Trends in temperature-dependent Schottky barrier formation: The Ga/GaAs and Mn/GaAs interfaces

K. Stiles, S. F. Horng, and A. Kahn
Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544

J. McKinley, D. G. Kilday, and G. Margaritondo
Department of Physics and Synchrotron Radiation Center, University of Wisconsin, Madison, Wisconsin 53706

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We use soft x-ray photoemission spectroscopy to study the Ga/GaAs and Mn/GaAs interfaces formed at room temperature (RT) and at low temperature (LT = 80 – 100 K). The LT Ga/GaAs interface exhibits the strongly inhibited clustering observed at other nonreactive metal/GaAs interfaces. The Mn–GaAs reaction is slowed somewhat. At both interfaces, the effect of temperature on $E_F$ movement is in accord with the trends previously set: initial band bending on n-GaAs is slowed at LT, whereas band bending on p-GaAs is not affected significantly. For both Ga and Mn/GaAs, $E_F$ movement at low coverages is consistent with the explanation proposed for the sp and noble metals: introduction of donor states from, e.g., the specific adsorbate levels. Studies of the noble metal interfaces with GaAs have showed that the establishment of the final $E_F$ position is related to the appearance of metallicity at the interface; Mn/GaAs provides direct evidence for that interpretation.

I. INTRODUCTION

A series of experiments on metal adsorption on cleaved GaAs(110) at low temperature (LT) has led to the understanding that the surface Fermi level ($E_F$) is controlled in part by adsorbate-derived levels in the low-coverage regime (0.01–1 Å).1–4 For the unreactive or mildly reactive metals Al, In, Ag, and Au, the conclusions drawn from these experiments is that these adsorbate levels are donors positioned several tenths of an eV above the valence band maximum (VBM) and, as such, yield rapid $E_F$ movement on p-GaAs in the low-coverage regime. The rate of $E_F$ movement and the maximum $E_F$ position in the gap depend quite sensitively on the metal.1,2 Very little movement of $E_F$ occurs on n-GaAs until the coverage reaches ~1–2 Å, as expected from the introduction of mostly donor levels. Above this coverage, a rapid movement of $E_F$ toward its final position occurs on n-GaAs. $E_F$ also stabilizes on p-GaAs at the same coverage.

These results prompt a number of questions. The first is whether some specific property of the metal can be related to the position of the observed donor levels. The trend observed in low-coverage $E_F$ movement on LT p-GaAs with Au, Ag, Al, and In, i.e., larger rate of band bending and increased overshoot in the order given here, has been explained in terms of metal work function and Schottky limit.2 Metal adatoms, however, are isolated or form very small clusters, at LT and low coverage, and the problem might be better treated in terms of parameters specific to the atom. The studies of Al, In, Au, Ag, and Sn presented at PCSI-1987,1,2 and of Sb,5 Ca,6 Y,7 and Tm8 indicate that the ionization energy of the adatom might constitute a better starting point. The details of adatom–substrate bonding and chemical interaction are unknown, however, and will be essential to achieve a quantitative description of these levels. In any case, it is important to extend the investigation of these trends to other metals such as Ga and Mn.

The second question relates to the transition (abrupt on LT n-GaAs) to the final $E_F$ pinning position observed at higher coverages (> 1 Å).1–4 There is clear evidence from several metal/GaAs interfaces that the final stabilization of $E_F$ is correlated with the onset of metallic character in the overlayer, in support of Schottky barrier models based on metal-induced gap states (MIGS).3,4,6,8,9 The LT deposition experiments were instrumental in reaching this conclusion, as it provided natural, nonperturbing means to slow down metal clustering and appearance of metallicity in the overlayer. The extension of these studies to other metal/GaAs interfaces would constitute a very important step toward a fundamental understanding of these systems.

Finally, Sb,5 Ca,6 Sn,9 and Ti10 deposited on LT n-GaAs display some variation of the temperature dependence of $E_F$ movement shown by the adsorbates mentioned above. Although the p-GaAs band bending behavior with these elements is compatible with that described above, the low-coverage n-GaAs band bending is not substantially inhibited at LT. Two explanations can be proposed to resolve this discrepancy. Sn and Sb form ordered two-dimensional overlayers and, as such, can introduce (acceptor) states through bonding to, and unrelaxation of, the first GaAs atomic layer. Ti and Ca react extensively with the substrate, even at 80 K. If acceptor defects are introduced by reaction, LT does not inhibit their formation as efficiently as with other interfaces. In view of these four examples, the trend in the low-coverage n-GaAs behavior observed with Al, In, Ag, and Au should be tested with other metals.

The present work describes the trends in temperature-dependent Schottky barrier formation, outlined above, as illustrated by the examples of Ga and Mn/GaAs. These interfaces display markedly different chemistry and morphology. Nevertheless, both confirm the LT low-coverage formation of donor levels due to metal adsorbates. The abrupt shift of $E_F$ on n-GaAs at higher coverages is examined in great detail.
for Ga/\(n\)-GaAs. Finally, both interfaces provide evidence linking this final \(E_F\) stabilization to the appearance of metalliclicity in the overlayer. For Mn/GaAs, this correlation is evident from the appearance of the Fermi edge in the valence band spectra.

**II. EXPERIMENTS**

Ga and Mn were deposited in amounts from 0.01 to 32 Å on ultrahigh vacuum cleaved bars of GaAs (\(n = 0.8 - 2 \times 10^{17}\), \(p = 0.9 - 2 \times 10^{16}\)) from Crystal Specialties. One monolayer (ML) on GaAs(110) is \(0.89 \times 10^{13}\) atoms/cm\(^{-2}\) and corresponds to 1.7 and 1.1 Å for Ga and Mn, respectively. The metals were evaporated from carefully outgassed W filaments in amounts monitored with a quartz crystal thickness monitor. Experiments were done both at RT and with the sample held at \(LT = 80-100\) K by a Cu braid connected to a closed cycle He refrigerator. Soft x-ray photoemission (SXPS) experiments were carried out at the Synchrotron Radiation Center at the University of Wisconsin. Photoelectrons were energy analyzed using a double-pass cylindrical mirror analyzer; the combined resolution of the analyzer and the monochromater was about 0.2 eV. The Ga 3d and As 3d core level spectra were taken using photon energies of 60 and 80 eV, respectively, and valence band spectra were taken using either 50 or 70 eV photons. Morphological information was obtained from the attenuation of relative core level intensities from the substrate. For Mn/GaAs, the core levels also show evidence of chemical reaction. Band bending was obtained from rigid shifts of both the Ga 3d and the As 3d core levels.

**III. RESULTS AND DISCUSSION**

**A. Ga/GaAs**

The physical and electronic properties of the room-temperature (RT) Ga/GaAs interface have been reported.\(^{11-13}\) This interface displays the extensive clustering that is typical of the \(sp\) and noble metals, as noted above. Clustering is manifested in the slow attenuation of the substrate As 3d core level peak as a function of Ga coverage (not shown). For abrupt interfaces, this type of plot yields a straight line with a slope characteristic of the electron escape length through the overlayer \(\lambda\); clustered growth causes a deviation from this line toward smaller slopes. In accord with the trend for In\(^{1}\) and Al\(^{14}\), the RT Ga clustering is inhibited at LT. The slope of the exponential attenuation yields \(\lambda \sim 2\) Å, indicative of an homogeneous layer-layer Ga growth.

The position of \(E_F\) vs Ga coverage at both RT and LT is shown in Fig. 1. The RT band bending agrees with that of an earlier study\(^{11}\) and extends the range into the low-coverage regime (\(< 1\) Å). The bands bend with Ga coverage at roughly the same rate on \(n\)- and \(p\)-GaAs, and the position of \(E_F\) is apparently stabilized by about 2 Å. At this coverage, the position of \(E_F\) differs by about 0.25 eV on \(n\)- and \(p\)-GaAs, a fact that has been taken as evidence of defect models of Schottky barrier formation.\(^{15}\) The band bending at LT is similar to that for Al, In, Ag, and Au.\(^{12}\) There is very rapid movement of \(E_F\) on \(p\)-GaAs, while nearly flat bands are maintained on \(n\)-GaAs up to about 2 Å. Above that coverage, there is an abrupt shift of \(E_F\) to its final pinning position.

We first examine the ultralow coverage range. We have argued that defects are very unlikely to cause the rapid band bending on \(p\)-GaAs observed at other metal–GaAs interfaces\(^{1,4,9}\) for two reasons: (i) the rate of defect formation is expected to decrease at LT, and this is incompatible with the increased rate of band bending observed with metals such as Al or In; (ii) native defects would not produce the metal-dependent band bending and \(E_F\) overshoot mentioned above. Therefore, defect formation is most likely not important in the early stages of Ga/GaAs interface formation. The Schottky limit argument\(^{2}\) is also difficult to reconcile with experiment: if it did apply to our highly dispersed overlayer at low coverage, the low-Ga work function (4.2 eV) should produce an \(E_F\) overshoot similar to those of Al (4.2 eV) and In (4.12 eV). The overshoot is very small (\(< 50\) meV), if it exists at all, whereas those due to Al and In are large (\(> 0.3\) eV). On the other hand, the observed behavior is consistent with the hypothesis that Ga adsorbed as isolated atoms or small clusters induces a discrete donor level, the position of which may depend sensitively on the configuration of the adatoms on the surface, i.e., the degree of Ga–Ga coordination, and on the adatom–substrate chemical interaction. From the initial rise of \(E_F\) on \(p\)-GaAs, one can infer that the Ga level should be \(< 0.6\) eV above the VBM below that of In (0.75 eV\(^{1}\)), Al (0.65 eV\(^{14}\)), and Ca (0.7 eV\(^{6}\)) and above those of Sn (0.5 eV\(^{9}\)) or Au (0.35–0.5 eV\(^{7}\)). As a side remark, we note that the idea of atom-specific energy level, as opposed to that of adatom-induced defect level, can be extended to the very electronegative oxygen and chlorine. Both elements are shown to introduce acceptor levels deep in the GaAs gap, which leave \(E_F\) essentially unmodified on \(p\-)GaAs before oxidation by O or surface etching by Cl sets in.\(^{16-18}\) These levels appear to be element specific: Cl moves \(E_F\) on \(n\)-GaAs down to 0.2 eV above the VBM, whereas O moves \(E_F\) only down to the middle of the gap. Here again, the specific chemisorption configuration of these elements must be understood before atomic parameters such as electron affinity can be used to evaluate quantitatively the position of these levels.

At low coverages, the metal adsorbate donor levels do not affect \(E_F\) on \(n\)-GaAs, and the bands remain flat until another
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mechanism takes over above 2 Å. The correlation between the start of the abrupt shift in $E_F$ above this coverage and the appearance of metallic behavior in other metal overlayers, has lent support to Schottky barrier models based on metal induced gap states (MIGS). Due to the low-photoionization cross section of Ga sp valence electrons, small signal-to-noise ratio prevented the use of the valence band and Fermi edge spectra to assess metallicity in the overlayer, as has been done with Ag and Au, and Ca and Mn (below). A correlation based on the shift of the adatom Ga 3d core level, however, is possible. Figure 2 shows that, at RT, a peak appears at lower binding energy than the Ga in GaAs peak; this peak is due to deposited Ga which forms metallic clusters. Above 1 Å, the chemical shift is constant at 0.9–1 eV, in good agreement with previous measurements. At LT and low coverages, however, the chemical shift is considerably less and the free Ga peak shows up as a shoulder of the bulk Ga peak. The slow increase in chemical shift indicates an evolution of the coordination of the free Ga, from quasi-isolated atom on the surface to part of a metallic overlayer at high coverages. The remarkable point is that the most pronounced shift over and beyond the band bending shift occurs between 2 and 6 Å when the Ga becomes truly metallic, and coincides with the abrupt movement of $E_F$ on $n$-GaAs. Above 6 Å, the GaAs Ga peak is buried by the

**Fig. 2.** Ga 3d core level as a function of Ga coverage on GaAs(110) at (a) RT and (b) LT.

**Fig. 3.** Ga 3d core level as a function of Mn coverage on GaAs(110) at (a) RT and (b) LT.
layer, and the chemical shift between Ga adatoms and Ga in GaAs must be deduced from the total band bending. This measurement again yields 0.9–1 eV, in accord with the presence of metallic Ga on the surface. In addition to coordination, size effects can also affect the shift. A charged final state in extremely small clusters shifts the core level to higher binding energy. The data show that at RT the clusters are large enough to be free of final state effects even at low coverages.

One last point is the final pinning position. As mentioned above, at LT $E_p$ pins at the same point in the band gap irrespective of doping type, in contrast to the two apparent pinning positions for $n$- and $p$-GaAs at RT. Although there is a 50–100 meV uncertainty in the absolute position of $E_p$, there is no room for doubt in this interpretation—the final kinetic energy of the As 3d core level at LT is exactly the same for $n$- and $p$-GaAs. It has been recognized that SXPS may not measure the full band bending at the interface for a highly clustered overlayer. This effect due to inhomogeneous band bending is particularly pronounced in the limit of large clusters and high doping. These results confirm this expectation. Thus, a 10 Å homogeneous Ga layer is thick enough to yield the full $E_p$ pinning, yet thin enough to allow the band bending to be probed by SXPS. Therefore, the interpretation of the final pinning of $E_p$ at the RT Ga/GaAs interface in terms of defects is most likely incorrect. Rather, the pinning is due to the development of a metal on the surface, as will be confirmed below in the discussion of the Mn/GaAs interface.

### B. Mn/GaAs

Unlike the sp and noble metals, the transition metals are very reactive with GaAs. Recent work on the Mn/GaAs interface at RT shows that it fits this trend. A conclusion of these studies is that Mn reacts with the As, liberating Ga in the process. The phase segregated Ga most likely exists diluted in the Mn overlayer, and stays close to the interface. The effect of the reaction can be best observed in the Ga core level spectra as a function of Mn coverage, which are shown in Fig. 3 (a). At RT, there is a broad peak at the low binding energy side of the main peak due to the reacted Ga. This peak is clearly resolved at 4 Å and above. The chemical shift, at 8 Å is $\sim$ 1.0 eV, and corresponds to partly diluted Ga in Mn. In contrast, Fig. 3 (b) shows that at LT the peak due to reacted Ga is much smaller, albeit not completely eliminated. The Ga 3d and As 3d, not shown) core level is attenuated with increasing Mn coverage, with only a very small peak due to reacted Ga remaining above 8 Å.

The RT band bending versus Mn coverage, shown in Fig. 4, also agrees well with that reported earlier. The movement of $E_p$ with Mn coverage is extremely rapid in the very low coverage regime ($< 0.01 Å$) for both $n$- and $p$-GaAs, and $E_p$ is found at the same position within the band gap for both doping types beyond $\sim 1 Å$. The situation at LT is markedly different. While there is no apparent temperature dependence of the $E_p$ movement for $p$-GaAs, $E_p$ moves very little at low coverages and shifts abruptly to its final position above $\sim 4 Å$ for $n$-GaAs. In this respect, the evolution of the band bending with coverage follows the trend of the less reactive metals, the difference in interface chemistry notwithstanding.

At low coverages, the observed behavior at LT is in accord with the explanation postulated for the other metals; adsorbed Mn atoms on the surface act as donors. From the initial $E_p$ movement on $p$-GaAs, the donor level can be approximately positioned at 0.55 eV above the VBM. The difference between RT and LT pinning on $n$-GaAs, however, must be explained in different terms than with Al, In, or Ag. For the sp and noble metals, adsorbed atoms cluster and become metallic at low coverages, leading to earlier $E_p$ pinning by MIGS. For Mn, on the other hand, faster pinning at RT may be related to reaction-related phenomena: metallic phase segregated Ga freed by the reaction and levels from Mn substitutional impurities. At any rate, the LT $E_p$ behavior on $n$-GaAs is related to cluster inhibition in sp and noble metal/GaAs interfaces, and inhibition of the reaction at the Mn/GaAs interface. This interpretation is supported by the fact that at the Ti/GaAs interface, cooling to 100 K is not sufficient to slow the reaction significantly. Likewise, there is no significant temperature dependence to the evolution of the $E_p$ position with Ti coverage. The evolution of the valence band spectra as a function of Mn coverage at LT is shown in Fig. 5. Extra valence band emission due to the Mn d band appears with the first coverage around 4.5–5 eV below $E_p$, and dominates the whole spectrum above 1 Å. At coverages up to and including 4 Å, $E_F$ is near the top of the gap, in a position where there are no occupied states (visible with PES). Between 4 and 8 Å, however, a large density of states appears at the Fermi level, clearly signaling the transition to metallic behavior in the overlayer. As Fig. 4 shows, this is just the coverage regime where EF exhibits a large shift to its final position. Therefore, earlier reports linking the final stabilization of $E_p$ at LT to the onset of metallicity in the overlayer are now supported by direct evidence. With similar findings for Ca/GaAs and Tm/GaAs, it is clear that this constitutes a definite trend in support of Schottky barrier models based on metal-induced gap states.
IV. CONCLUSIONS

Temperature-dependent reaction, morphology, and $E_F$ pinning at metal/GaAs interfaces are discussed using two very different metals, Ga and Mn, as examples to illustrate the trends. For the $sp$ and noble metal/GaAs interfaces, the effect of formation at LT is to suppress the overlayer clustering. For the Mn/GaAs interface, it is the reaction that is inhibited at LT. The evolution of $E_F$ with metal coverage at LT is explained by distinct mechanisms that control the position of $E_F$ in two coverage regimes. At low coverages, donor levels due to the metal adsorbates dominate. Above $\sim 2$ Å, there is an abrupt transition to the final $E_F$ pinning position as the overlayer becomes metallic.

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31. The difference between Ti and Mn is to be expected from the large heat of formation of TiAs, which is $-35.8$ kcal/mol, compared to $-14$ kcal/mol for MnAs and $-17$ kcal/mol for GaAs (Langes Handbook of Chemistry, 13th ed. (McGraw-Hill, New York, 1985)).