

PHOTOEMISSION STUDIES OF ATOMIC REDISTRIBUTION AT COMPOUND SEMI-  
CONDUCTOR INTERFACES

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New phenomena at compound semiconductor interfaces reveal a general and systematic relationship between local atomic bonding and the chemical and electronic structure of the extended interface. Local bond strength and charge transfer determine stoichiometry of interdiffusion, measured electrical properties, and reacted width of the interface.

We have used the extreme surface sensitivity achievable with tunable synchrotron radiation, coupled with x-ray and UV sources, to probe with monolayer spatial resolution the rearrangement of semiconductor and metal atoms at their interface. Atomic rearrangements are extracted from peak intensities and chemical shifts of core and valence band features and are correlated with the Fermi level stabilization that occurs with less than a few monolayers of metal deposited on a UHV-cleaved semiconductor surface [1,2,3,4].

We have employed "interlayers" [5] of monolayer thickness to modify the microscopic bonding at compound semiconductor-Au interfaces and thereby to alter the macroscopic chemical structure of the junctions at room temperature. Figure 1 shows As 3d and In 4d core level spectra obtained with high surface sensitivity using 130 and 80eV incident photon energy respectively. For Au on cleaved InAs (110), significantly more As than In diffuses through the Au overlayer to the vacuum interface. This nonstoichiometry is reversed by a 10Å Al interlayer between the InAs and Au. Note the chemically-shifted peaks in Fig. 1 corresponding to free As (In) at higher (lower) binding energy without (with) the Al interlayer. Al interlayers produce similar effects at Au interfaces with GaAs(110), GaSb(110), and InP(110).

Monolayer thicknesses of Al, Ti, In, and Zn at interfaces of UHV-cleaved GaAs(110) [ $n=3 \times 10^{17}$  Te] with Au films produce dramatic modulations of the Ga vs. As diffusion into Au. Figure 2 illustrates the integrated Ga to As peak height ratio R as a function of Au overlayer thickness for various 10Å metal interlayers. Ga and As 3d core-level spectra were taken with  $h\nu = 130\text{eV}$  for Al, Ti, and Au studies. Ga and As 2p core-level spectra were taken with  $h\nu = 1486.65\text{eV}$  for Zn and In interlayers. The kinetic energies of all core levels lie in the range corresponding to minimum escape depth ( $\sim 4-6\text{\AA}$ ) [6], thereby yielding maximum surface sensitivity.

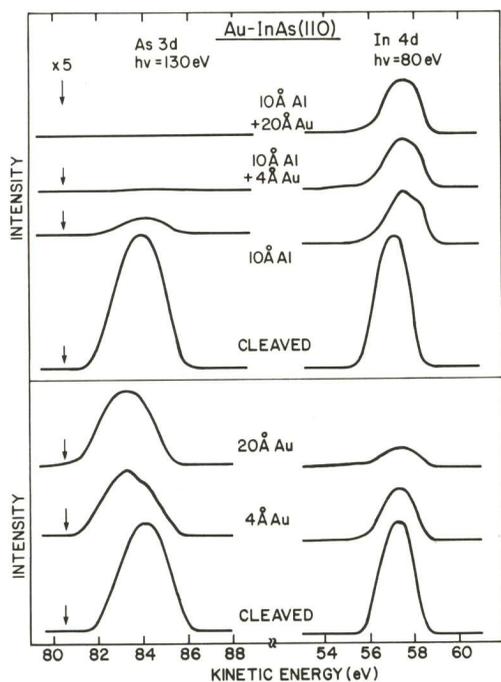


Fig. 1 As 3d and In 4d core-level spectra for various metal overlayers on cleaved InAs(110)

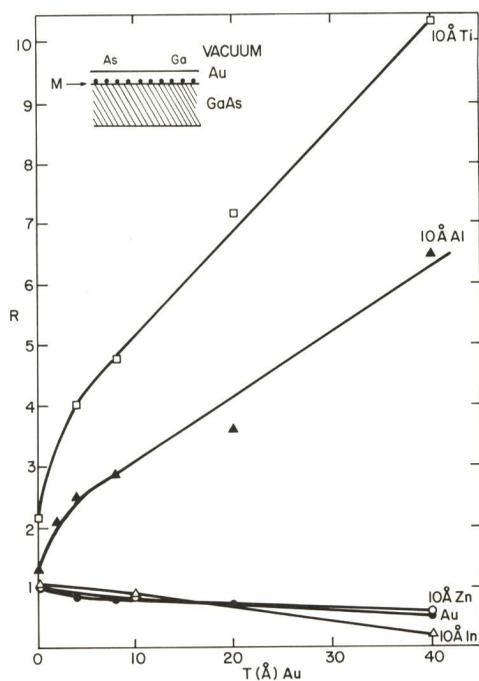


Fig. 2 Integrated Ga/As core-level intensity ratio  $R$  relative to cleaved GaAs surface vs. Au overlayer thickness  $T$  for different  $10\text{\AA}$  metal overlayers

The Ga and As concentrations within the metal overlayers depend both on the As-metal bond strength as well as the interface electric field induced by the initial metal chemisorption. These "chemical trapping" (CT) and electromigration (EM) [7] processes produce increases or decreases in  $R$  at the Au overlayer surface which depend on the interlayer metal. Both CT and EM processes act to increase  $R$  by over an order of magnitude for  $40\text{\AA}$  Au- $10\text{\AA}$  Al-GaAs relative to  $40\text{\AA}$  Au-GaAs. Here Al bonds strongly with interface As atoms (interface heat of reaction  $\Delta H_R = -0.43\text{eV/metal atom}$ ) [8] and produces a negative dipole on GaAs(110) (as measured by Kelvin probe techniques [3]) which further retards As outdiffusion. Conversely, In and Zn form no strong bonds with As ( $\Delta H_R = +0.13$  and  $+0.48\text{eV/metal atom}$  respectively) and induce positive dipoles on GaAs(110). For these metals, the reverse EM field and lower CT effects act to decrease  $R$  significantly. A similar decrease in cation/anion intensity ratio occurs at Au-CdS( $10\bar{1}0$ ) interfaces with Al interlayers, where Al also induces a positive dipole. Likewise, Au monolayers on GaAs(110) induce a positive dipole and an  $R$  decrease. Finally, Ti bonds strongly to As interface atoms ( $\Delta H_R = -0.82\text{eV/metal atom}$ ) yet induces a positive dipole on GaAs(110). The CT and EM are opposite in effect and appear to balance at  $\sim 1/2$  monolayer Ti coverage. At  $10\text{\AA}$  Ti coverage, however, the CT process clearly dominates:  $R$  ( $10\text{\AA}$ Ti) exceeds  $R$  ( $10\text{\AA}$ Al) at all Au coverages due to the stronger interface reaction and chemical trapping of As.

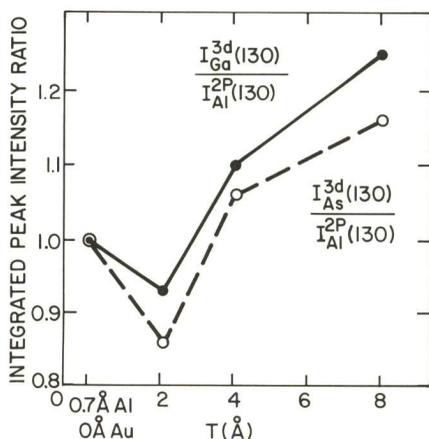


Fig. 3 Integrated Ga 3d, As 3d, and Al 2p core-level intensity ratios at  $h\nu = 130\text{eV}$  for Au/0.7ÅAl/GaAs(110)

Schottky barrier heights measured on these large area ( $0.25\text{cm}^2$ ) interfaces using I-V and C-V techniques are 0.4eV for  $R>1$  and grouped 0.1-0.2eV higher for  $R<1$ . These results suggest that interface states associated with Ga and As vacancies are separated by 0.1-0.2eV, consistent with Fermi level "pinning" observations at monolayer metal coverages [9]. Thus the strength of interface bonding and charge transfer determine the different Schottky barrier heights on the same n-type GaAs surface.

Coupling soft x-ray photoemission spectroscopy (SXPS) with submonolayer Al interlayers as markers [6], we demonstrate that Au diffuses into GaAs with initial monolayer deposition. Figure 3 illustrates the decrease in Ga 3d and As 3d vs. Al 2p core level intensity, consistent only with Au in diffusion. Al remains bonded at the GaAs interface since no chemical shift to lower binding energy is observed. With further Au coverage, both intensity ratios increase as Ga and As diffuse into the overlayer.

We observe analogous intensity variations for Au on GaSb(110), InP(110), InAs(110), and CdS(10 $\bar{1}$ 0) with initial Au deposition. For this wide range of semiconductors, measured interface states and Fermi level variations induced by Au monolayers must be associated with metal atoms within the semiconductor lattice rather than with semiconductor defects alone.

SXPS and XPS core level features also establish that compound semiconductor-metal interfaces are in general not atomically abrupt. Figure 4 illustrates that interface widths of semiconductor anions bonded to metal increase linearly with decreasing heat of interface reaction - from 3Å for Al-InP(110) to 22Å for Zn-GaAs(110) with

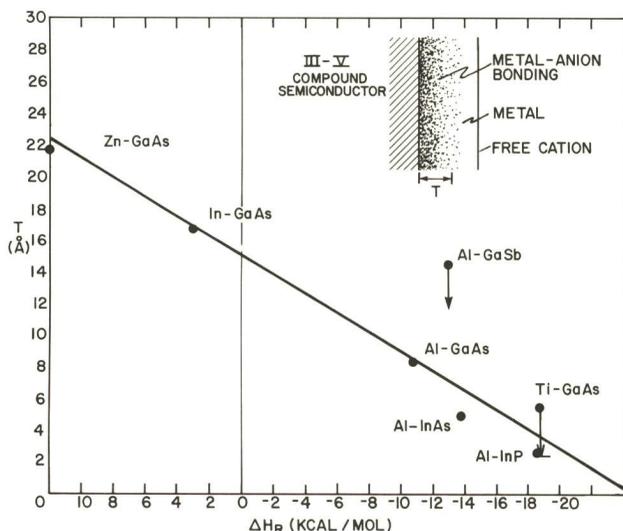


Fig. 4 Interface width vs. interface chemical reactivity for various metal/III-V compound semiconductor junctions

a linear slope of  $0.65\text{\AA}/\text{kcal}\cdot\text{mol}^{-1}$ . Interface width  $T$  is derived assuming that the metal overlayer attenuates the semiconductor anion concentration  $A$  as  $A = A_0 e^{-x/T}$ , where  $x$  is the overlayer thickness. The Al-GaSb width is probably lower than shown since metal-GaSb interfaces exhibit anomalously high Sb outdiffusion [4]. The monotonic decrease in interface width with increasing chemical reactivity shown in Fig. 4 describes not only different metals - Ti, Al, In, and Zn - on GaAs but also the same metal (Al) on different semiconductors - GaAs, GaSb, and InP. The interface width vs. reactivity curve predicts that hyperabrupt III-V compound semiconductor-metal junctions will be restricted to systems with strong metal-anion bonding and that interfaces with little chemical bond strength will be extended over tens of atomic layers.

In conclusion, the strength and character of microscopic interfacial bonding is a central factor in determining the chemical and electrical characteristics of the extended compound semiconductor-metal interface.

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Supported in part by NSF grant DMR 78-22205.

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