# Formation of Schottky Barrier at the Tm/GaAs(110) Interface

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Detailed photoemission studies of the Tm/GaAs(110) interface give clear evidence for an abrupt change in Fermi-level position at a relatively high Tm coverage ($\simeq 2.6$ Å) by 0.22 eV towards the value expected from current-voltage measurements. This observation together with the strongly increasing density of states at the Fermi level around this coverage indicates that the Schottky barrier is not established until the overlayer assumes metallic character. The results are interpreted within the concept of metal-induced gap states defining the final Fermi-level position in Schottky barriers.

Detailed studies of the chemical, electronic, and spatial structure of metal/semiconductor interfaces have attracted considerable interest in the recent past mainly as a result of technological aspects.[1] Despite these efforts, several features of such interfaces are still not well understood on a microscopic level, in particular the mechanism of Schottky-barrier formation. Three major theories of the Schottky-barrier height have been formulated, including work-function,[2,3] metal-induced gap-state (MIGS),[4-6] and localized-state[7] models. Core-level photoemission (PE) studies of thin metal overlayers grown on semiconductor surfaces, which serve as model systems for metal/semiconductor interfaces, provide detailed information on chemical and electronic structure of the interfacial region as well as on band bending during interface formation.

In the present Letter we report on a detailed study of the reactive Tm/GaAs(110) interface by normal-emission PE spectroscopy. Using synchrotron radiation, we were able to follow the As-$3d$, Ga-$3d$, and Tm-$4f$ core levels of both the unreacted GaAs substrate and the reacted overlayer up to relatively high Tm coverages. Besides information on the chemical structure of the interface and the initial band bending for Tm coverages below 0.5 Å, we observe abrupt additional shifts of all core-level PE lines to lower binding energies (BE's) by $\simeq 0.22$ eV for a Tm coverage of $\theta \simeq 2.6$ Å. These additional shifts occur when the valence-band spectrum signals a metallization of the overlayer through an increasing density of states at the Fermi level. The final Fermi-level position derived from the PE spectra agrees well with the value expected from current-voltage measurements. These observations show that the Schottky barrier is not established until the overlayer assumes metallic character and are interpreted in support of the MIGS model.

The measurements were performed with a hemispherical electron analyzer (acceptance angle $\simeq 10°$), with use of synchrotron radiation (BESSY/SX700) or light from a He resonance lamp. The total-system resolution was $\simeq 0.15$ eV, and BE changes were determined with an accuracy of $\pm 0.03$ eV (synchrotron radiation) or 0.01 eV (He II). All data were taken in normal-emission geometry at room temperature under UHV conditions ($\leq 10^{-10}$ mbar). Clean GaAs(110) surfaces were prepared by cleaving of Si-doped $n$-GaAs ($2.8 \times 10^{18}$ atoms/cm$^3$) or Zn-doped $p$-GaAs ($1 \times 10^{18}$ atoms/cm$^3$). Interfaces were prepared only on mirrorlike cleavage planes by evaporation of 99.99% pure Tm metal from a tungsten basket. The evaporation rates of $1-5$ Å/min were measured with a quartz-crystal microbalance (accuracy: absolute $\pm 30\%$; relative $\pm 15\%$).

PE spectra of the As-$3d$ and Ga-$3d$ core levels are shown in Fig. 1 for various Tm coverages on $p$-GaAs(110). The spectra are composed of spin-orbit-split doublets at different BE's, which stem from bulk ($b$) and surface ($s$) atoms of the GaAs substrate (separated by the surface core-level shift)[8] as well as from the reacted phase ($r$). While the intensities of the components from substrate surface atoms (dash-dotted) decrease strongly with Tm coverage, additional components (dashed) emerge at lower BE, which are assigned to As and Ga atoms that have reacted with Tm at the interface. The important point in the context of the present paper is that the signals from the substrate (dotted subspectra) may be followed across the whole range of Tm coverages up to 7.2 Å. A closer inspection of the energetic positions of the subspectra in Fig. 1, indicated by the vertical bars, reveals both a parallel shift of the substrate core levels to higher BE's at $\theta < 0.8$ Å, and additional shifts of all core levels by $\simeq 0.22$ eV in opposite direction at coverages between 2.0 and 2.8 Å.

The corresponding PE spectra from the Tm-$4f$ core-level and valence-band regions are shown in Fig. 2. While the clean GaAs spectrum shows emission from the GaAs valence band, the spectra from Tm-covered GaAs are dominated by the Tm-$4f^{11}$ final-state multiplet with lines at BE's between 5 and 12 eV, characteristic for a trivalent Tm-$4f^{12}$ initial state.[9] The Tm-$4f$ lines exhibit also a BE decrease of similar size as the As and Ga core levels at coverages between 2.0 and 2.8 Å, superimposed on a gradual decrease with increasing Tm coverage. The
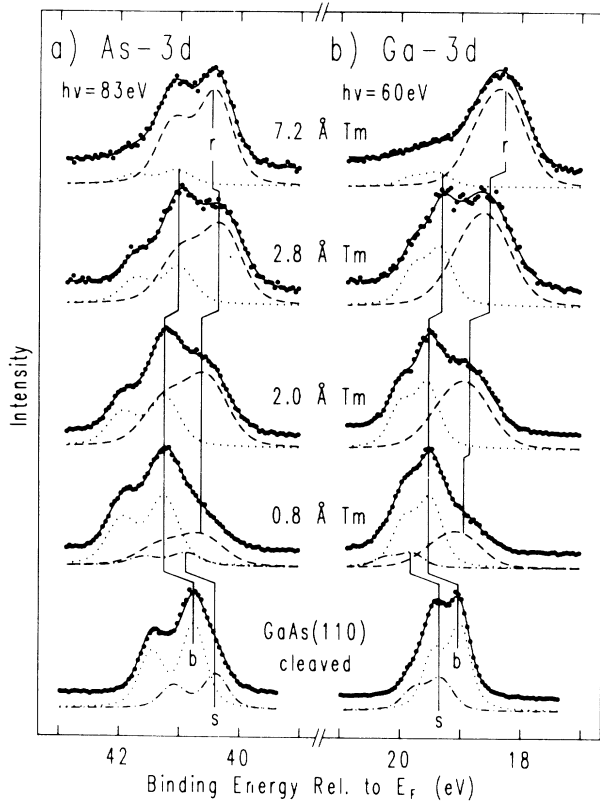
FIG. 1. As-$3d$ and Ga-$3d$ core-level PE spectra of the Tm/$p$-GaAs(110) interface as a function of Tm coverage. The solid curves through the data points represent the results of least-squares fits. The dotted subspectra ($b$) represent the bulk signal from the unreacted GaAs substrate, while the dash-dotted components ($s$) stem from the substrate surface atoms and are observed only for low Tm coverages. The dashed subspectra ($r$) originate from atoms in the reacted phases. Vertical bars mark the positions of the $3d_{5/2}$ components. All spectra are normalized to equal heights.



FIG. 2. Tm-$4f$ and valence-band PE spectra of the Tm/$p$-GaAs(110) interface as functions of Tm coverage. The solid curves through the data points represent the results of least-squares fits. At Tm coverages between 2.0 and 2.8 Å, an increasing density of states at $E_F$ becomes visible. The two subspectra shown for $\theta=7.2$ Å are assigned to surface (dashed) and bulk (dash-dotted) Tm atoms. The spectra are normalized to equal heights.

second important piece of information in Fig. 2 is the fact that the upper valence-band edge reaches the Fermi level in the same coverage range, signaling metallization of the surface region. The appearance of a finite density of states at $E_F$ was also confirmed by detailed PE studies with He I and He II radiation (not shown here).

The spectra in Figs. 1 and 2 were quantitatively analyzed by least-squares fits. For the As-$3d$ and Ga-$3d$ core-level spectra, spin-orbit splittings of 0.70 eV (As) and 0.44 eV (Ga) were assumed,[8] with a fixed ratio (2:3) of the intensities of the two doublet components. The spectral shapes were approximated by Lorentzians with 0.20-eV lifetime width (FWHM), convoluted by a Gaussian, and superimposed on a linear background. The spectra in Fig. 2 were fitted with the well-known $4f^{11}$ multiplet structure[9] with Gaussian lineshapes, added to a $4f$-derived integral background and emission from valence-band states.
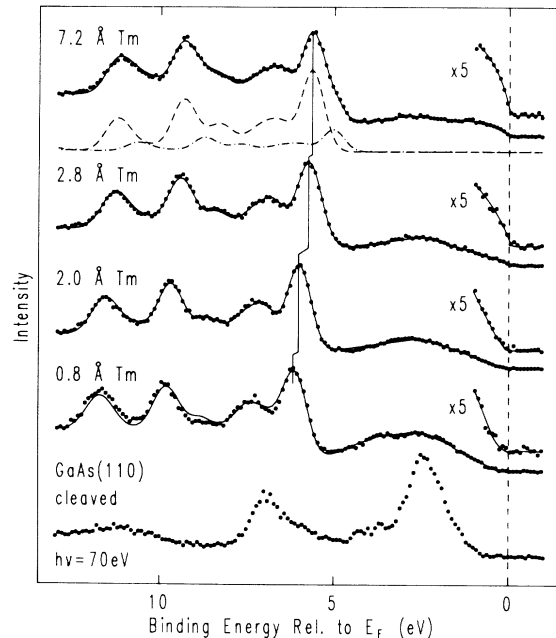
The resulting BE's as functions of Tm coverage are summarized in Fig. 3(a) for the As-$3d$ and Ga-$3d$ core levels of the unreacted GaAs substrate ($n$- and $p$-type), and in Fig. 3(b) for the core levels from all three elements in the reacted layer. The most striking information in Fig. 3 is the initial band-bending–induced shifts of the substrate core levels for $\theta < 0.5$ Å, and an additional parallel shift of all core levels to lower BE's occurring abruptly at $\theta \simeq 2.6$ Å.

These additional shifts were studied with synchrotron radiation for $p$-GaAs(110) only, while the initial band-bending shifts were investigated also with He II radiation for both $n$- and $p$-type substrates. The differences of 0.12 eV, clearly observed for the initial Ga-$3d$ BE's for $n$- and $p$-type GaAs(110) (see Fig. 3), are readily explained by the known variation of band bending in the GaAs substrate over the sampling depth of the PE measurements.[10] To this end, the band-bending variation is given in linear approximation[11] by $\Delta\Phi_B = \Delta x (2ne\Phi_B/\epsilon\epsilon_0)^{1/2}$; here, $\epsilon$ is the dielectric constant of GaAs ($\epsilon=10.4$),[11] $n$ stands for the doping concentration, and $\Delta x$ is the distance from the interface. The observed BE's in the PE spectra are then weighted mean values over the PE sampling depths (mean free path $\lambda \simeq 10$ Å in GaAs), leading to BE deviations of $+0.08$ eV for $n$-GaAs and $-0.05$ eV for $p$-GaAs from the correct interfacial Fermi
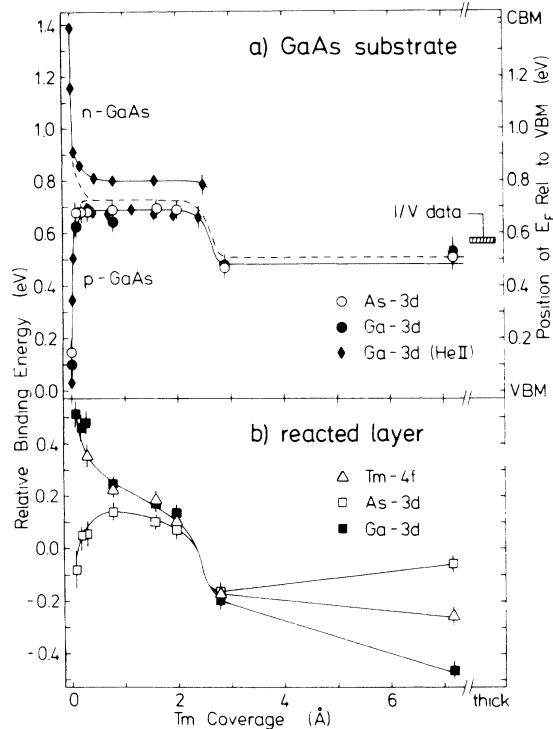
FIG. 3. Core-level BE shifts of the Tm/GaAs(110) interface as functions of Tm coverage for both $n$- and $p$-type substrates: (a) As-$3d$ and Ga-$3d$ from atoms in the GaAs substrate; (b) Tm-$4f$, As-$3d$, and Ga-$3d$ core levels from atoms in the reacted interfacial region. Note the parallel shifts of all core levels to lower BE's at a Tm coverage of $\simeq 2.6$ Å. The additional smooth BE variations for the reacted atoms reflect changes in chemical composition or coordination. The dashed line represents the common Fermi-level position for $n$- and $p$-type GaAs obtained from the PE data after correction for finite sampling depths (right-hand scale). The Fermi-level position derived from $I$-$V$ measurements on thick diodes is indicated by the dashed horizontal bar.

level [dashed line in Fig. 3(a)]. With these corrections, a single Fermi-level position at $0.72 \pm 0.03$ eV (for $0.5$ Å $< \theta < 2.6$ Å) above the valence-band maximum is obtained for both $n$- and $p$-type GaAs(110).

The main point of this Letter concerns the additional parallel shifts of all core levels to lower BE's at $\theta \simeq 2.6$ Å, when the overlayer metallizes (see Fig. 3). Similar shifts were previously observed for interfaces of other rare-earth metals (Ce, Sm, and Yb) with $n$-GaAs(110), but only for the reacted phases, since substrate core levels were not monitored at relevant coverages.[12] These shifts, however, were interpreted in terms of chemical effects, which may be excluded in the present case because of the parallel shifts of all core levels including those of substrate atoms.

We may also exclude charging of the whole sample as well as shifts due to a possible cluster formation as origins of these additional shifts: Charging ought to depend

on photon flux, and we have observed no additional shifts when varying the photon flux by a factor of 4. The reported self-energy effect[13] of a charged metallic cluster on top of an insulating substrate would influence core levels of cluster atoms and the position of the Fermi level in a similar way, but with smoothly decreasing shifts to lower BE as a function of cluster size (exposure). This is clearly not seen in the present system.

We thus end up with two further possible origins for the additional BE shifts: (1) A change in band bending due to metallization of the overlayer; (2) metallic screening of core holes in the PE process that would also lead to shifts to lower BE.[14] The second mechanism is unlikely to cause the main effect, since both substrate-atom and overlayer-atom core levels are affected in almost the same way. On the other hand, a change in band bending is expected to shift all interface levels in the same way.[15]

Further support for a change in band bending at $\theta \simeq 2.6$ Å is obtained from a comparison of the PE results with the Fermi-level position derived from current-voltage ($I$-$V$) measurements on Schottky diodes of the trivalent rare-earth metals Tb, Dy, and Er with $n$-GaAs(001): $\Phi_B = 0.85 \pm 0.01$ eV.[16] The same Fermi-level position may be assumed for the Tm/GaAs(110) interface because of chemical similarity of the trivalent rare-earth metals and the known independence of barrier height from substrate orientation.[7] As shown in Fig. 3(a), the Fermi-level position from $I$-$V$ data agrees within our experimental accuracy of $\simeq 0.05$ eV only with the PE BE's for thick Tm overlayers with metallic character, but not with the initial Fermi-level position. This is a strong argument against metallic screening as the main mechanism of the observed shifts, and supports directly the occurrence of a change in band bending when the overlayer metallizes.

A closer inspection of Fig. 3(a) reveals a minor deviation of $\simeq 0.05$ eV between the Fermi-level positions derived from $I$-$V$ measurements and our PE data for relatively thick metallic rare-earth overlayers. Such a small deviation, if real, could be caused by an additional metallic-screening shift of the core-level BE's upon metallization of the overlayer.[14]

The initial band-bending saturation at very low coverages can be described by defect-level pinning.[7] This model, however, is unlikely to be capable of accounting for the abrupt change in band bending at $\theta \simeq 2.6$ Å, since a switching between different defect levels, as discussed for InP,[17] (1) is unexpected for GaAs and (2) would require much stronger chemical changes than reflected in our PE spectra. We therefore conclude that the abrupt shifts at $\theta \simeq 2.6$ Å are caused by metallization of the overlayer leading to an overcompensation of defect states. One such mechanism, proposed by Heine,[4] Tersoff,[5] and Flores and Tejedor,[6] is based on metal-induced gap states (MIGS) in the band gap of the semiconductor close to the interface. This MIGS model of Schottky-

barrier formation is consistent with the present results. It is noted, however, that these arguments in support of the MIGS model are not totally excluding other metallization-induced mechanisms, like, e.g., the effective work-function model.[3] Even though a final decision on these issues seems not possible at present, the new experimental results are expected to strongly stimulate further work on Schottky-barrier formation.

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