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Photoemission from metal dots on GaAs(110): Surface photovoltages and conductivity

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Photoemission results from isolated dots on GaAs(110) demonstrate a temperature-dependent nonequilibrium surface photovoltage (SPV), even when the dots are metallic. Flat-band conditions are observed beneath isolated metallic dots at low temperature, while measurements for fully metallized surfaces show midgap pinning. Significantly, the SPV is shorted and approximate equilibrium is established for the dots when the electrical isolation is reduced by a thin conducting layer over the surface. We conclude that the steplike Fermi-level movement into the gap that has been associated with metallization is related to surface conductance rather than to changes in fundamental metal-semiconductor interactions.

Recent photoemission studies of metal layers grown at low temperature T on lightly doped semiconductor surfaces have shown that the surface Fermi level E_F remains close to the band edge until overlayer "metallicity" is reached.[1-4] A step is then observed, as sketched in Fig. 1, as E_F moves deep into the gap. There have been many attempts to explain this step into the gap.[5-8] Initially, it was believed that low-temperature E_F movement was fundamentally different for n- and p-type samples since the step was observed only for n-type samples. However, we recently showed symmetric movement for n- and p-type samples with matched dopant concentrations N, with the step occurring only for lightly doped (LD) samples.[9] Faster, nearly T-independent E_F movement was observed for heavily doped (HD) samples. Several authors have associated the step with the onset of metallicity, suggesting that adatom-adatom interactions produce delocalized gap states that pin E_F.[5-7] Others attributed T-dependent E_F movement to differences in defect formation.[3,8]

Most recently, discussions of N- and T-dependent E_F movement have focused on the communication between states at the surface and in the bulk. Aldao *et al.*[10] were the first to demonstrate the importance of surface-to-bulk coupling. They described the coupling as an equilibrium process, but Hecht[11] noted that it should be considered as a nonequilibrium process associated with a surface photovoltage (SPV). The SPV results from the separation of electron-hole pairs created by incident photons by fields in the depletion region, producing an accumulation of minority carriers at the surface. The result is a flattening of the bands in the absence of a compensating current from the bulk. Studies of the dependence of the E_F position on the photon (or electron) flux N and T have confirmed the importance of the SPV. In the inset of Fig. 1 we sketch equilibrium E_F movement in the gap as dashed lines (300 K), and deviation from this behavior is a measure of the T-dependent SPV, shown at 50 K by solid lines.

The SPV explanation raises intriguing questions related to surface recombination sites and their character.[12] The SPV can explain the T-dependent E_F movement for LD samples since bulk-to-surface coupling through the depletion is strongly temperature dependent. Furthermore, the SPV can explain the N-dependent E_F movement at low T since, for the same amount of band bending, the depletion region is narrower for HD samples and coupling is easier. The SPV does not, however, establish the mechanism responsible for the step in Fig. 1 at low T and low N.

This paper demonstrates that the movement into the gap is related to the presence of a surface layer that shorts

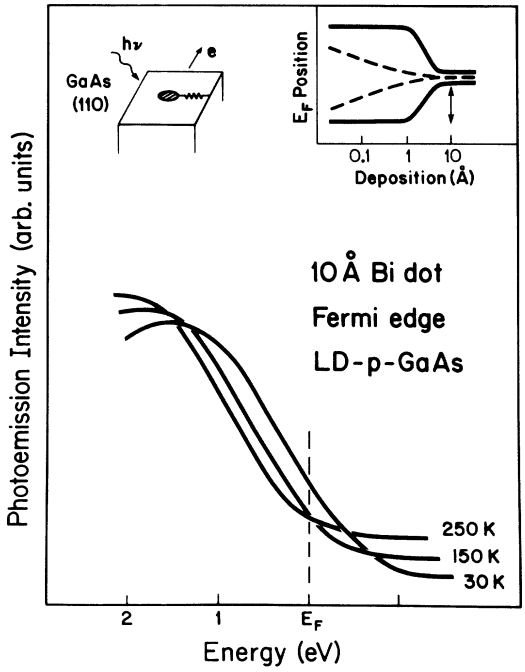

FIG. 1. Photoemission results showing spectra near the Bi Fermi cutoff as a function of substrate temperature for a 10-Å Bi dot deposited near the center of a LD p-type GaAs(110) surface, as sketched in the left inset. E_F is the equilibrium Fermi level of the spectrometer. The right inset shows qualitatively the band bending behavior as a function of deposition onto LD GaAs at 300 (dashed line) and 50 K (solid line). The photoemission spectra show emission from above E_F at low temperature that is due to a nonequilibrium SPV that flattens the bands beneath the Bi dot. The temperature-dependent movement of the Bi cutoff follows the arrow at 10 Å in the right inset.

out the SPV effect. These experiments were motivated by suggestions by Hecht and Tersoff that overlayer growth and metallization provide a conduction path from the illuminated (flat-band) region of the surface to a location on the surface or at its edge where more Ohmic contact is made. To test this intriguing idea, we formed metallic dots on GaAs(110), illuminated those dots with synchrotron radiation, and used photoemission to measure the Fermi cutoff and the binding energies for Ga 3*d*, As 3*d*, and the metal core levels. For dots confined to pristine regions of the surface, the SPV prevailed to coverages above the metallization limit and the step was not observed. Temperature cycling demonstrated that flat band conditions existed beneath the dots at 30 K but that approximate equilibrium pinning was established at 300 K. However, when conducting layers were established between the dots and the remainder of the sample, the Fermi cutoff returned to the equilibrium position, even at 30 K. We conclude that full surface coverage allows compensation of the SPV and that the step is a consequence of surface conduction.[11]

The synchrotron radiation photoemission experiments were done with a fixed photon energy of $h\nu = 65$ eV. The photon flux of $\sim 10^{12}$ photons/cm^{2}sec did not vary enough to affect the measurements.[10] Posts of GaAs were cleaved *in situ* at operating pressures of $\sim 5\times 10^{-11}$ Torr. Measurements at 300 K demonstrated that the surface was unpinned (samples with E_F more than ~ 60 meV from the band edges were discarded). All samples were doped at 1×10^{17} cm^{-3} (Si doping for *n* type, Zn doping for *p* type). After cleaving, they were cooled to 30 K and core-level spectra were again acquired. Overlayers of Bi and Ti were deposited onto these cold substrates through a $\sim$2-mm-diam aperture placed < 1 mm from the surface (the cleaved surface was typically 4×4 mm^2). In this way, a dot isolated from the sample edges was formed, and its character could be identified by observation of a Fermi cutoff and the binding energies of the core levels. The inset of Fig. 1 schematically shows the experimental arrangement. The dots produced with this simple masking technique were not uniform in thickness around the perimeter, but they sufficed very well for our measurements. Indeed, the low density of atoms that migrated away from the dots provided a way of directly comparing very low coverage results with those for metallized regions by moving the sample in the beam.

In Fig. 1 we show photoemission spectra near E_F for a 10-Å Bi dot on *p*-type GaAs(110). The spectra at different temperatures are offset vertically for clarity, and they are referenced in energy to the equilibrium E_F position determined from a $\sim$100-Å-thick Ti film. These results clearly demonstrate nonequilibrium *T*-dependent movement of the emission cutoff of semimetallic Bi that is consistent with the SPV model and charging of the dot. This charging is due to the open circuit voltage at the interface resulting from accumulation of minority carriers at the surface. It serves to oppose band bending for both *n*- and *p*-type substrates. It is important to note that 10 Å of Bi would result in near-midgap pinning at 30 K for conventional experiments where the surface is fully exposed to the evaporant (see arrow in inset of Fig. 1 at 10 Å). The fact that this is not observed for the dot indicates that a unique nonequilibrium configuration has been achieved and the bands become increasingly flat upon cooling despite the coverage being above the "metallization" step. The *T*-dependent movement of E_F (or the metal core levels) is a measure of band flattening beneath the dot.

Previously, we showed reversible E_F movement in the band gap as a function of *T* for a given amount of metal coverage across the surface.[9,10] This prompted examination of surface-to-bulk coupling and, ultimately, the SPV model.[10,11] Figure 2 gives the corresponding movement of E_F for metallic dots. In the upper panel of Fig. 2 we show *T*-dependent results for a 10-Å Bi dot on LD *p*-type GaAs(110). The solid line represents the change in band bending derived by the Bi Fermi-level emission and the dashed line corresponds to the shift in the Ga and As core levels. Both reflect the same trends, but the magnitude of the shift is greater for the Bi dot. The smaller shift for Ga and As emission can be understood by recognizing that the Bi dot is opaque to photoelectrons emitted beneath it and that the Ga and As 3*d* photoelectrons were emitted

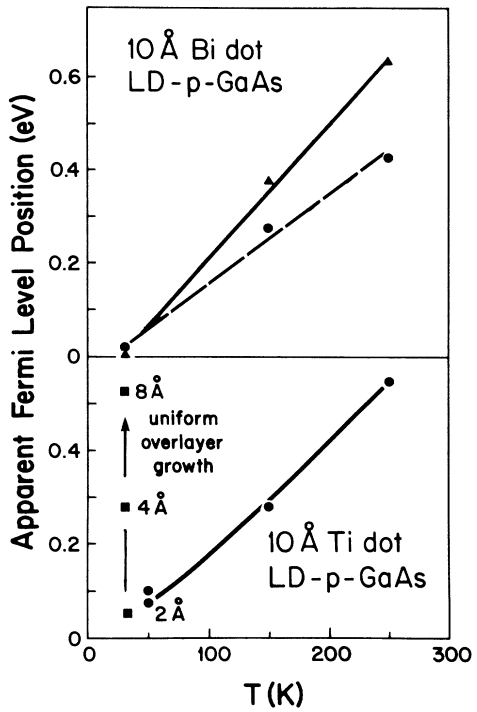

FIG. 2. Apparent Fermi-level position in the gap for 10-Å Bi and 10-Å Ti dots on LD *p*-GaAs(110). The energy zero represents flat bands with E_F within $\sim$30 meV of the valence-band maximum. The dashed line was obtained from shifts of the Ga and As 3*d* emission; it is indicative of the SPV in regions near the dot covered by $\sim$0.1 Å of Bi where the amount of band bending was less. The lower panel shows results for the Ti dot derived from Ga and As 3*d* spectra. The squares show that Ti deposition at 30 K over the entire surface induces movement of the apparent Fermi level to its final position by 8 Å. Hence, the SPV is large for isolated metallic dots at low temperature, but similar depositions across the full surface produced a shunted diode with no appreciable SPV.

from the surface region near the dot where the Bi coverage is very small. In this case, the Bi-induced equilibrium band bending would be much less and the temperature dependence would correspond to that for ~0.1 Å rather than 10 Å (see inset of Fig. 1).

We stress that when 10 Å of Bi is deposited across the entire surface, the Fermi level is pinned near midgap, even at 30 K, and no SPV effect is observed (inset Fig. 1).[13] In the absence of such a conducting layer, our results clearly demonstrate a substantial SPV at coverages well above the metallization threshold. This suggests that the step for lightly doped samples at low temperature is a consequence of the changing conductivity of the surface.

To test the idea that surface conductance could alter the apparent Fermi-level position, we first formed a metallic 10-Å Ti dot on *p*-type GaAs and then deposited Ti incrementally across the surface at 30 K. The bottom panel of Fig. 2 shows the change in band bending for the Ti dot upon cycling from 30 to 250 and back to 30 K. The results are again derived from Ga and As 3*d* core-level spectra and represent changes in SPV in the regions of the surface around the Ti dot, i.e., regions covered only by submonolayer amounts of Ti. As previously established, cycling between low and high T results in reversible E_F movement for submonolayer metal coverages.[9,10] As for Bi, the Ti valence-band features exhibit emission above the Fermi level at low T because of nonequilibrium band flattening beneath the Ti dot. Again, for uniform Ti deposition across a GaAs(110) surface, a 10-Å film is sufficient to pin E_F at its final position at 30 K because it exceeds the metallization threshold of Fig. 1. This establishes that the Ti dot is electrically isolated from the sample edge.

To better understand the differences between the dot experiment and the fully exposed surface experiments, we deposited 2 Å of Ti on the 10-Å dot surface at 30 K. From Fig. 1 (and Ref. 14), the apparent E_F position for a uniform 2-Å film would be close to the band edge at 30 K and metallization should not have been observed. From Fig. 2, the effect of this uniform 2-Å deposition was negligible (square symbol labeled 2 Å). When 4 Å of Ti were deposited onto the dot and the surface, band bending changed by ~200 meV. Note that uniform coverage of 4 Å corresponds to partial movement over the metallization threshold of Fig. 1. When the uniform overlayer thickness was increased to 8 Å, the amount of band bending equaled that for a conventional metallized surface *and* for the 10-Å dot at 250 K (Fig. 2). No SPV was observed. While these measurements predominantly sample regions of the surface not directly beneath the dot (due to photoelectron attenuation by the dot), they establish that uniform metallic coverages are sufficient to pin E_F at low temperature but isolated metallic coverages are not.

The results of Fig. 2 make it clear that metallic dots of Bi and Ti are charged during the photoemission process at low temperature. This SPV is reduced for the isolated dot as the temperature increases because a compensating current is established through the depletion region beneath the dot. Remarkably, the SPV for the dot is shorted at low temperature when the extended surface exhibits metallicity. These results therefore demonstrate that the metallization threshold reflects the ability of the surface to pass a current able to compensate the SPV. Such shorting would occur for both *n*- and *p*-type samples, explaining the symmetric movement of E_F observed at low temperature. Moreover, the SPV would account for the apparent spread in the pinning position above the metallization threshold and its dependence on the bulk dopant concentration. Thus, the metallization threshold of Fig. 1 is important, but not for the reasons previously thought.[1-10] It appears unrelated to an alteration of the fundamental interactions of the overlayer with the substrate as the overlayer becomes metallic.

It is interesting to speculate about the nature of the contact that is established upon uniform surface metallization because this contact is clearly different from that beneath an isolated metallic dot. The metallization threshold has now been observed at low temperature for metals ranging from the semimetals like Bi (which does not disrupt the surface) to metals like Ag (which does not disrupt the surface) and Sm and Ti (where disruption and intermixing is pronounced). Despite differences in surface morphology, reactivity, and the conductivity of the species that evolve, the halfway point for the step falls between ~0.8 ML for Co and ~4 ML for Cr (or ~6.8 ML for Al) and the step width is generally less than ~4 ML. At this point, we see no clear correlation between surface reactivity and the metallization parameters. Moreover, the SPV is able to maintain essentially flat band conditions during overlayer growth, starting at very low coverage and extending beyond the metallization limit, indicating that direct recombination rates are very small.

Hecht recently postulated that a uniform film could establish a shunt resistance such that the metallized surface represents a leaky diode with a shorting of the open circuit voltage that leads to band flattening.[11] The present results establish the importance of such a conducting layer. One must assume, therefore, that there are sites on the cleaved surface or at its edge where an Ohmic contact is established. Presumably, these contacts occur at heavily steeped regions of the surface where the density of states in the gap is large. Investigations are under way to determine the nature of these contacts.

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