. 1(a) we show E_F movement in the surface band gap upon Ti deposition at 60 K onto HD and LD GaAs(110). The points represent bulk- and surface-sensitive spectra for both Ga 3d and As 3d core-level emission. There are almost no Ti-induced changes in E_F from 0.006 to $\sim$1 ML for LD n-type GaAs. Between 1 and 4 ML, E_F moves to its final position 0.67 eV below the CBM. For LD p-type GaAs, the movement of E_F is highly symmetric with that for LD n-type GaAs, with almost no change below $\sim$1 ML and then a step toward midgap. Although this step behavior has been observed previously for n-type GaAs, it has not been seen for p-type GaAs and the remarkable symmetry has gone unnoticed. For HD Ti/GaAs, E_F moves monotonically towards its final position with adatom deposition for both n-type and p-type GaAs, starting at the lowest coverage. For HD n-type GaAs, there is a vestigial step at the same coverage as for LD GaAs, $\sim$1 ML. We stress that core-level and valence-band analyses indicate equivalent substrate disruption for LD and HD n-type and p-type GaAs. Indeed, while Ti/GaAs is the most reactive system studied to date, the symmetry is clearly independent of surface reactivity and disruption.

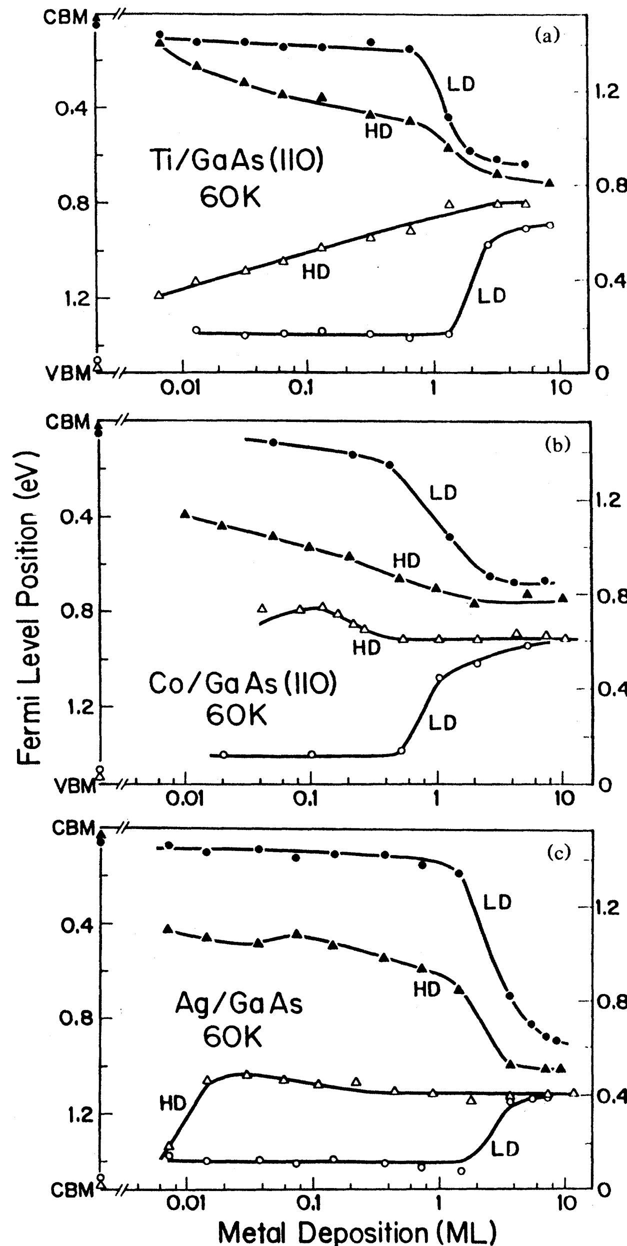

FIG. 1. Fermi-level position at the interface as a function of metal deposition at 60 K. Circles correspond to LD substrates (1×10^{17} cm^{-3}) and triangles correspond to HD ones (2×10^{18} cm^{-3}). The LD samples exhibit symmetric movement into the gap with a step at 1–2 ML. Vestiges of this step can be observed for HD n-type samples. The results for Ag/n-type GaAs at 60 K exhibit an undershoot equivalent to that observed for p-type GaAs at low temperature. The results of Fig. 1 are quite general, regardless of differences in reactivity and morphology.

To demonstrate the generality of this symmetric Fermi-level movement, we investigated Co and Ag atom deposition on GaAs(110) at 60 K. Previous studies have shown that Co induces limited disruption and forms an epitaxial bcc overlayer at 300 K.[8] At 60 K, an equivalent amount of disruption is observed, but liberated As atoms are kinetically trapped near the buried interface.[9] For Ag, atom deposition leads to spontaneous island formation at 300 K with no evident surface disruption. Thermally activated Ag surface diffusion is negligible at 60 K, and approximately layer-by-layer growth is observed.[1,2,10]

Figures 1(b) and 1(c) show the Co and Ag adatom-induced E_F movement. For LD n-type and p-type GaAs(110), there is little change at low coverage, but rapid shifting toward the final pinning position starting at $\sim$1 ML. For Co (Ag), the transition is completed by $\sim$6 ML ($\sim$10 ML). As for Ti/GaAs, the half-way point occurs at approximately the same coverage for LD n-type and p-type GaAs, emphasizing a common mechanism for each metal. In contrast, movement is evident by 0.01 ML for both metals for HD n-type GaAs, and like Ti, exhibits a vestigial step as E_F drops in the gap. The vestigial step for HD n-type GaAs, suggests that the mechanism responsible for movement into the gap at lower coverage is supplemented by that which causes the step for LD samples. For HD p-type GaAs, the previously observed overshoot of the Fermi-level position is seen at low coverage, followed by relatively little change.[1,2] We note that HD p-type GaAs results do not show a step near $\sim$1 ML because of the overshoot but that the corresponding HD step is observed for Au/p-type GaAs (to be discussed elsewhere). The Ag results for HD n-type GaAs also reveal an intriguing *undershoot* with a minimum for Ag depositions of $\sim$0.03 ML that is the counterpart of the overshoot for HD p-type GaAs.

In considering effects which might account for the Fermi-level movement of Fig. 1, we note that the dopant-concentration dependence is *opposite* from that expected for the charged defects at the surface. In particular, vari-

ations in the dopant-concentration would lead to better screening for HD samples than LD samples, inhibiting Fermi-level movement. Such a dependence is clearly not observed because the LD samples respond more slowly.

We propose that the results of Fig. 1 can be understood from the perspective of electron dynamics and transport involving overlayer states and states of the semiconductor. Our model suggests that the formation of a depletion region will only occur when charge transfer is possible. The limiting factor is not the existence of states formed by chemical bonding, but rather their occupancy by electrons contributed by the adatoms and electrons from the semiconductor conduction band.

Electron transport can be understood in terms of Fig. 2 where an adatom-induced state at energy E_a develops at a fixed energy relative to the CBM, independent of the position of the Fermi level. (That this energy referencing is correct can be demonstrated by investigating the position of adatom-energy levels for *n*-type and *p*-type GaAs, as will be discussed elsewhere using the *d*-band maximum for Ag or the Al 2*p* core levels.) In the presence of these adatom-induced states, semiconductor band bending occurs when electron exchange is possible and the condition of Fermi-level equilibrium can be achieved. When the overlap between the wave functions of the adatom-induced state and substrate is very small, then the wave function of the adatom-induced state can be treated as localized, giving a well-defined energy E_a. In this case the occupation of that state is either zero or one, the energy needed to add or remove an electron is large, and there will be no band bending (i.e., no redistribution of charge so that the adatom level is effectively neutral). When there is overlap of the wave functions of the adatom-induced state and the substrate, tunneling between the two states can occur and the wave functions become delocalized. The result is a broadening of the energy level, as shown in Fig. 2, and a lowering in energy of its centroid.[11-13] In this case, the adatom-induced state assumes the role of a donor or an acceptor that is activated by the delocalization process. Electron tunneling through the barrier is a natural consequence of such wave-function overlap, and an arbitrarily small amount of charge transfer can occur to accommodate movement of the Fermi level. Indeed, such coupling of adsorbate wave function to metallic substrates was discussed long ago by Newns,[11] Gadzuk,[12] and Lang and Williams.[13] To our knowledge, such a model has not been considered for adatoms interacting with semiconductor surfaces.

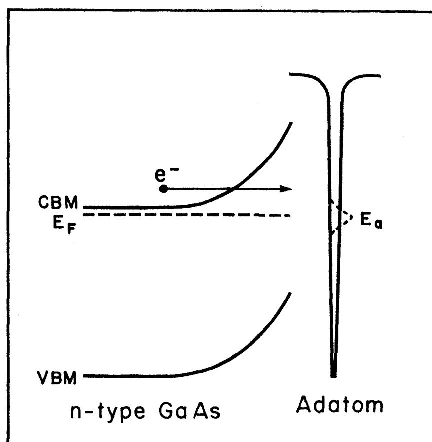

FIG. 2. Schematic of the tunneling process responsible for differences in low-coverage Fermi-level movement for high- and low-doped GaAs. This tunneling depends strongly on the dopant concentration and temperature. For an isolated adatom, E_a is sharp and tunneling is suppressed. Overlap of the adatom-induced state with states of the semiconductor produces broadening and tunneling.

The results of Fig. 1 show that the coupling between the adatom-induced levels and the semiconductor is small at low coverage for LD but is much larger for HD. This can be understood in terms of tunneling because it is well known that tunneling becomes important in metal-semiconductor junctions at HD. In Si, for example, tunneling dominates thermionic emission across a Schottky barrier for a doping concentration of 10^{17} cm^{-3} at 100 K.[14] Using the Wentzel-Kramers-Brillouin (WKB) approximation, the transmission probability for tunneling can be calculated through

$$P = \exp[-(4\pi\Phi/h)(m^*\epsilon/N)^{1/2}] ,$$

where Φ is the amount of band bending, N is the dopant concentration, and ϵ is the static dielectric constant of the semiconductor.[15] For GaAs with a band bending of 0.3 V, the transmission probability for the LD samples (10^{17} cm^{-3}) is more than 15 orders of magnitude smaller than that for the HD material (2×10^{18} cm^{-3}). This provides a natural explanation for the neutral character of adatoms on LD samples compared to HD samples, regardless of the formation of a disrupted region or novel interface states.

There are several factors which provide corrections to this simple tunneling picture. First, ionized impurities in the semiconductor may affect the electron occupancy of metal adatoms through Coulomb interaction. Adatoms near ionized donors will be somewhat more likely to receive and hold an electron than adatoms which are far from any ionized donors. Second, the inclusion of image-force effects would lower the barrier. Third, at high dopings impurity atoms tend to interact with each other (Mott transition). The impurity ionization energy then becomes smaller and disappears completely above a critical density. Fourth, the above equation considers only tunneling by carriers from outside the depletion region at the energy position of the CBM (for *n*-type) or the VBM (for *p*-type), whereas the actual energy distribution of these carriers will certainly affect the tunneling probability.[16] While the above factors are expected to enhance the tunneling, their relative importance for the low-coverage band-bending behavior needs further theoretical investigation.

This tunneling model also agrees with the room-temperature band-bending trends. At 300 K, previous results have demonstrated the formation of metal clusters or the tendency to form patches of the reaction products.[8] Hence, the amount of delocalization of the adatom-

induced states is greater at any given (low) coverage than at 60 K. We expect that this would enhance the coupling of the adsorbate-induced levels with the semiconductor. At the same time, the contribution from thermionic emission increases exponentially and tunneling also increases, leading to rapid pinning at room temperature.

The high coverage results can be understood in terms of metallization of the overlayer[1,2,5] with the transition from isolated atoms to a metallic character occuring near 1 ML. The resulting change in Fermi-level position is then related to the delocalization of adatom states via adatom–adatom bonding. Such delocalization makes it possible to couple these metallic states with the semiconductor regardless of the dopant concentration, with the exchange of incremental amounts of charge to accommodate E_F movement. The effect is most obvious for LD GaAs because of the small band bending at low coverages. The sharp step shows the importance of adatom-adatom interaction even for HD.

The final E_F positions are not identical, as would be expected based on discussions of bulk metal-semiconductor interfaces by Zur, McGill, and Smith.[17] (For Hd GaAs, the final values are within 0.12 eV of each other for Ti, 0.16 eV for Co, and 0.10 eV for Ag after deposition of ~10 ML. For LD GaAs, the final positions are separated by 0.2–0.25 eV.) At present, there is no clear explanation for the dopant-dependent final pinning positions. We note that preliminary results for *n*-type GaAs doped at 10^{16} cm^{-3} show that E_F lies even closer to the CBM at low coverage and the drop in E_F occurs at higher depositions, and we speculate that differences may be related to the width of the depletion region. In that case, the transport of charge to the surface may be sufficiently poor so that final surface Fermi-level positions increasingly deviate from the expected common level for *n*-type and *p*-type doped samples. Corrections of the sort described by Tang and Freeouf[18] to account for the finite probe depth of the measurements, shift the HD results toward each other a greater amount than the LD results. They will not lead to a common final Fermi-level position.

We note that the calculations of Mönch[19] and Klepeis and Harrison[20] implicitly assumed that charge transfer was possible and then predicted the energy positions of the adatom-induced levels. Therefore, those calculations are most applicable to the HD regime of Fig. 1. Klepeis and Harrison reproduced the observed step for *n*-type GaAs at ~1 ML and the overshoot for *p*-type GaAs. Reevaluation to take into account the symmetric behavior for LD *n*-type and *p*-type GaAs may shed light on the coupling mechanism, and should recognize that low-temperature deposition leads to surface disruption.

The results of Fig. 1 are quite general for reactive and nonreactive metal GaAs(110) and equivalent behavior has been obtained for InP(110). Moreover, vestigial steps have been seen at 60 K for Au adatoms on LD *n*-type and *p*-type GaAs. We conclude that the dependence of E_F on bulk dopant concentration reveals the importance of coupling of the semiconductor and adatom-induced wave functions in the low-coverage regime. In the high-coverage limit, adatom–adatom bonding and metallic delocalization are responsible for charge transfer at the interface. In all cases, delocalization of the adatom wave functions is critical for charge redistribution and related Fermi-level movement.

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[1]K. Stiles, A. Kahn, D. G. Kilday, and G. Margaritondo, J. Vac. Sci. Technol. B **5**, 987 (1987); K. Stiles, S. F. Horng, A. Kahn, J. McKinley, D. G. Kilday, and G. Margaritondo, J. Vac. Sci. Technol. B **6**, 1392 (1988), and references therein.

[2]R. Cao, K. Miyano, T. Kendelewicz, K. K. Chin, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. B **5**, 998 (1987); For a detailed discussion, see W. E. Spicer *et al.*, in *Metallization and Metal-Semiconductor Interfaces,* NATO Advanced Study Institute, Series B Physics, Vol. 195, edited by I. P. Batra (Plenum, New York, 1989).

[3]W. Mönch, J. Vac. Sci. Technol. B **6**, 1270 (1988).

[4]G. D. Waddill, C. M. Aldao, I. M. Vitomirov, Y. Gao, and J. H. Weaver, J. Vac. Sci. Technol. (to be published); For discussion of line-shape analysis, see J. J. Joyce, M. del Giudice, and J. H. Weaver, J. Electron. Spectrosc. (to be published).

[5]M. Prietsch, M. Domke, C. Laubschat, and G. Kaindl, Phys. Rev. Lett. **60**, 436 (1988); R. Ludeke, G. Jezequel, and A. Taleb-Ibrahimi, *ibid.* **61**, 601 (1988).

[6]M. W. Ruckman, M. del Giudice, J. J. Joyce, and J. H. Weaver, Phys. Rev. B **33**, 2191 (1986); D. M. Hill, F. Xu, Z. Lin, and J. H. Weaver, *ibid.* **38**, 1893 (1988).

[7]C. M. Aldao, G. D. Waddill, S. G. Anderson, and J. H. Weaver (unpublished) have studied 60 and 300 K Ti/GaAs(110) interfaces.

[8]F. Xu, J. J. Joyce, M. W. Ruckman, H.-W. Chen, F. Boscherini, D. M. Hill, S. A. Chambers, and J. H. Weaver, Phys. Rev. B **35**, 2375 (1987); scanning tunneling microscopy measurements for the related Fe/GaAs(110) system have been reported by J. A. Stroscio, P. N. First, D. T. Pierce, R. A. Dragoset, and R. J. Celotta, J. Vac. Sci. Technol. (to be published).

[9]G. D. Waddill, I. M. Vitomirov, C. M. Aldao, and J. H. Weaver, Phys. Rev. Lett. **62**, 1568 (1989).

[10]G. D. Waddill, C. M. Aldao, I. M. Vitomirov, S. G. Anderson, C. Capasso, and J. H. Weaver, J. Vac. Sci. Technol. (to be published), and references therein.

[11]D. M. Newns, Phys. Rev. **178**, 1123 (1969).

[12]J. W. Gadzuk, Surf. Sci. **6**, 133 (1967).

[13]N. D. Lang and A. R. Williams, Phys. Rev. B **18**, 616 (1978).

[14]C. Y. Chang and S. M. Sze, Solid State Electron. **13**, 727 (1970).

[15]S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981), Chap. 5.

[16]C. R. Crowell and V. L. Rideout, Solid State Electron. **12**, 89 (1969).

[17]A. Zur, T. C. McGill, and D. L. Smith, Phys. Rev. B **28**, 2060 (1983).

[18]J. Y.-F. Tang and J. L. Freeouf, J. Vac. Sci. Technol. B **2**, 459 (1984).

[19]W. Mönch, Europhys. Lett. **7**, 275 (1988).

[20]J. E. Klepeis and W. A. Harrison, J. Vac. Sci. Technol. (to be published); and (private communication).