Correlation between E_F Pinning and Development of Metallic Character in Ag Overlayers on GaAs(110)

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Ag is deposited on room-temperature and low-temperature GaAs(110). Correlation is found between the appearance of metallicity in the Ag layer, as inferred from the width of the Ag-4*d* band, and the pinning of the Fermi level at the GaAs surface. These results suggest the importance of metal-induced gap states at high coverage (> 2 Å) in the formation of the Schottky barrier.

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The models proposed to date to explain the formation of Schottky barriers at metal-semiconductor interfaces still provoke much controversy.[1-5] The complexity of the interface morphology,[6] microscopic structure,[7] and chemistry[2] has prevented unambiguous identification of the nature and origin of the states that pin the Fermi level (E_F), near midgap for GaAs. We have recently followed an approach that consists of depositing the metal on GaAs surfaces cooled to 70–100 K.[6,8-10] Metal clustering and interdiffusion are substantially inhibited at low temperature (LT), as inferred from low-energy electron diffraction (LEED) and Auger-electron spectroscopy. Chemical reactions are somewhat slowed down, but are not eliminated even at $T < 100$ K. We attempt to correlate these changes with changes observed in the formation of the Schottky barrier, in particular with E_F pinning during the initial stages of overlayer growth. As a result, we suggest the role of metal-induced gap states at the Ag/GaAs(110) interface in the high-coverage regime.

Experiments performed with Al, In, Au, and Ag evaporated on LT GaAs(110) give concordant results.[8-12] All these metals cluster to various degrees on room-temperature (RT) GaAs. Particularly significant are the soft x-ray and ultraviolet photoemission spectroscopy (SXPS and UPS) measurements which show that the coverage-dependent surface-band bending is affected differently by temperature on *n*- and *p*-GaAs.[8-12] After a small initial band bending at ultralow coverage, final pinning is *substantially* retarded on *n*-GaAs with respect to the RT case. Band bending occurs as fast on *p*-GaAs as in the RT case, faster with Al and In.[10-12] The Ag data are shown in Fig. 1. The asymmetry in the E_F movement on LT *n* and *p* samples and the LT transition around 2 Å on *n*-GaAs suggest that several mechanisms responsible for band bending at the semiconductor surface are active during the formation of the interface, in opposition to the traditional picture of a single mechanism inferred from the rapid and symmetric band bending observed at RT (Fig. 1). Our assumption is that the differences between the LT and RT data reflect a slowdown, or decomposition, of the overlayer formation process at temperatures below 100 K.

The experiments presented here were done with $n = 3\times10^{17}$–3×10^{18} cm^{-3} (Si or Te) and $p = 4\times10^{18}$–1×10^{19} cm^{-3} (Zn) doped GaAs surfaces cleaved in ultrahigh vacuum. The sample temperature was maintained at 300 K (RT) or 70–100 K (LT) during evaporation and measurements. Ag was evaporated from a W filament in equivalent coverages ranging from less than 0.01 to 32 Å. Measurements of overlayer morphology and structure with use of LEED and Auger-electron spectroscopy have been reported elsewhere.[10] In this paper, we emphasize UPS measurements of the GaAs valence band and Ag-4*d* band as functions of Ag coverage, using the He II (40.8 eV) radiation line. In the text and figures below, these measurements are correlated with surface-band bending obtained from SXPS and UPS measurements of Ga-3*d* and As-3*d* core-level energy shifts.[10]

Although this paper deals mostly with the high-coverage pinning mechanism, comments concerning the difference between the low-coverage E_F movements on *n* and *p* samples should be made. This asymmetry is difficult to reconcile with current Schottky-barrier mod-

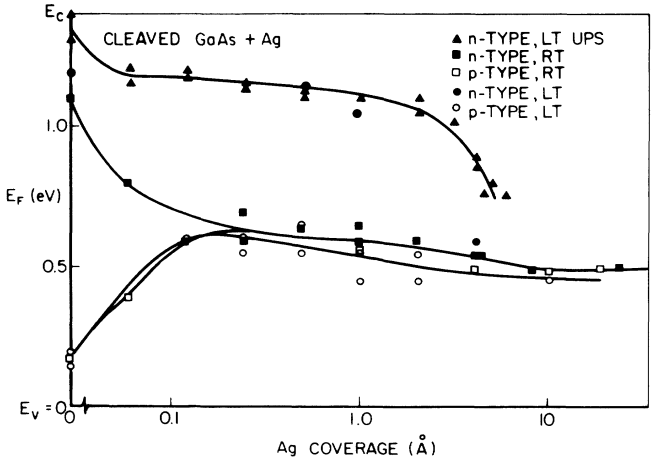

FIG. 1. Position of E_F at the (110) surface of *n*- and *p*-GaAs as a function of Ag coverage at RT and LT.

els based on near-midgap acceptor and donor defects,[1] or on metal-induced gap states.[4] In particular, the former model would require a ratio of 2 orders of magnitude between the rates of LT formation of donor and acceptor defects, e.g., As and Ga antisites, whereas these same defects would form at the same rate at RT. This is highly unlikely in the case of GaAs. Several factors could, however, contribute to this asymmetry. First, the fast initial rise of E_F on LT p-GaAs has been modeled, for the similar case of Al, in terms of small adatom charged clusters and their size-dependent Coulomb energy and Fermi level.[13] A good fit between theory and experiment was obtained at ultralow coverage (<0.1 Å). Whether this model can reproduce the n data up to the 1–2-Å transition coverage is unknown, however. Second, it has been observed (at LT) that metals such as Al[6] and Ag[10] unrelax the (110) GaAs surface. Dangling bonds at unrelaxed sites could generate gap states, donors in the present case, which are otherwise swept out of the gap by the surface relaxation.[7] Finally, and perhaps most important, the fast low-coverage movement of E_F on LT p-GaAs generally exhibits an overshoot above its final pinning position (Fig. 1). The magnitude of this overshoot depends on the metal[12]: It is large with low-electronegativity metals (Al and In), smaller with Ag and Au,[10] and nonexistent with Pd.[14] In the low-coverage regime (<0.5 Å) at LT, the overlayer consists of isolated atoms or very small clusters, as we discuss below. The low-coverage asymmetry could therefore be the manifestation of the real nature of the surface states induced by the very dilute overlayer.[15] Yet knowledge of the atomic and electronic structures (adsorption sites, substrate relaxation, bonding, and antibonding states) of atoms or small clusters on the surface must be determined before a quantitative justification of the asymmetry can be presented.

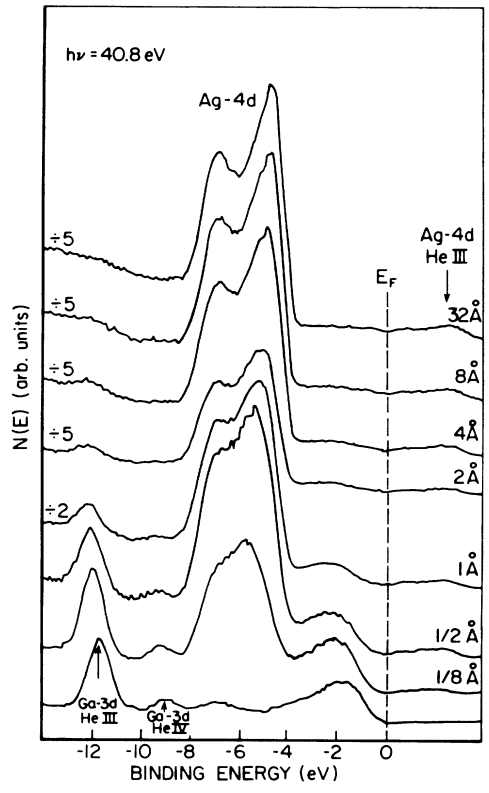

FIG. 2. GaAs valence band as a function of Ag coverage on the RT (110) surface. Extra Ga and Ag peaks are due to He III (48.4 eV) and He IV (51.0 eV) lines.

Beyond these ultralow-coverage results, the LT data indicate that another mechanism comes into play around 2 Å (Fig. 1) and pins the Fermi level on n- and p-GaAs in the high-coverage limit. Figure 2 shows the GaAs valence band and the Ag-4d level as a function of Ag coverage on a p-type RT surface. The large cross section of the Ag-4d level produces a peak that dominates the valence-band spectrum even at coverages below 0.5 Å. Contributions to the width of the 4d band come from the spin-orbit split (0.4 eV), inhomogeneities in the Ag layer (especially at LT), and the size of the Ag clusters. The evolution of the shape and width of the Ag-4d band has been studied as a function of Ag deposition on RT amorphous carbon (a-C).[16] Band narrowing, due to loss in long-range periodicity, is observed in small clusters. Other parameters such as alloy composition can affect the bandwidth equally. The Ag-GaAs interface is abrupt, however, and little if any alloying is expected, especially at LT. We can therefore attribute bandwidth variations to inhomogeneities and mostly to changes in adatom cluster size.

Two parameters become important in the evaluation of the size of the clusters in our Ag deposition: the density of nucleation sites on the GaAs surface, and the temperature-dependent surface diffusion of Ag. The typical density of nucleation sites on a-C substrates is $d_c = 3\times10^{12}$ cm^{-2}, much larger than on the well cleaved surfaces used here. As Ag is highly mobile on RT GaAs, clustering is not limited by surface diffusion, and we can expect cluster sizes larger than those obtained on a-C at equivalent coverage. A comparison of the shape and width of the 4d bands of Fig. 2 with those of Ref. 16 confirms this expectation. The full width at half maximum (FWHM) of our $\frac{1}{8}$-Å (7.4×10^{13} cm^{-2} Ag atoms) band is 2.85 eV, very close to the 3.0-eV value obtained with a much larger coverage of a-C (10^{15} cm^{-2} Ag atoms). A lower bound for the mean number of atoms per cluster, n_{Ag}, for $\frac{1}{8}$ Å can therefore be estimated with the nucleation site density on a-C: $n_{Ag} > 10^{15}$ cm$^{-2}/d_c \simeq 300$, well above the number of Ag atoms necessary to produce metallic behavior.[16] Thus, Ag clusters on RT GaAs are metallic early on, at coverages equal to or lower than $\frac{1}{8}$ Å. This estimation is probably more reliable than that obtained from the measurement of the Fermi edge. The d band has a very large cross

section in UPS, and its width can be measured accurately. The Fermi edge, on the other hand, is weak at low coverage. Final-state charging effects in small (although metallic) clusters[16] can shift it to higher binding energy by a substantial amount (0.3–0.5 eV), away from the bulk Ag Fermi level and toward the top of the GaAs valence band, thus making its observation and correlation with metallicity more difficult.

The high-binding-energy peak of the Ag-4*d* doublet shows little dispersion with respect to coverage, as was shown by Chin *et al.*,[17] and the low-binding-energy peak shifts to lower binding energy, in agreement with the Ag/*a*-C data. The FWHM of the band (Fig. 3) increases smoothly as a function of coverage, indicating an increase in the long-range periodicity in the Ag clusters, with results from LEED and SXPS.[10]

The evolution of the FWHM during deposition on the LT GaAs surface is different (Figs. 3 and 4). The FWHM at $\frac{1}{8}$ Å is only 1.6 eV, about half of its high-coverage value (3.25 eV). This severe band narrowing corresponds to a small effective size of the Ag clusters. A comparison with the data of Ref. 18 indicates that the LT $\frac{1}{8}$-Å clusters are substantially smaller than those corresponding to a deposition of 2.0×10^{14}-cm^{-2} Ag atoms on *a*-C. Using again the density of nucleation sites on *a*-C, we can estimate the upper bound for n_{Ag} to be substantially less than sixty Ag atoms at $\frac{1}{8}$ Å. The clusters are therefore mostly *nonmetallic*. This corresponds to the predominance of very small AG clusters, or perhaps isolated Ag atoms, dispersed on the surface, as expected from reduced adatom diffusion at 100 K. The FWHM increases suddenly around 1 Å toward the final 3.0-eV RT value. From the considerations given above, we conclude that, at LT, the average cluster becomes metallic only with a coverage between 1 and 2 Å. Instead of the RT Volmer-Weber growth mode, the Ag overlayer grows in a quasi-2D first layer followed by 3-D nucleation and formation of metallic clusters at higher coverage. The 2D character of the first layer is compatible with LEED measurements showing *complete unrelaxation* of the GaAs surface with 1.5 Å (=1 monolayer) of Ag deposited at LT.[10]

We propose that the 2-Å drop of E_F on LT *n*-GaAs is due to the appearance of metallicity in the overlayer. The onset of this transition occurs when the FWHM of the *d* band indicates metallic character in the clusters, i.e., FWHM > 2.6–2.8 eV between 1 and 2 Å, suggesting that the two are correlated (Figs. 1 and 3). The movement of E_F continues, however, up to a coverage of 6–8 Å. This is due to several factors. First, there is a broad distribution of cluster sizes, especially at LT where equilibrium is more difficult to achieve. Although the broad line shape of the 4*d* band of the larger clusters precludes the determination of this distribution, some clusters must remain nonmetallic up to high coverages (> 6–8 Å). Though E_F may be pinned locally under metallic clusters, the lateral extent of the depletion region is limited by the doping. This leads to inhomogeneous band bending.[18] Second, inhomogeneities in the Ag layer can also lead to bandwidth broadening unrelated to the metallic character of the overlayer.

A more fundamental question concerns the rapid movement of E_F at ultralow coverage on LT *p*-GaAs. As mentioned previously, this movement is due to an independent mechanism, i.e., charged clusters,[13] small density of defects, interface structural changes,[10] or metal-adsorption-induced states, which brings E_F close to its final position and precludes a drop or rise similar to

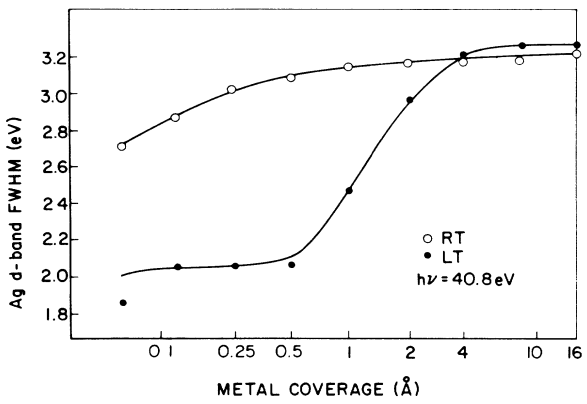

FIG. 3. Full width at half maximum (FWHM) of the Ag-4*d* band as a function of Ag coverage on RT and LT GaAs(110).

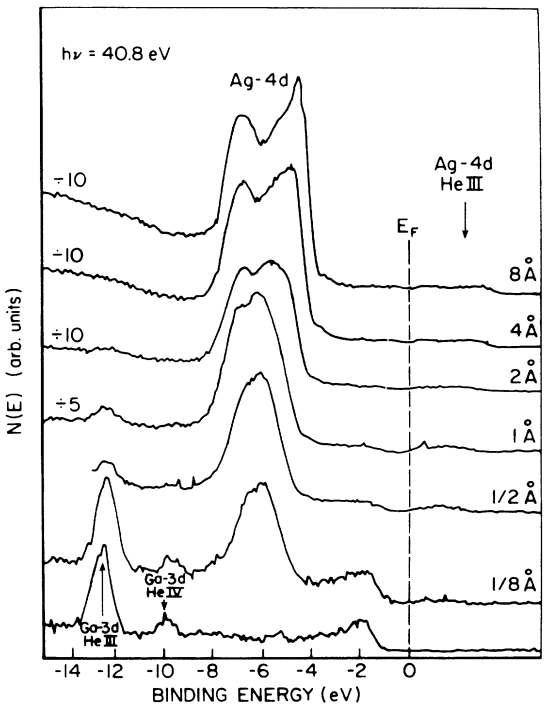

FIG. 4. Same as Fig. 2, but at LT.

that observed on *n*-GaAs. Yet a movement down from the overshoot position is always observed around the transition coverage. Similar movements are observed with other metals, i.e., Al, In, and Au, and by another group.[8-12] It suggests that a common pinning mechanism is active on both *n*- and *p*-type samples beyond the ultralow-coverage regime, although its manifestation is not as dramatic on LT *p*- as it is one *n*-GaAs.

Our conclusions concerning the possible pinning mechanisms are therefore the following. Mechanisms put forward in models such as the unified-defect model[1] or the effective-work-function model[3] are not likely to play a dominant role in the abrupt transition described above and the resulting E_F position at this interface. The energy necessary for defect formation, i.e., heat of condensation of the metal or energy released upon formation of small clusters (even below 1 Å at LT) should be available and produce pinning at much lower coverage than the observed transition coverage. Pinning beyond 2 Å seems to be more compatible with the appearance of metal-induced gap states which develop when delocalization of the cluster conduction electrons occurs. In other words, LT pinning is delayed until the overlayer acquires a metallic character, which does not happen until the coverage reaches 1–2 Å. At that coverage, the density of metal-induced gap states becomes sufficient to screen any interface states formed at low coverage, and to move E_F close to the GaAs charge-neutrality level. The abrupt transition is not observed at RT because of the early formation of large metallic clusters, as demonstrated from the FWHM data in Fig. 3, and RT pinning is expected to be rapid on *n* and *p* samples, as is indeed observed. We therefore suggest a correlation between E_F pinning and appearance of overlayer metallic character at the Ag/GaAs interface.

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[1]W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, J. Vac. Sci. Technol. **16**, 1427 (1979).

[2]L. J. Brillson, Surf. Sci. Rep. **2**, 123 (1982).

[3]J. L. Freeouf and J. M. Woodall, Appl. Phys. Lett. **39**, 727 (1981).

[4]J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984), and references therein.

[5]W. Mönch, Phys. Rev. Lett. **58**, 1260 (1987).

[6]C. R. Bonapace, K. Li, and A. Kahn, J. Phys. (Paris), Colloq. **45**, C5-409–C5-418 (1984).

[7]A. Kahn, Surf. Sci. Rep. **3**, 193 (1983).

[8]M. K. Kelly, A. Kahn, N. Tache, E. Colavita, and G. Margaritondo, Solid State Commun. **58**, 429 (1986).

[9]K. Stiles, A. Kahn, D. Kilday, N. Tache, and G. Margaritondo, in *Proceedings of the Eighteenth International Conference on the Physics of Semiconductors, Stockholm, 1986,* edited by O. Engström (World Scientific, Singapore, 1987), p. 121.

[10]K. Stiles, A. Kahn, D. Kilday, and G. Margaritondo, J. Vac. Sci. Technol. B **5**, 987 (1987).

[11]K. K. Chin, T. Kendelewicz, C. McCant, R. Cao, K. Miyano, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. A **4**, 969 (1986).

[12]R. Cao, K. Miyano, T. Kendelewicz, K. K. Chen, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. B **5**, 998 (1987).

[13]S. Doniach, K. K. Chin, I. Lindau, and W. E. Spicer, Phys. Rev. Lett. **58**, 591 (1987).

[14]K. Stiles and A. Kahn, unpublished.

[15]The *n* vs *p* asymmetry can result from adsorbate-induced states if a gap opens in the density of states of the overlayer for isolated adsorbates or very small clusters (donor states in the semiconductor gap, acceptor states near or above the conduction-band minimum). The gap vanishes when the adatom clusters grow and become metallic.

[16]G. K. Wertheim, S. B. DiCenzo, and D. N. E. Buchanan, Phys. Rev. B **33**, 5384 (1986).

[17]K. K. Chin, S. H. Pan, D. Mo, P. Mahowald, N. Newman, I. Lindau, and W. E. Spicer, Phys. Rev. B **32**, 918 (1985).

[18]J. Y. F. Tang and J. L. Freeouf, J. Vac. Sci. Technol. B **2**, 459 (1984).