

Abruptness of Semiconductor-Metal Interfaces

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A predictive relation between reacted interface width and heat of interface reaction is presented for III-V-compound-semiconductor-metal interfaces. Soft-x-ray photoemission measurements reveal that the thickness of chemically reacted species and the extent and stoichiometry of atomic interdiffusion are determined by the strength and nature of metal-semiconductor bonding. Chemical bond strength directly influences the macroscopic electronic properties as shown by transport measurements.

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The interaction between metals and semiconductors at their microscopic interface plays a central role in Schottky-barrier (SB) formation. New electronic states and Fermi-level changes induced by monolayers or less of metal atoms on clean semiconductor surfaces in ultrahigh vacuum (UHV) can account for macroscopic barrier heights.¹ No states associated only with the semiconductor or with the metal account for these electronic features.¹ In this Letter, we have correlated the interface electronic features with atomic rearrangement and chemical bonding for a wide range of III-V-compound-semiconductor-metal interfaces. These interfaces exhibit a general relation between their widths and interface heats of reaction. The width of the region over which metal-semiconductor bonding occurs and the extent and stoichiometry of atomic interdiffusion are determined by the strength and nature of semiconductor-metal bonding. Correspondingly, these metal-semiconductor bond properties are found to determine the electronic barriers at the interface as measured by transport techniques.

We have used soft-x-ray photoemission spectroscopy (SXPS) and Al $K\alpha$ XPS to monitor core-level intensities and chemical shifts of semiconductor and metal atoms during the initial stages of SB formation. Interfaces were formed from clean, visually smooth semiconductor surfaces obtained by UHV cleavage with successively increasing coverages of metal deposited by evaporation. Pressure during evaporation rose from the 10^{-11} to the 10^{-10} Torr range.

For III-V compounds, anion intensities exhibit monotonic decreases with metal coverage which depended strongly on the particular metal-semiconductor combination. Figure 1 illustrates P

$2p$ integrated core-level intensities $I_p^{2p}(h\nu=185 \text{ eV})|_T$ obtained with incident photon energy $h\nu=185 \text{ eV}$ at a metal coverage T and normalized to the cleaved surface. The strong initial attenuation for metal coverage $T < 10 \text{ \AA}$ argues against island formation in all cases. We obtain similar effects for metals on GaAs, GaSb, and InAs. In contrast, cation intensities display no strong metal-coverage (T) dependence in general. At metal coverage T over several angstroms, cation peaks shift to lower binding energy, indicating dissociated cations within the metal. For all core levels reported here, $h\nu$ was selected to yield photoelectron kinetic energies of $\sim 50\text{--}100 \text{ eV}$. In this range, scattering lengths $\lambda_e \sim 4\text{--}6 \text{ \AA}$,² resulting in extreme surface sensitivity.

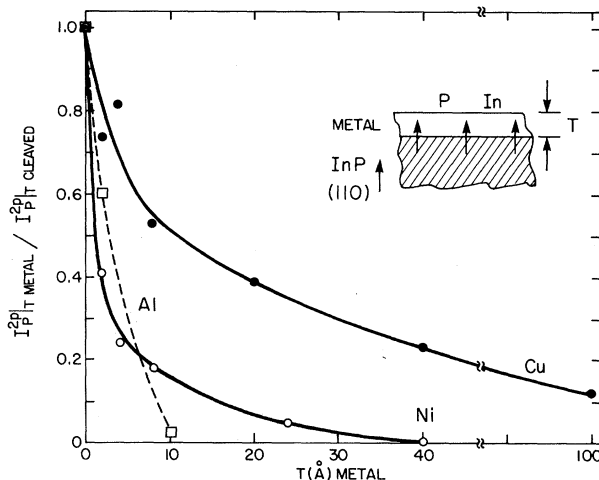


FIG. 1. P $2p$ core-level intensity $I_p^{2p}(185)$ at $h\nu=185 \text{ eV}$ vs metal overlayer coverage T on cleaved InP(110) for Cu, Al, and Ni.

We define the interface abruptness as the length over which cation-anion bonding changes to metal-metal bonding. For III-V compounds, this is just the metal overlayer thickness required to achieve a characteristic (e.g., $1/e$) anion attenuation. This attenuation depends strongly upon "chemical trapping" (CT) of the anion by metal atoms near the interface.³ In general, *the larger the heat of interface reaction* $\Delta H_R [\equiv H_F(\text{semiconductor}) - H_F(\text{metal-anion complex})]$,⁵ *the stronger the anion attenuation rate*. Here H_F values are a measure of bond strength⁶ but do not imply formation of stoichiometric bulk compounds at the interface.

The role of chemical trapping in forming semiconductor-metal interfaces is confirmed experimentally in Fig. 2, where interface widths T_0 vs ΔH_R increase with a slope of 0.65 kcal/mol. Here anion concentration $N_A = N_0 e^{-T/T_0}$, although this functional dependence is secondary. Figure 2 encompasses not only different metals with the same semiconductor (GaAs, InP), but different semiconductors with the same metal (Al). The apparently large Al-GaSb width is due to the anomalously large Sb outdiffusion at metal-GaSb interfaces. N_A values based on I_{anion} are not corrected for substrate photoemission at metal coverage $T < \lambda_e$. This correction is model dependent and reduces T values by $\sim 2-3 \text{ \AA}$. Thus Al-InP and Ni-InP interfaces are in fact atomically abrupt. Figure 2 predicts that hyperabrupt III-V-compound-semiconductor interfaces will be restricted to systems with strong metal-anion bonding ($\Delta H_R < -18 \text{ kcal/mol}$) and that interfaces

with little bond strength will be extended over tens of angstroms. Au-semiconductor junctions typically have width $>10 \text{ \AA}$ with $\Delta H_R \sim 0 \text{ kcal/mol}$ but diffusion is dominated by Au-cation versus anion bonding. The data in Fig. 2 are not due to any metal-dependent differences in island formation since (a) the same metal with different semiconductors exhibits a monotonic T_0 vs ΔH_R variation, (b) outdiffusion is not stoichiometric in general, and (c) T_0 does not scale with metal heats of condensation. To our knowledge, Fig. 2 is the first predictive guide to atomic structure at metal-semiconductor interfaces.

SXPS and XPS studies of CdS-, CdSe-, CdTe-, and ZnS-metal junctions further confirm that compound-semiconductor-metal interfaces are not abrupt in general. For these II-VI-compound interfaces, atomic redistribution depends systematically on interlayer bonding as well. However, the model shown in Fig. 2 cannot be applied because of the mixed metal-anion-cation bonding.⁷ Some evidence suggests that abruptness of Si-metal interfaces increases with reactivity as well.⁸

Chemical trapping can radically alter the stoichiometry of anion versus cation diffusion within metal overlayers. Figure 3 illustrates In 4d and As 3d core-level spectra taken at 80 and 130 eV, respectively, with and without an Al interlayer between InAs and increasing coverages of Au. The appearance of In and As for Au coverages well above the 4-6- \AA escape depth in Fig. 3(a) indicates that significant diffusion of both anion and cation occurs. An anomalously low Au 5d splitting indicates that the Au overlayer does not form islands below 8-20 \AA .⁹ The As 3d spectra exhibit broadening to lower kinetic energy, characteristic of free As formation. Figure 3(b) shows that the presence of a 10- \AA -thick Al interlayer strongly attenuates As diffusion into the Au overlayer. Furthermore, the In 4d spectra exhibit broadening to higher kinetic energy, characteristic of free In formation. The anion versus cation nonstoichiometry is now reversed. Since Al bonds strongly with As while Au does not, As intensity decreases dramatically in Fig. 3(b). Similar effects occur for GaAs, InP, and GaSb, varying monotonically with interlayer thickness. All intensities reported here are room-temperature equilibrium values which change $<10\%$ over $\sim 15 \text{ h}$.

Local charge transfer between metal and semiconductor surfaces with initial deposition can also affect semiconductor outdiffusion, particular-

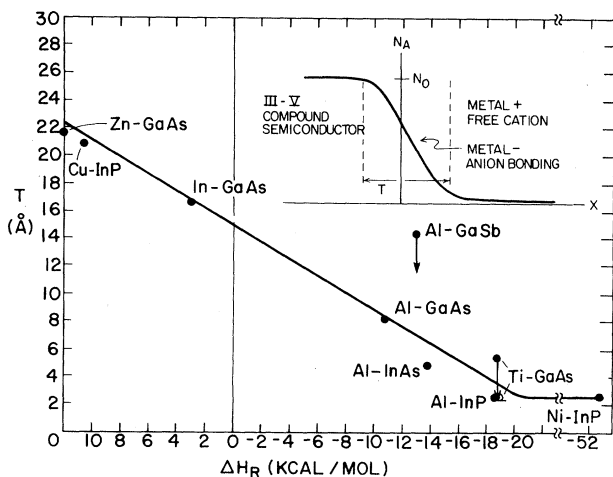


FIG. 2. Interface width vs interface heat of reaction for metal/III-V-compound-semiconductor junctions. Inset shows anion profile schematically.

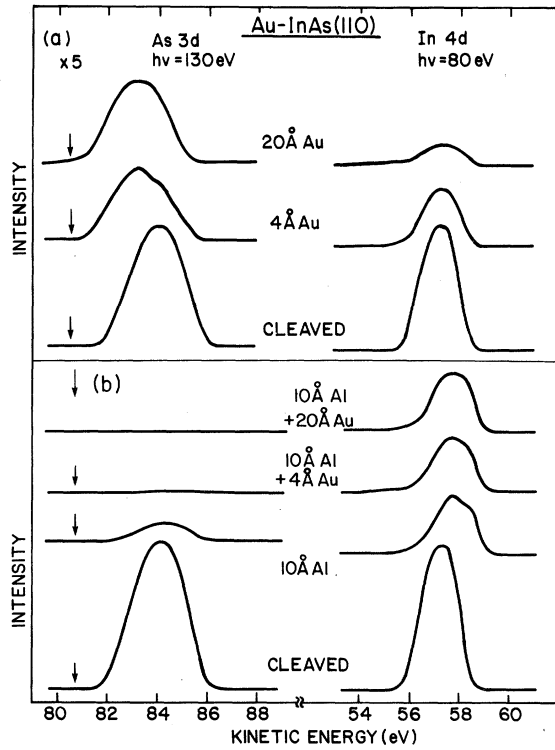


FIG. 3. In 4d and As 3d core-level spectra for (a) Au and (b) 10 Å Al + Au on cleaved InAs(110).

ly when metal-anion bonding is not strong. Dipole voltages ($\sim 0.1-0.3$ eV) set up across only a few angstroms can produce extremely high electric fields ($\sim 10^7$ V/cm) which can enhance or retard ionic motion near the interface. Table I contains evidence for such electromigration (EM). The positive dipole $\Delta\chi$ of Ti on GaAs(110) (positive end out of the surface, as measured by Kelvin techniques) acts to retard Ga-ion outdiffusion, while the large negative ΔH_R acts to re-

tard As outdiffusion. At low (0.7 Å) coverage, EM dominates— I_{Ga} decreases while I_{As} remains relatively unchanged with respect to the interlayer-free case. At higher coverages, CT dominates and I_{As} decreases dramatically. For Al, both CT and EM act to decrease I_{As} , as observed.³ I_{As} decreases less for 10 Å of Al than for 10 Å of Ti, scaling with ΔH_R . For In, Zn, and Au, no strong reactions occur and $\Delta\chi$ is expected to dominate. This is confirmed by the dominant I_{Ga} decreases which change relatively little between 2 and 10 Å. Similar EM effects are evident for metals on other III-V and II-VI compound semiconductors. For the 40 Å Au-10 Å metal-GaAs interfaces here, the resultant I_{Ga}/I_{As} ratios are >1 for Ti and Al; <1 for In, Zn, and no interlayer; and vary over two orders of magnitude between Ti and In. Thus the relative anion versus cation concentrations depend directly on the strength and nature of interface bonding.

Both CT and EM affect dN_A/dx , the profile of anion attenuation versus metal overlayer thickness (Fig. 2, inset). To first order, anion free energy at the interface may be written as $G = \mu_A N_A + Z_A e E x$, where μ_A , N_A , Z_A , and E are anion local chemical potential, concentration, ionic charge, and electric field. At thermal equilibrium, $\Delta G = 0$ so that $dN_A/dx = -N_A/\mu_A (d\mu_A/dx) - Z_A e E/\mu_A$. CT dominates at all but monolayer or lower coverages, and μ_A is linearly proportional to H_F ,⁶ so that $dN_A/dx \propto -dH_F/dx$, which is linearly proportional to ΔH_R . Thus the stronger is the interface metal-anion reaction, the sharper the profile, as observed.

The interface atomic structure determined by chemical bond strength directly influences macroscopic electronic properties. Schottky-barrier height (ψ_B) measurements by $I-V$ and $C-V$ techniques show that the defect model of Spicer *et al.*¹⁰

TABLE I. Ga or As 3d photoemission intensity $I(T)$ for 40 Å Au/(2 or 10 Å) metal interlayer/GaAs(110) interfaces with corresponding interlayer reactivity ΔH_R and dipole $\Delta\chi$. $I(T)$ is normalized to interlayer-free interface. Chemical trapping (electromigration) determines dominant $I(T)$ change—Ga vs As decrease—at 10 Å (2Å).

Interlayer	Bond	ΔH_R (eV/mol)	$\Delta\chi$ (eV)	I (2 Å)	I (10 Å)
None	Au-Ga	+ 0.66	+ 0.2	1.0 Ga	1.0 Ga
Ti	TiAs	- 0.82	+ 0.22	0.9 Ga ^a	0.03 As
Al	AlAs	- 0.43	- 0.24	0.4 As	0.1 As
In	InAs	+ 0.13	+ 0.14	0.2 Ga	0.1 Ga
Zn	Zn ₃ As ₂	+ 0.48	+ 0.2	0.6 Ga	0.5 Ga

^a 0.7 Å Ti.

must be integrated into a chemical framework which accounts for the ΔH_R dependence emphasized by Fig. 2 and Ref. 4. For example, φ_B of large-area (0.25 cm^2) Au-2 Å metal-GaAs(110) interfaces yield $\varphi_B = 0.4 \text{ eV}$ for Ti, In, Zn, and Au ($I_{\text{Ga}}/I_{\text{As}} < 1$) and 0.1–0.2-eV higher values for Al ($I_{\text{Ga}}/I_{\text{As}} > 1$). This result would be consistent with the defect model in which Fermi-level (E_F) pinning levels associated with Ga or As vacancies are separated by 0.1–0.2 eV. Contrary to this defect model, however, E_F pinning at different levels can be produced with different adsorbates on the same semiconductor. For Au-InP(110) interfaces with small-area ($2 \times 10^{-3} \text{ cm}^2$) contacts, a 10-Å Al interlayer shifts φ_B from 0.43 to 0.36 eV.¹¹ Cu and Au (Al and Ni) overlayers on InP(110) cause P (In)-rich outdiffusion, resulting in a high (low)¹² φ_B . This association of high and low φ_B with qualitatively different chemical structure provides a detailed background to explain the transition⁴ in φ_B with ΔH_R for III-V compound semiconductors.

In summary, compound-semiconductor-metal interfaces are not atomically abrupt. Instead they include a reacted interface of finite width and/or an interdiffused region extending into the semiconductor. The reacted region can have local potential gradients and new dielectric properties. The interdiffused region can alter the surface space-charge region near the interface in a non-parabolic way, depending on the type of diffusion which dominates. Both regions can contribute to φ_B and both depend on the chemical bond strength and charge transfer at the local interface.

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