Absence of Fermi level pinning at metal-$In_xGa_{1-x}As$ (100) interfaces

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Soft x-ray photoemission spectroscopy measurements of clean, ordered $In_xGa_{1-x}As$ (100) surfaces with Au, In, Ge, or Al overlayers reveal an unpinned Fermi level across the entire In alloy series. The Fermi level stabilization energies depend strongly on the particular metal and differ dramatically from those of air-exposed interfaces. This wide range of Schottky barrier height for III-V compounds is best accounted for by a chemically induced modification in metal-alloy composition.

Schottky barrier formation at metal interfaces with III-V compound semiconductors has been of considerable ongoing interest because of the apparently weak dependence of barrier height on metal work function and its consequences for high-speed and optoelectronic devices.[1] Fundamental studies of Schottky barrier mechanisms for III-V compounds have been directed primarily to GaAs and especially the (110) cleavage surface of bulk single crystals. In this case, the energy at which the surface Fermi level E_F stabilizes appears to be relatively insensitive to the particular metal contact and to ambient contamination, lying in a range of only a few tenths of eV near the band-gap center. To account for this E_F "pinning," researchers have proposed gap states due to defects formed by metal atom condensation,[2] alloy work functions involving As precipitates,[3] chemically formed dipole layers,[4] and metal-induced gap states defined by the semiconductor band structure[5] or by chemisorption and charge transfer involving metal atoms and clusters.[6] Studies of InP (110)[7] and GaAs (100) metal interfaces suggest somewhat wider ranges of E_F gap position which are sensitive to chemical changes on an atomic scale.[8–10]

Until now, the ternary alloy series $In_xGa_{1-x}As$ has also been viewed in terms of a narrow E_F "pinning" range.[11] This is suggested by capacitance versus voltage (C-V) measurements on Schottky barrier diodes[12] [air-exposed, etched $In_xGa_{1-x}As$ (100) surfaces with Au contacts] and gate-controlled galvanometric measurements on metal-insulator-semiconductor (MIS) capacitor and transistor test structures.[13] These data have been used to support theoretical calculations of anion vacancies[14] or antisite (cation replacing anion)[15] defect states.

Here we use soft x-ray photoemission spectroscopy (SXPS) measurements of metals on clean, ordered $In_xGa_{1-x}As$ (100) surfaces to demonstrate that the surface E_F stabilization energy (and thereby the band bending) depends strongly on the particular metal and that, for $x > 0$, the range of E_F movement is comparable to or greater than the band gap. For the same metal on different alloys, we observe regular trends in E_F position with respect to the band edges which effectively contradict the models based on simple vacancy or antisite defects as well as the "common-anion rule"[16] of III-V barrier formation. Instead, the results suggest that E_F is not "pinned" by interface states but that interface chemical reaction and diffusion lead to a range of metal-alloy compositions whose work functions determine the E_F gap position.

$In_xGa_{1-x}As$ layers 7500 Å thick ($n = 5\times10^{16}$ Si/cm^3) were grown by molecular beam epitaxy (MBE) over 2000 Å $In_xGa_{1-x}As$ ($n = 10^{19}$ Si/cm^3) on top of 1000 Å GaAs ($n = 10^{19}/cm^3$) and an n^+ GaAs (100) substrate. This configuration provided unstrained $In_xGa_{1-x}As$ (100) films with Ohmic contacts. Following growth, the specimens were capped with As as protection against ambient contamination. Using a sequence of vacuum annealing steps,[17] we desorb this As cap, leaving clean and ordered (1×1) surfaces as determined from valence-band photoemission spectroscopy and low-energy electron diffraction, respectively. The resultant surface appeared not to have an excess of surface As as gauged by surface versus bulk (photoelectron kinetic energy 50–100 eV vs 10–20 eV)[18] ratios of Ga $3d$ and As $3d$ SXPS core level intensities at appropriate excitation energies. The energies of SXPS features with varying alloy concentration agree systematically and reproducibly with the changes in semiconductor band gap.[19] Thus, if we assume a constant E_F position with respect to the band edges for each clean alloy (for $n = 5\times10^{16}/cm^3$, $E_C - E_F \sim 0.1$ eV), the SXPS valence-band edges exhibit the correct decrease in band gap with increasing x_{In} to within ± 0.17 eV. For each alloy composition, $E_C - E_V$ is reproducible to within ± 0.05 eV. We evaporated metals in ultrahigh vacuum (base pressure 8×10^{-11} Torr) from W filaments (pressure rise no higher than mid 10^{-9} Torr) and monitored depositions with a quartz crystal oscillator.

We have measured the rigid As $3d$, Ga $3d$, and In $4d$ core level shifts as a function of Au, Al, In, and Ge depositions for $In_xGa_{1-x}As$, where $x = 0$, 0.25, 0.50, 0.75, and 1.00. Figure 1 illustrates surface-sensitive spectra for As $3d$ and Ga $3d$/In $4d$ core levels obtained with 100 and 80 eV, respectively. Rigid shifts of all core levels with increasing metal deposition correspond to E_F shifts with respect to the band edges. In general, the relatively sharp In $4d$ and Ga $3d$ peak features provided clearer indications of E_F movement than the As $3d$ feature. Figure 1 illustrates these features for atoms localized within the top few angstroms of the deposit-

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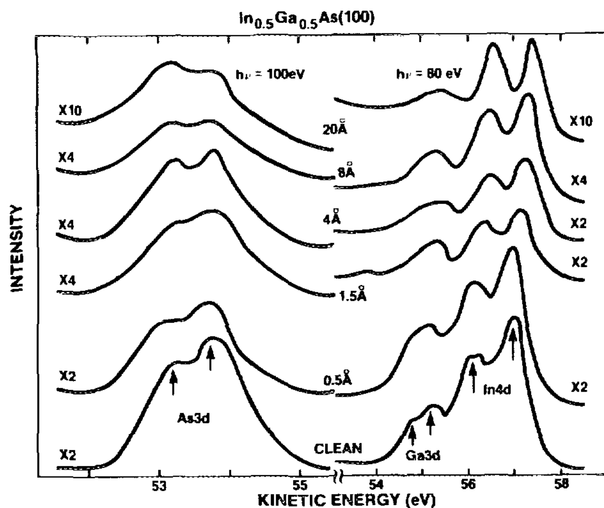

FIG. 1. SXPS core level spectra for As $3d$ at $h\nu = 100$ eV and Ga $3d$ and In $4d$ at $h\nu = 80$ eV as a function of increasing Au deposition.

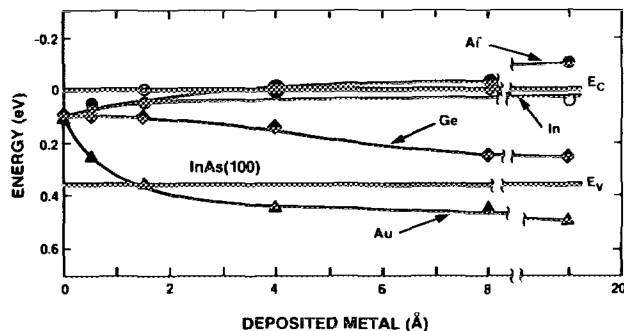

FIG. 2. Fermi level movements for clean InAs (100) as a function of Au, In, Ge, or Al deposition.

ed surface. The 0.3 eV rigid shift to higher kinetic energy corresponds to an E_F movement toward the valence-band maximum E_V. Integrated peak areas of these three structures reveal a slower attenuation of the As $3d$ peak with Au coverage, indicating As outdiffusion. Indeed the As $3d$ spectra display at least one additional component at lower kinetic energy due to Au deposition, corresponding to dissociated As. The As $3d$ and Ga $3d$/In $4d$ spectra obtained with $h\nu = 60$ and 40 eV respectively yield more bulk-sensitive spectra which minimize any surface chemical effects on core line shape and whose rigid spectral shifts agree with those of Fig. 1. In general, we used both surface and bulk-sensitive spectra to determine the rigid core level shifts reported here.

The E_F shifts with metal coverage extracted from SXPS features indicate a wide range of Schottky barrier positions for metals on $In_xGa_{1-x}As$ (100). For example, Fig. 2 illustrates E_F position as a function of metal coverage on InAs (100) for Au, Al, In, and Ge deposition. Each metal exhibits a different E_F movement with increasing metal coverage. Furthermore, the thickness over which each E_F position evolves to its final value range from 1 to 10 Å, reflecting chemical and electronic differences in the metal-semiconductor interaction. At 20 Å metal coverage, the final E_F positions extend from above the conduction-band minimum E_C to below E_V over a range of 0.5 eV. By comparison, the InAs band gap E_g is only 0.36 eV. Analogous plots for other alloy semiconductors yield ranges of 0.85 eV for $In_{0.75}Ga_{0.25}As$ ($E_g = 0.53$ eV), 0.65 eV for $In_{0.50}Ga_{0.50}As$ ($E_g = 0.76$ eV), 0.67 eV for $In_{0.25}Ga_{0.75}As$ ($E_g = 1.05$ eV), and ~ 0.4 eV for GaAs ($E_g = 1.43$ eV). Thus the range of E_F stabilization energies becomes comparable to or greater than the semiconductor band gap with increasing In alloy concentration.

The E_F stabilization energies for a given metal on different alloy semiconductors follow regular trends with respect to the band edges. Figure 3 illustrates these trends for Au, Al, and In across the $In_xGa_{1-x}As$ (100) alloy series. Here, the valence-band energies are referred to a common vacuum level as determined by photoemission threshold measurements[20] (e.g., 5.42 eV for InAs and 5.56 eV for GaAs). The wide E_F ranges for each In alloy demonstrate that E_F is not "pinned." Furthermore, the E_F trends appear to parallel the conduction band, especially for In and Al. The data are in reasonable agreement with what little results have been measured previously for clean interfaces. Grant *et al.* measured an $E_C - E_F$ of 0.75 eV for Au on GaAs (100) as well as a range of $E_C - E_F$ energies ranging from 0.75 to 0.2 eV with surface treatment.[8] The significantly higher position of In versus Au ($E_C - E_F = 0.35$ vs 0.75 eV) for GaAs (100) agrees with SXPS results of Daniels *et al.*[21] for cleaved GaAs (110) (e.g., 0.4 vs 0.9 eV[2]).

There is a large discrepancy between those ultrahigh vacuum results for InAs and InGaAs alloys and the previous air-exposed results,[12,13] which showed E_F pinning within the conduction band for Au on InAs and a relatively constant position with respect to E_V across the entire alloy series. Also, Baier *et al.*[22] have measured an E_F position 0.13 eV above the conduction-band edge for both cleaved and oxidized InAs (110). To address these apparent differences, we have performed SXPS experiments for Au on MBE-grown InAs (100), thermally cleaned and then exposed to air. Under these conditions, E_F indeed stabilized within the conduction band. Similarly, we measured for In on thermally cleaned air-exposed $In_{0.50}Ga_{0.50}As$ (100) an E_F stabilization 0.25 eV below E_C, again in agreement with Kajiyama *et al.*[12] Also supporting our results are Schottky barrier data

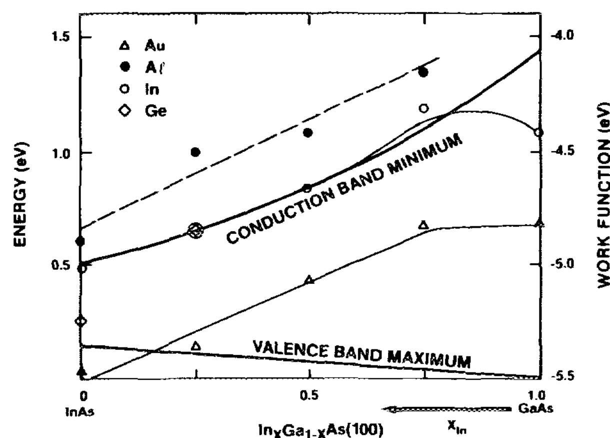

FIG. 3. Fermi level stabilization energies for Au, In, Ge, and Al deposited on clean $In_xGa_{1-x}As$ (100), $0 \leq x \leq 1$. Left-hand scale relative to GaAs valence-band maximum. Right-hand scale relative to vacuum level.

for MBE-deposited Al on n-$In_{0.50}Ga_{0.50}As$ (100), which display Ohmic behavior.[23] The apparent discrepancy between our clean InAs (100) and Baier's cleaved (110) results is likely due to the different surface preparations, i.e., As passivation and subsequent reevaporation for (100) MBE-grown versus cleavage for (110) melt-grown InAs. An analogous difference in E_F movement between (110) melt-grown and (100) MBE-grown surfaces has already been reported for GaAs.[24]

The E_F trends for different metals in Fig. 3 are at variance with a number of Schottky barrier models. The large energy differences with metals do not support models based on "pinning" in a narrow energy range, where the effect of the metal is secondary. These include models involving high densities of closely spaced defect energy levels[2] or metal-induced state "pinning" at a midgap position.[5] Indeed, the latter yields a large error for the Au-InAs (100) E_F position, even after taking the metal electronegativity and band structure effects into account. The E_F movements parallel to the conduction band are contrary to theoretical calculations of native defects reported thus far. Both simple vacancies[14] and anion-on-cation antisite defects[15] display trends which parallel the valence rather than the conduction band and which lie above the conduction band for $x_{In} < 0.5$. Within a localized state model, the conduction-band trends are consistent only with cation-derived states. Finally, the conduction-band trend in Fig. 3 is contrary to a common anion rule,[16] where the same $E_C - E_F$ would obtain for all III-V compounds with the same anion. Hence, a unified theoretical model of all experimental observations to date (let alone a predictive model) is not yet at hand.

Several studies of $Ga_{0.47}In_{0.53}As$ MIS structures suggest that the densities of any interface states on dielectric-coated GaInAs surfaces are relatively low and are reduced further by thermal annealing.[25,26] Nevertheless, it was argued that the E_F position depended on the position and density of surface donors and acceptors. Without involving such surface charge states, one can account for the observed E_F stabilization energies via differences in overlayer work function. The trends in Fig. 3 do not reflect pure metal work function values, for which the stabilization energies would be at constant energies below the vacuum level. Instead they are accounted for by overlayer work functions of changing composition.

Based on the relative composition of outdiffusing species observed via SXPS, we observe a trend with Au on $In_xGa_{1-x}As$ (100) from an As-rich to an *As-deficient* interface with increasing x_{In}.[17] This is in sharp contrast to both In and Al on $In_xGa_{1-x}As$ (100), where we observe a trend toward an increasingly *As-rich* interface with increasing x_{In}.[17] On the premise that the interface work function varies with increasing x_{In} from $\varphi_{As} = 4.8$ eV (Ref. 3) to $\varphi_{Au} = 5.2$–5.4 eV (Ref. 27) for Au overlayers and varies from $\varphi_{In, Al, Ga} \sim 4.1$–$4.3$ eV (Ref. 27) to $\varphi = 4.8$ eV for In or Al overlayers, one obtains reasonable fits to the data points in Fig. 3 using only straight lines (not shown) between end point values of work function (right-hand scale). Higher φ interfacial Ga versus In may account for the In-GaAs variation.[17] Thus, we are able to account for a large set of interface data on both an absolute and relative scale using only a classical work function approach and observations of interface chemical species. Hence, chemically induced changes in metal-alloy composition rather than interface defect levels appear to be the most direct explanation for the large range of E_F stabilization energies for metals on $In_xGa_{1-x}As$ alloys.

Beyond any theoretical model relating the position of the equilibrium Fermi level and Schottky barrier formation, the data presented here yield an unambiguous result: within the $In_xGa_{1-x}As$ alloy system, the metal-semiconductor barrier depends upon the chemically induced modification of the interface.

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[1] A. G. Milnes, *Semiconductor Devices and Integrated Electronics* (Van Nostrand, New York, 1980).

[2] W. E. Spicer, I. Lindau, P. Skeath, C. Y. Su, and P. Chye, Phys. Rev. Lett. **44**, 420 (1980).

[3] J. L. Freeouf and J. M. Woodall, Appl. Phys. Lett. **39**, 727 (1981).

[4] L. J. Brillson, J. Vac. Sci. Technol. **16**, 1137 (1979).

[5] J. Tersoff, Phys. Rev. B **32**, 6968 (1985).

[6] R. Ludeke, T.-C. Chiang, and T. Miller, J. Vac. Sci. Technol. **B 1**, 581 (1983).

[7] R. H. Williams, V. Montgomery, and R. R. Varma, J. Phys. C **11**, L735 (1978).

[8] R. W. Grant, J. R. Waldrop, S. P. Kowalczyk, and E. A. Kraut, J. Vac. Sci. Technol. **19**, 477 (1981).

[9] L. J. Brillson, C. F. Brucker, A. D. Katnani, N. G. Stoffel, and G. Margaritondo, Appl. Phys. Lett. **38**, 784 (1981); C. F. Brucker and L. J. Brillson, *ibid.* **39**, 67 (1981).

[10] V. Montgomery, R. H. Williams, and G. P. Srivastava, J. Phys. C **14**, L191 (1981).

[11] W. E. Spicer and S. J. Eglash, in *VSLI Electronics: Microstructure Science* (Academic, New York, 1985), Vol. 10, p. 79.

[12] K. Kajiyama, Y. Mizushima, and S. Sakata, Appl. Phys. Lett. **23**, 458 (1973).

[13] H. H. Wieder, Appl. Phys. Lett. **38**, 170 (1981).

[14] M. S. Daw and D. L. Smith, Appl. Phys. Lett. **8**, 690 (1980).

[15] R. E. Allen and J. D. Dow, Phys. Rev. B **25**, 1423 (1982).

[16] J. O. McCaldin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. **36**, 56 (1976).

[17] L. J. Brillson, M. L. Slade, R. E. Viturro, M. Kelly, N. Tache, G. Margaritondo, J. M. Woodall, P. D. Kirchner, G. D. Pettit, and S. Wright (unpublished).

[18] M. P. Seah and W. A. Dench, Surf. Interface Analysis **1**, 2 (1979).

[19] E. W. Williams and V. Rehn, Phys. Rev. **172**, 798 (1969).

[20] J. van Laar, A. Huijser, and T. L. van Rooy, J. Vac. Sci. Technol. **14**, 894 (1977).

[21] R. R. Daniels, T.-X Zhao, and G. Margaritondo, J. Vac. Sci. Technol. A **2**, 831 (1984).

[22] H.-U. Baier, L. Koenders, and W. Mönch, J. Vac. Sci. Technol. (to be published).

[23] K. H. Hsieh, M. Hollis, G. Wicks, C. E. C. Wood, and L. F. Eastman, Inst. Phys. Conf. Ser. **65**, 165 (1983).

[24] P. Chiaradia, A. D. Katnani, H. W. Sang, Jr., and R. S. Bauer, Phys. Rev. Lett. **52**, 1246 (1984).

[25] H. H. Weider, A. R. Clawson, D. I. Elder, and D. A. Collins, IEEE Electron Device Lett. **EDL-2**, 73 (1981).

[26] H. H. Weider, Surf. Sci. **132**, 390 (1983).

[27] H. B. Michaelson, J. Appl. Phys. **48**, 4729 (1977) and references therein.