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Defects and metal states: Towards a predictive model for the Schottky barrier

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In the presence of metallic states, deposition-generated midgap levels at the semiconductor surface evolve into resonances that accommodate the fractional charge density that ultimately determines the Fermi level and hence the Schottky-barrier height. This concept is applied to calculate both the barrier heights of GaAs for nonalloyed metal-semiconductor interfaces, and the index-of-interface behavior for 15 tetrahedrally coordinated semiconductors.

Presently discussed Schottky-barrier models that attempt a microscopic description of observed barrier characteristics fall into two, mutually exclusive groups. Models of one group, jointly referred to as metal-induced gap state (MIGS) models,¹⁻⁵ essentially consider only the effects of jellium metal states on the intrinsic band structure of the semiconductor, that is, interface rebonding of semiconductor-metal states is ignored. A common shortcoming of the MIGS models is their inability to account for the often-strong dependence of barrier heights on the metal work function or electronegativity. On the other extreme of conceptual models are the defect models proposed by Spicer and co-workers,^{6,7} which are based on the observation of unique, metal-independent pinning positions of the interface Fermi level E_F during the early stages of interface formation. The pinning of E_F was attributed to defects intrinsic to the semiconductor. This model, however, can neither account for the large variations in Schottky-barrier heights for different metals on GaAs (~ 0.5 eV),^{8,9} nor is it capable of making predictions for other metal-semiconductor systems. We have recently proposed¹⁰ a new concept of metal-semiconductor interface behavior to explain variations of E_F in the intermediate coverage region between the adsorbate stage and full metallic coverage. This model contains aspects of MIGS models, but requires the existence of defect and/or impurity states at the interface which are generated during the formation process of the interface through rehybridization of interface bonds or substitutional reactions. This duality of the model will be further developed here to account for observed work-function-dependent variations of Schottky-barrier heights for GaAs, as well as the index-of-interface behavior for the tetrahedrally coordinated semiconductors.¹¹ A viable Schottky-barrier model should agree semiquantitatively with this index; full agreement cannot be expected for

any model, since the database from which the index is calculated is presently not entirely reliable.¹²

The delocalization model is based on the notion that a localized defect or impurity state on the surface of the semiconductor becomes delocalized in the presence of a metallic overlayer. This effect is a consequence of the overlap of impurity and metal wave functions, which causes the formerly localized level to become a broadened resonance. The resonance can be described in terms of a local density of states $\rho_i(E)$ of Lorentzian form:^{10,13} $\rho_i(E) = \Gamma/2\pi \{ [E - E_i^0 + \Delta E_i(q_{\text{eff}})]^2 + (\Gamma/2)^2 \}^{-1}$, where E_i^0 is the energy of the deposition-induced defect and/or impurity level prior to the onset of metallic properties in the overlayer, Γ is the full width at half maximum of the broadened resonance following the interaction of the defect level with the metallic states, and $\Delta E_i(q_{\text{eff}})$ is the image force lowering of E_i^0 due to an average effective charge q_{eff} residing in the resonance. q_{eff} can be calculated in the low-temperature limit from $q_{\text{eff}} = \int_{-\infty}^{E_F} \rho_i(E) dE$:

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

Upon contact, the disparate Fermi levels in the metal and semiconductor equilibrate, as charge flows into the interface states to establish an interface dipole $\Delta\phi$. The driving potential is the difference between the ionization energy I_{sc} of the semiconductor and the metallic work function ϕ_m . At contact E_F , measured relative to the semiconductor valence-band edge, is given by

$$E_F = I_{\text{sc}} - \phi_m - \Delta\phi = I_{\text{sc}} - \phi_m - 4\pi e^2 \lambda_{\text{eff}} N_i q_{\text{eff}}, \quad (2)$$

where the dipole parameters include the density of de-

fects N_i , and the effective separation λ_{eff} of q_{eff} and its countercharge near the ion potential of the metal. Since both $\Delta E_i (\propto q_{\text{eff}}^2)^{10}$ and E_F depend on q_{eff} , Eq. (1) must be obtained self-consistently. With the exception of E_i^0 the parameters in Eqs. (1) and (2) are readily calculated.¹⁰ Thus $\lambda_{\text{eff}} \sim \xi + s/\epsilon(s) \sim 1 \text{ \AA}$,² where s is the defect-metal separation, $\epsilon(s)$ the dielectric function of the semiconductor, and ξ the Thomas-Fermi screening length. Γ can be calculated from a procedure described by Gadzuk¹⁴ for an adatom on a metal surface. For an atomlike defect potential on the semiconductor side of the interface, $\Gamma = \Gamma_0(s)/\bar{\epsilon}^2(s)$, where $\Gamma_0(s)$ is the unscreened broadening function of value comparable to that of an adatom on a metal surface,¹⁴ and $\bar{\epsilon}(s)$ is the dielectric function of the semiconductor averaged over the region of wave-function overlap.¹⁰ For GaAs, with $s = 2 \text{ \AA}$ and $\bar{\epsilon}(s) \sim 4$. In analogy to the adatom case, the defect level can be viewed as an atomic valence level embedded in a medium of dielectric constant $\bar{\epsilon}$ and in close proximity to a metal surface. It should be noted that due to this proximity to the metal $\bar{\epsilon}$ is considerably reduced from the macroscopic value of the dielectric constant (~ 11 for GaAs).

We will first apply the model to calculate the Schottky-barrier height $\Phi_b^0 = E_F$ for (*p*-type GaAs)-metal interfaces. To do this, we must first estimate a value for E_i^0 . Although ionized defect and/or impurity levels in the bulk semiconductor can vary over the region of the band gap,¹⁵⁻¹⁷ the Fermi level for most adsorbates, for example, on *n*-type GaAs, lie within $\pm 0.1 \text{ eV}$ of midgap for coverages of ~ 0.1 monolayers.^{6,18} Consequently, we will initially make the simplifying assumption that E_i^0 lies at midgap for all metals near monolayer coverages. We will subsequently discuss the implications of this premise and conclude that this assumption produces negligible errors over all but the lowest work-function range when compared to a calculation for which E_i^0 varies by 0.4 eV . A value of E_i^0 near midgap can also be argued from theoretical considerations: midgap for GaAs also coincides with the charge-neutrality level (CNL),^{5,19} to which transition-metal impurity levels²⁰ and cation vacancy levels²¹ in III-V semiconductors are effectively "pinned." The density N_i of impurity and/or defects is set at $\frac{1}{2}$ the atomic density of the GaAs surface, a choice that is premised on the notion that only rehybridized metal-cation bonds and cation substitutions contribute to states in the gap.²² Moreover, the solutions for E_F are relatively insensitive on N_i in the density range of choice.¹⁰ For GaAs the choice of $N_i = 5 \times 10^{14} \text{ cm}^{-2}$ is also consistent with previous estimates.²

The results of the calculations are shown in Fig. 1; experimental values are shown as well.^{9,18,22-24} The calculated values of Γ used for the solutions varied from the 0.016 eV for Cs to 0.081 eV for Cu.²² The solid line represents a solution with a "universal" $\Gamma = 0.062 \text{ eV}$, which is the average value for the metals considered. The good agreement of the two approaches indicates a relative insensitivity to the precise value for Γ . A description in terms of a single, narrow defect level may not adequately describe the bonding variations of a real interface, which nevertheless may be simulated by using in-

stead a discrete set of levels, centered at E_i^0 whose sum is limited to N_i . Such a simulation for seven levels distributed within a Gaussian envelope and spaced 0.03 eV is shown by the dashed curve in Fig. 1. With the exception for $\phi_m \lesssim 2.5 \text{ eV}$, where image force effects (large q_{eff}) produce additional deviations, the generally good agreement between single level (solid) and "broadened" solutions appears to justify our earlier and computationally simpler use of a single defect level. The effective charge q_{eff} per resonance is also shown in Fig. 1. Its value decreases rapidly with increasing ϕ_m , as less charge is needed to equalize the Fermi levels of metal and semiconductor. For small q_{eff} the model predicts a high Φ_b^0 for *n*-type GaAs, as E_F lies low in the tail of the Lorentzian resonance, which remains centered at E_i^0 . Overall, the model predictions appear to be in reasonable agreement with experiment. In particular, the model accounts for the near constancy of E_F for $\phi_m \lesssim 4 \text{ eV}$, and the large barrier height recently reported for Au.⁹ It should be emphasized that the model assumes a nonalloyed interface, a situation not often realized in practice. For reacted interfaces, ϕ_m should correspond to an effective value intermediate between that of the metal and the reaction product. The latter may be the frequently observed elemental Ga ($\phi_m = 4.3 \text{ eV}$),^{18,25} or an arsenide.²⁶ The effect of alloying is not apparent for $\phi_m \lesssim 4 \text{ eV}$ because of the shallow slope of E_F versus ϕ_m . In contrast, when $\phi_m \gtrsim 4 \text{ eV}$, for which the slope is steep, the effects of intermixing should exhibit strong deviations from model predictions, with E_F moving towards midgap. The different values reported for Au shown in Fig. 1 can be attributed to interface reactions,^{27,28} with the results reported by Kaiser *et al.*⁹ representing selected areas of high Φ_b^0 , which were electrically probed with a modified scanning tunneling microscope.

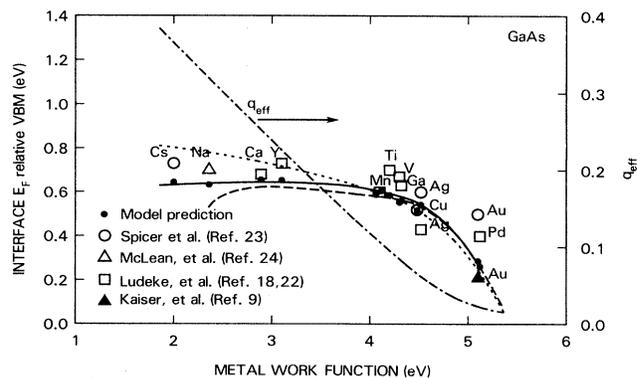


FIG. 1. Position of the interface Fermi level E_F as function of ϕ_m for GaAs: solid circles and solid line are model predictions for a unique midgap defect level; the dashed curve depicts the solutions when this level is inhomogeneously broadened. The dotted line indicates solutions that include metal-dependent values of the defect levels. The other data points are experimental values. The dotted-dashed line represents q_{eff} .

The discrepancies between model and experiment can be mainly attributed to the following uncertainties: (i) a lack of knowledge of an effective ϕ_m for real systems, (ii) neglect of Coulombic effects in E_i^0 ($\propto q_{\text{eff}}$), which would "raise" the defect level for metals of low ϕ_m (large q_{eff}), and (iii) the assumption of a unique E_i^0 for all metals. An upper estimate of the error due to the latter assumption can be readily made by use of existing data for GaAs. Mönch²⁹ has compiled the values for the low-coverage (~ 0.01 monolayer) plateaus of E_F for a broad range of metals on GaAs, and has associated these values with adsorbate-induced defect levels. A remarkable linear energy dependence over ± 0.2 eV about the CNL was observed when plotted against the atomic ionization energy. Using these values for our starting E_i^0 we obtain the dotted curve in Fig. 1, which deviates appreciably from the single-valued E_i^0 curve (solid line) only for $\phi_m < 3$ eV. The addition of inhomogeneous broadening would furthermore lower this end of the curve in closer agreement with the solid curve and the experimental data.

We will evaluate next the index of interface behavior $S \equiv d\Phi_0^0/d\chi_m$,¹¹ where χ_m represents the Pauling electronegativity of the metal. χ_m and ϕ_m exhibit an empirically determined relationship:³⁰ $\phi_m = 2.27\chi_m + 0.34$. Previous attempts to relate S to physical parameters of the interface have been made in the framework of MIGS models, with success ranging from fair^{3,12} to poor.⁴ In general, a unique value of S is assumed to exist for each semiconductor, implying a linear relationship between Φ_0 and χ_i . In practice, the data are quite scattered and a least-squares linear fit is used to obtain S .^{11,12} Our model does not predict a unique S for the abrupt, nonalloyed interface. However, for intermediate values of $\phi_m \sim 4$ eV for GaAs in Fig. 1, the effects of intermixing on $dE_F/d\phi_m$ are minimal, as discussed above. Hence a comparison of model predictions and measured values of S can be tried.

Since $S = d\Phi_0^0/d\chi_m = -2.27 dE_F/d\phi_m$, solving Eq. (1) for E_F and differentiating it, one obtains

$$S = \frac{2.27}{1 + [1.15\bar{\epsilon}^2(\lambda)\lambda_{\text{eff}}N_i\sin^2(\pi q_{\text{eff}})]/\Gamma_0(s)}, \quad (3)$$

where N_i is expressed in units of 10^{14} cm^{-2} and λ_{eff} in \AA . The dominant parameter that contributes to the variation of S for different semiconductors is $\bar{\epsilon}^2$.³¹ For a given semiconductor $\bar{\epsilon}^{\text{sc}}$ can be approximated by scaling the calculated value for GaAs ($\bar{\epsilon}^{\text{GaAs}} = 4$) with the ratio of the dielectric constants: $\bar{\epsilon}^{\text{sc}} = 4\epsilon_{\infty}^{\text{sc}}/\epsilon_{\infty}^{\text{GaAs}}$. Thus $\bar{\epsilon}$ reflects the screening of the defect potential from the encroaching metallic states. If this screening weakens, as for the more ionic semiconductors with lower ϵ_{∞} , the delocalization and broadening (Γ) of the defect resonance is enhanced. A broader resonance for a given change in q_{eff} (due to a variation in ϕ_m) promotes a larger variation of E_F , and consequently an increase in S .

In order to calculate q_{eff} from Eq. (1) the value of E_i^0 is needed for each metal-semiconductor combination. Since these values are now known, we will make the simplifying assumption that E_i^0 lies, as for GaAs, at the CNL. Using Tersoff's calculated values for the CNL relative to the

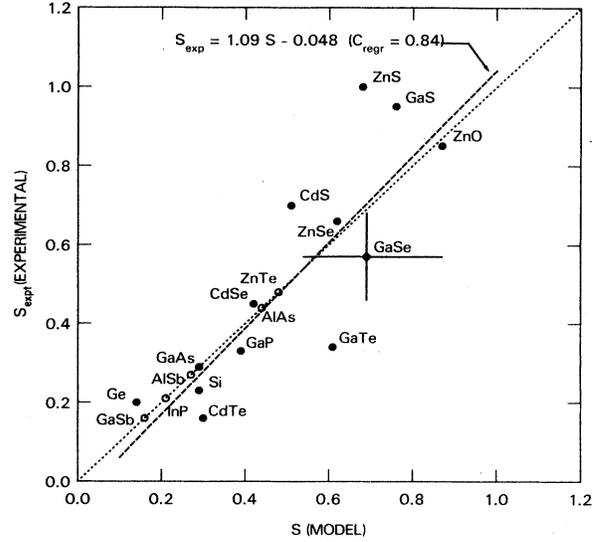


FIG. 2. Comparison of experimental value and model prediction for the index-of-interface behavior S . The dashed line is a least-squares fit.

valence-band maxima for six III-V and four II-VI compound semiconductors,³² and subtracting these from the corresponding, experimentally determined ionization potentials I_{sc} ,^{33,34} we noted that all CNL's lie 5.0 ± 0.2 eV from the vacuum level. Consequently the additional assumption was made of a "universal" position for E_i^0 at 5 eV below the vacuum level for all semiconductors discussed here.³⁵ This notion has a precedent with transition-metal impurity levels in III-V and II-VI compound semiconductors, some of which exhibit a universality in energy among the different hosts when referenced to the vacuum level.¹⁷

The metallic parameters for the present calculations were those for Al ($\phi_m \sim 4.3$ eV). With N_i set at $\frac{1}{2}$ the atomic surface density of the semiconductor, and $\lambda_{\text{eff}} \approx 0.6 + (0.43a_0 - 0.75)/\bar{\epsilon}^{\text{sc}}$, where a_0 is the lattice constant, S was calculated at $\phi_m = 4.3$ eV for 15 tetrahedrally coordinated semiconductors and three Ga chalcogenides. The model predictions are plotted against experimental observations³⁶ in Fig. 2; agreement is indicated by a data point lying on the dotted diagonal of unit slope. A least-squares fit through the solid points has a slope of 1.09 and a regression coefficient of 0.84. The open circles are model predictions for which experimental data were not available. The vertical bar through the GaSe point represents a $\pm 20\%$ uncertainty in the experimental values,¹² whereas the horizontal bar represents the range of model predictions for a variation for $4.0 \leq \phi_m \leq 4.6$ eV. In general the agreement is quite satisfactory, particularly in view of the scatter of values in the database.^{2,11,12,36} Only ZnS and the Ga chalcogenides are outside the uncertainty range. The assumptions made here for tetrahedrally coordinated compounds may be questionable for the Ga chalcogenides, which are layered materials, in which only the Ga is tetrahedrally coordinated.

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