Absence of Fermi level pinning at metal-In\(_x\)Ga\(_{1-x}\)As (100) interfaces

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(Received 24 January 1986; accepted for publication 1 April 1986)

Soft x-ray photoemission spectroscopy measurements of clean, ordered In\(_x\)Ga\(_{1-x}\)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. 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, alloy work functions involving As precipitates, chemically formed dipole layers, and metal-induced gap states defined by the semiconductor band structure or by chemisorption and charge transfer involving metal atoms and clusters. Studies of InP (110) and GaAs (100) metal interfaces suggest somewhat wider ranges of \(E_F\) gap position which are sensitive to chemical changes on an atomic scale.

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

Here we use soft x-ray photoemission spectroscopy (SXPS) measurements of metals on clean, ordered In\(_x\)Ga\(_{1-x}\)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" of III-V barrier formation. Instead, the results suggest that \(E_F\) is not "pinning" 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\(_x\)Ga\(_{1-x}\)As layers 7500 Å thick \((n = 5 \times 10^{16} \text{Si/cm}^2)\) were grown by molecular beam epitaxy (MBE) over 2000 Å In\(_x\)Ga\(_{1-x}\)As \((n = 10^{19} \text{Si/cm}^2)\) on top of 1000 Å GaAs \((n = 10^{19} \text{Si/cm}^2)\) and an \(n^+\) GaAs (100) substrate. This configuration provided unstrained In\(_x\)Ga\(_{1-x}\)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, we desorb this As cap, leaving clean and ordered (1 x 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) 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. Thus, if we assume a constant \(E_F\) position with respect to the band edges for each clean alloy (for \(n = 5 \times 10^{16} \text{cm}^3\), \(E_C - E_F \approx 0.1 \text{eV}\)), the SXPS valence-band edges exhibit the correct decrease in band gap with increasing \(x\) to within \(\pm 0.17 \text{eV}\). For each alloy composition, \(E_C - E_V\) is reproducible to within \(\pm 0.05 \text{eV}\). We evaporated metals in ultrahigh vacuum (base pressure \(8 \times 10^{-11} \text{Torr}\)) from W filaments (pressure rise no higher than mid \(10^{-9} \text{Torr}\) 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\(_x\)Ga\(_{1-x}\)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.
ed surface. The 0.3 eV rigid shift to higher kinetic energy corresponds to an $E_F$ movement toward the valence-band maximum $E_F$. 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$_3$Ga$_{1-x}$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 $E_F$ 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$_3$Ga$_{1-x}$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 $E_F$ 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.$^{13}$ Also supporting our results are Schottky barrier data.
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 or metal-induced state “pinning” at a midgap position.\(^{25,26}\) 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\(^{27}\) and anion-on-cation antisite defects\(^{28}\) display trends which parallel the valence rather than the conduction band and which lie above the conduction band for $x_{\text{In}} < 0.5$. 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$_{0.5}$In$_{0.5}$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$_{0.5}$Ga$_{0.5}$As (100) from an As-rich to an As-deficient interface with increasing $x_{\text{In}}$.\(^{27}\) This is in sharp contrast to both In and Al on In$_{1-x}$Ga$_x$As (100), where we observe a trend toward an increasingly As-rich interface with increasing $x_{\text{In}}$.\(^{27}\) On the premise that the interface work function varies with increasing $x_{\text{In}}$ from $\varphi_{\text{As}} = 4.8$ eV (Ref. 3) to $\varphi_{\text{Al}} = 5.2-5.4$ eV (Ref. 27) for Au overlayers and varies from $\varphi_{\text{In}}, \varphi_{\text{Ga}} \sim 4.1-4.3$ 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 $\varphi$ interfacial Ga versus In may account for the In-GaAs variation.\(^{27}\) Thus, we are able to account for a large set of interference 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$_{1-x}$Ga$_x$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$_{1-x}$Ga$_x$As alloy system, the metal-semiconductor barrier depends upon the chemically induced modification of the interface.

Partial support by the Office of Naval Research (ONR N00014-80-C-0778) is gratefully acknowledged. The Synchrotron Radiation Center is supported by the National Science Foundation. We wish to express special appreciation to the Aladdin staff for their outstanding efforts in implementing these experiments.


\(^{27}\) H. B. Michaelson, J. Appl. Phys. 48, 4729 (1977) and references therein.