# Delocalization Effects at Metal-Semiconductor Interfaces

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Changes with onset of metallic behavior in the position of an impurity-stabilized Fermi level at the GaAs-Ag interface are interpreted in a model based on delocalization of the impurity levels. The resulting energy broadening of interface states appears to be an important mechanism underlying the Schottky behavior; in particular the model obviates the need for separate donor or acceptor properties of the impurity levels.

We have observed substantial changes ($>100$ meV) of the Fermi-level position $E_F$ with the onset of metallic behavior of Ag sequentially deposited on cleaved GaAs(110) surfaces. Unexplained reversals in the direction of the movement of $E_F$ for $p$-type GaAs near the onset of metallic behavior have been reported in the past[1-3] [an example is the dashed curve in Fig. 1(b) for Ag]. These effects, which are especially pronounced for low-temperature deposition of the metal,[4,5] cannot be adequately explained by existing Schottky-barrier models.[6-14] The changes reported here are particularly noteworthy because they occurred even after the semiconductor surface was thought to be "pinned" by impurity densities far exceeding those estimated to overcome metallic screening effects.[15,16] Our results are interpreted in terms of a new model based on broadening and energetic shifts of impurity levels in close contact with the metal. The broadening is the result of wave-function overlap which leads to a delocalization of the impurity states at the interface. The delocalization allows partial charge occupancy which accounts for the observed shifts of $E_F$ during the metal-semiconductor interface formation.

The experiments were designed to study the role of metallic screening on the interface charge density, in particular the minimum density required to maintain a constant $E_F$ near midgap independent of metal coverage. Calculations predicted this density to be $\simeq 10^{14}$ $|e|$ cm$^{-2}$,[15,16] which is $\sim 100$ times the value needed for the bare surface. Surface impurities were generated by deposition of V on cleaved $n$- and $p$-type GaAs [doped to $(5-10) \times 10^{17}$ cm$^{-3}$] to coverages of 0.1–1 monolayers (ML) [1 ML refers to the atomic density of the GaAs(110) surface or $8.86 \times 10^{14}$ cm$^{-2}$]. V reacts strongly with GaAs,[3] creating deep impurity levels which pin $E_F$. Ag was subsequently deposited in steps on the "doped" surfaces. Ag was chosen because of its low reactivity with GaAs,[1] which minimizes potential confusing chemical interactions. All metal depositions were made with the substrate at room temperature. The band bending was measured from changes in kinetic energy of the bulk components of the photoemission spectra of the

Ga and As $3d$ core levels excited with synchrotron radiation of energy $h\nu = 90$ eV.[1,3] The results are shown in Fig. 1. The starting values of $E_F$ (no Ag coverage) de-
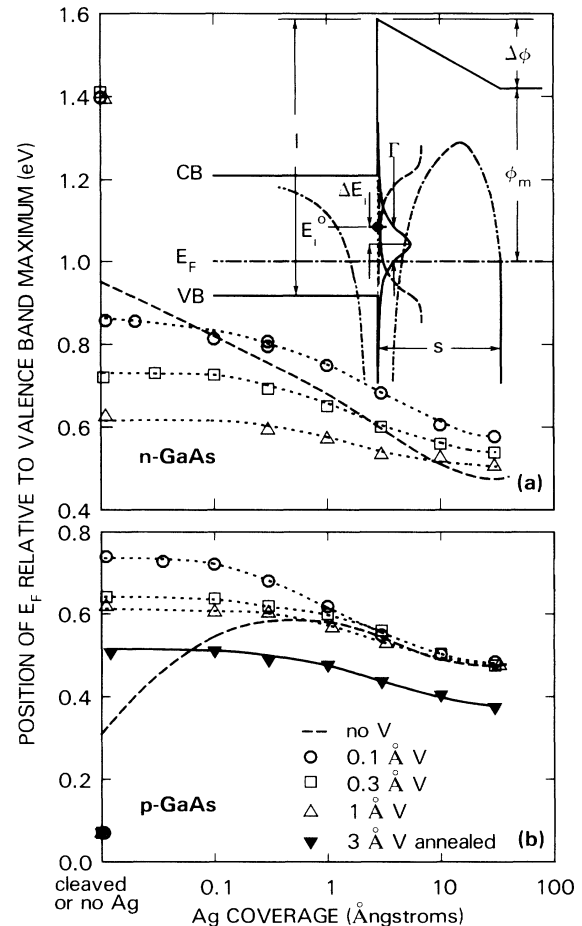


FIG. 1. Changes in the interface Fermi level with Ag coverage for (a) $n$-type GaAs(110) and (b) $p$-type GaAs(110) for indicated thicknesses of V interlayers. Open data points are for unannealed samples; filled data points are for an annealed sample. Dashed curves represent the behavior for Ag without V at the interface. An energy diagram for the proposed delocalization model is shown at the top.

pend on the initial V coverage; they decrease monotonically on $n$-type GaAs to a value 0.63 eV above the valence-band maximum (VBM), which is obtained for coverages near and above 1 Å. On $p$-type GaAs $E_F$ rises, reaches a maximum near 0.1 Å of V, and then decreases to the saturation value for $n$ type. We will discuss first the results for V-covered surfaces which were not annealed. The data are represented in Fig. 1 by open symbols. With the addition of Ag, changes in $E_F$ are initially small to coverages of $\simeq 0.5$ Å. Beyond this value $E_F$ dips and levels off near the highest coverages shown. The onset of the dip correlates with the onset of metallic character in the Ag near 0.5 Å, which was ascertained by the broadening of the Ag $4d$ levels and the appearance of a metallic Fermi edge.[1] The curves show similar shapes and a rather surprising trend for both $n$- and $p$-type materials: The final $E_F$ values (and consequently the Schottky-barrier heights) on unannealed surfaces are nearly those of Ag for coverages up to $\simeq 1$ ML of V (we did not exceed this value for unannealed samples because of inherent accuracy problems in the analysis of core-level spectra for chemically reactive systems). Thus it appears at first glance that the Ag almost totally screens the impurity levels of the V (we have spectroscopic evidence that the V is not removed from the interface). If screening were this pervasive, it alone would have substantial consequences on existing Schottky-barrier models, in particular, the relevance of defects and impurities in the determination of barrier heights.[9-11] However, it is difficult to reconcile, even with consideration of the metal-induced gap-state (MIGS) models, that the barrier height would be oblivious to defect densities exceeding $\simeq 10^{15}$ cm$^{-2}$.[17] Evidence that indicated the need for new approaches to the description of interface behavior was obtained by our repeating the experiments on samples annealed at $\simeq 330$°C after the deposition. The annealing improves the surface stoichiometry through partial removal of excess metallic Ga, and lowers $E_F$ relative to the unannealed case. The latter effect is clearly shown in Fig. 1(b). If the role of Ag were strictly to screen, for example, via the MIGS models, one would expect only a small change in $E_F$ towards coincidence with the other curves. Instead, $E_F$ follows a nearly identical trend as before, but with the important difference that it dips below the saturation value of Ag at maximum coverage. Clearly, neither MIGS models in their present formulation nor the chemical characteristics of Ag alone can account for this unusual behavior. Instead, we attribute these observations to correlation and delocalization effects of the impurity states in the presence of a metal. We develop this model next.

Let us consider the effect of a metal approaching a semiconductor which has a localized deep level at its surface. For simplicity, we assume it to be a substitutional defect or impurity. Near contact the wave functions of the impurities and the metal begin to overlap and elec-

trons can tunnel between the two systems. A finite lifetime $\tau$ can be assigned to the former stationary defect state, which in the close presence of the metal delocalizes and assumes the character of a resonance. The uncertainty principle dictates that a finite lifetime leads to an energy uncertainty $\Delta E \sim \hbar/\tau$. This broadening can be several electronvolts for valence levels of metal atoms adsorbed on metal surfaces.[18,19] Because of the dielectric response of the semiconductor, these effects are considerably reduced in the present case by screening effects. They remain nevertheless significant and comparable with general chemical effects that affect Schottky-barrier heights. The inset in Fig. 1 shows schematically the energy diagram for the system at intimate contact. The potential of the discrete defect level of energy $E_i^0$ is represented by a deep impurity potential (dash-dotted curves) that is separated from the metal potential by a barrier, through which the electrons can tunnel. The delocalized level is shown to have broadened by an amount $\Gamma$ and shifted downward in energy by $\Delta E_i$. The shift is the consequence of metallic screening of the net charge $q_{eff}$ in the defect level, and can be considered as an image-force effect. Simultaneously, a redistribution of electronic charge between the metal and semiconductor is required to equalize the differences in their Fermi levels which existed prior to contact. This is achieved by the formation of a dipole potential $\Delta\phi$, which satisfies the energy balance $E_F = I - \phi_m - \Delta\phi$, where $I$ and $\phi_m$ represent the ionization energy of the semiconductor and the metal work function, respectively. $\Delta\phi = 4\pi N_i e^2 q_{eff}\lambda_{eff}$, where $N_i$ is the surface density of impurity sites and $\lambda_{eff}$ is the effective separation between $q_{eff}$ and its counterpart near the positive-ion cores of the metal.[12] The broadened and delocalized defect level can be considered a local density of states $\rho_i(E)$, with the property $\int_{-\infty}^{+\infty} \rho_i(E)dE = 1$. The effective charge $q_{eff}$ at the impurity site can be obtained by integration of $\rho_i(E)$: $q_{eff} = \int_{-\infty}^{+\infty} F(E)\rho_i dE$, where $F(E)$ is the Fermi function. The functional dependence of $\rho_i(E)$ will be assumed to be analogous to that of an adsorbate-metal system, which in the framework of the Newns-Anderson formalism is a Lorentzian[20,21]:

$$\rho_i(E) = \frac{1}{\pi}\frac{\Gamma/2}{\{E - [E_i^0 - \Delta E_i(q_{eff})]\}^2 + (\Gamma/2)^2}. \quad (1)$$

The following approximations are made to calculate the parameters: (a) The metal is treated as a jellium; (b) metal-semiconductor interactions (bond formation) are neglected; and (c) the unperturbed impurity state is isolated and represented by a single energy level. The latter approximation assumes the absence of broadening effects, which may arise both through variations in the impurity bonding environment and, to a lesser extent, from the formation of impurity bands, which require extended wave functions normally associated with shallow impurity levels. The underlying physics will not be

changed with neglect of broadening, as the metal states delocalize all states on the semiconductor surface. For convenience and simplicity we will assume the low-temperature limit, for which integration of (1) gives

$$q_{\text{eff}} \overset{T \to 0}{=} \int_{-\infty}^{E_F} \rho_i(E)\,dE$$

$$= \frac{1}{\pi}\left[\tan^{-1}\left|\frac{E_F - [E_i^0 - \Delta E_i(q_{\text{eff}})]}{\Gamma/2}\right| + \frac{\pi}{2}\right]. \quad (2)$$

Since both $\Delta E_i$ and $E_F$, the latter now expressed as

$$E_F = (I - \phi_m) - 4\pi\lambda_{\text{eff}}e^2 N q_{\text{eff}}, \quad (3)$$

depend on $q_{\text{eff}}$, Eq. (1) must be solved self-consistently. The image force lowering $\Delta E_i(q_{\text{eff}})$ can be approximated by the image-force potential $q_{\text{eff}}^2 e^2/4\epsilon(s+\xi)$, where $s$ is the distance between the impurity site and the metal surface and $\xi$ is the Fermi-Thomas screening length in the metal.[22,23] From Fermi's "golden rule" $\Gamma = \Delta E$ $\propto |\langle m|V|i\rangle|^2$, where $\langle m|$ and $\langle i|$ are the eigenvectors of the unperturbed metal and impurity states and $V \sim e^2/\epsilon r$ is the screened impurity potential. With $|i\rangle$ represented by a hydrogenic $2s$-like wave function matched to a model deep impurity wave function[24] in GaAs, and a free-electron-like $|m\rangle$, we obtain an expression for the broadening $\Gamma$ similar to that of Gadzuk,[19] but with the important addition of an inverse square dependence on $\epsilon$. Now $\lambda_{\text{eff}} \sim s/\epsilon + \xi$.[12] Hence $\Gamma$, $\Delta E_i$, and $E_F$ are all inversely dependent on the effective dielectric function $\epsilon = \epsilon(s)$. We estimate its value to be half the bulk dielectric function[25] $\epsilon_\infty(r)$ weighted by the square of the unperturbed, $s$-dependent impurity wave function $\phi_i^2(s)$.[21] In the range of interest here $(1.5 \leq s \leq 2.5 \text{ Å})$ $\epsilon$ varies between 3.5 and 4.5 for GaAs.[21] We believe this to a conservative estimate. Louie, Chelikowsky, and Cohen[12] estimated a value of $\epsilon \simeq 2$, which is probably too low in view of the more recent calculations of $\epsilon_\infty(r)$.[25]

We can now calculate the changes in $E_F$ from Eqs. (2) and (3). We chose $s \sim r_{\text{sc}} + r_m - d_m/2 = 1.84$ Å, where the constants represent half the GaAs bond length, the Ag metallic radius, and the Ag interplanar spacing, respectively. The electrically active density $N_i$ is estimated to be limited near $\frac{1}{2}$ ML $(\simeq 5 \times 10^{14} \text{ cm}^{-2})$, a value consistent with previous estimates.[12] With $\lambda_{\text{eff}} = 1$ Å, $I = 5.56$ eV,[26] and $\phi_m = 4.52$ eV,[27] we obtain the following numbers: $\Gamma = 0.062$ eV, $q_{\text{eff}} = 0.065$, and $\Delta E_F = 0.15$ eV, where $\Delta E_F$ is the change of $E_F$ with the onset of metallic behavior in the Ag overlayer. Because of the small $q_{\text{eff}}$, $\Delta E_i$ is of the order of a few millielectronvolts; hence most of the shift in $E_F$ is due to the broadening of the impurity level. The good agreement with our experiment findings of $\Delta E_F \simeq 0.14\text{–}0.17$ eV without the use of fitting parameters may be somewhat fortuitous in view of the approximations, but nevertheless strongly supports the viability of the model.

A salient feature of this model is that the delocalized impurity or defect level can act both as an acceptor or donor. In the present calculation the net charge density is $q_{\text{eff}} \times N_i \approx 3 \times 10^{13}$ cm$^{-2}$. In contrast, the net charge difference at the interface necessary to maintain the potential difference for $n$- and $p$-type conductivity of the semiconductor is only $\simeq 2 \times 10^{12}$ cm$^{-2}$, which is readily accommodated in the resonance level without appreciably changing $E_F$. The broadened level may be viewed as an initially unoccupied (neutral) density of states, into which charge can be added or removed to accommodate the potential differences of the system as a whole. Thus the concept of separate donor and acceptor levels, which underlies the defect models,[9,10] is no longer a limitation in the present model. However, the strong delocalization effects obviate those models that rely strictly on bulk defect levels,[10,28] because their evolution in the presence of the metal makes an assignment in terms of unperturbed bulk levels meaningless. Although derivatives of bulk-related defects may contribute to an overall delocalized density of interface states, we believe that the actual metallic bonds provide sufficient density of states at the interface to accommodate the needed charge densities. Lack of the latter consideration is also a shortcoming of the MIGS models,[6–8,12,14] since all ignore the rehybridization of the semiconductor bonds at the interface and consequently lose contact with the ongoing chemistry and chemical trends. Contact with the MIGS models can be regained by consideration of only delocalization of the semiconductor valence- and conduction-band states in immediate contact to the metal. The resulting bulk band delocalization is conceptually shown in the inset of Fig. 1. This tailing in of the band edges has long been recognized and calculated[12]; however, the notion of its origin in terms of delocalization is generally not appreciated.[14,29] It should be emphasized that this effect is not the band narrowing described by Inkson,[13] which is based on exchange and correlation effects extending over several atomic distances into the semiconductor. Qualitatively the model can also account for Schottky-barrier reductions on $n$-type semiconductors with nonmetallic components at the interface, for example, oxides[6] or As.[30] Their principal effect is to increase the separation between metal and semiconductor and thereby reduce $\Gamma$ and $\Delta E_F$ to a few millielectronvolts. In contrast, an enhancement of the delocalization appears to dominate for metals deposited at low temperature. Chemical interactions are generally weaker than at room temperature, and the tendency for the metal to cluster is reduced as well. Low-temperature metallization experiments on $p$-type GaAs show[4,5] an initial strong rise of $E_F$ followed by a plateau extending to metal coverages of $\simeq 0.1$ ML. Over the same coverage range, the Fermi level on $n$-type material remains near its unpinned value at the conduction-band edge. Thus isolated atoms or small clusters appear to form donor states only. With the on-

set of metallic behavior both Fermi levels drop similarly as those in Fig. 1. On $n$-type GaAs the effect is generally larger than observed here because the adsorption-induced defect level lies higher in the band gap, which requires a smaller charge transfer to equilibrate $E_F$. The smaller $q_{eff}$ results in a larger $\Delta E_F$ with onset of metallic behavior. Stiles et al.[4] recently reported a $\Delta E_F = 0.4$ eV for Ag deposited at low temperature on $n$-GaAs. For a value of $E_i^0 = 1.15$ eV, to correspond to their plateau value prior to the appearance of the metallic phase of Ag, and otherwise identical parameters as in our previous calculation, our model predicts $\Delta E_F = 0.36$ eV. This excellent agreement further supports the basic premises of the proposed model.

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