# Schottky-like correction terms in heterojunction band lineups

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Thin Al intralayers induce changes in the valence-band discontinuities for the Ge/ZnSe(110) and the Ge/CdS(10$\bar{1}$0) heterojunctions, but not for the Si/GaP(110) heterojunction. We studied the dependence of the changes on the intralayer thickness, and their correlation to the local chemical reactions. The changes saturate for intralayers thicknesses $\sim\frac{1}{2}$ monolayer. For these thin intralayers, the Al is highly reacted with the anion of the compound semiconductor. The results indicate that the band lineup at heterojunction interfaces is affected by a Schottky-like term, as recently suggested by several theories. However, they also show that such a term does not imply the formation of a metallic Al phase.

The properties of metal-semiconductor devices are determined by the Schottky barrier. Similarly, the band discontinuities are the most important parameters of semiconductor-semiconductor heterojunctions. Very extensive experimental and theoretical research has explored the nature of these parameters.[1] The discovery of correlations between heterojunction band lineups and Schottky barriers was a major recent step towards the clarification of these fundamental problems.[2] We describe here a series of experiments that directly explored such correlations.

We recently demonstrated that thin Al intralayers at the Si/CdS(10$\bar{1}$0), Ge/CdS(10$\bar{1}$0), and Ge/ZnSe(110) heterojunction interfaces induce changes in the band lineups, while they do not affect the Si/GaP(110) heterojunction.[2,3] The changes saturate for submonolayer thicknesses of the Al intralayer, i.e., they are not related to the appearance of Al metallic character. We will see, on the other hand, that they can be interpreted as due to Schottky-like corrections to general semiconductor interface models.

After many years of theoretical work, two main classes of general semiconductor interface theories have emerged. The *unified defect model* attributes the interface properties to Fermi-level pinning by interface defects.[4,5] The *midgap energy theories* explain them in terms of induced gap states, not due to defects but to the tailing of wave functions.[6–8] Both kinds of theories are affected by limits due to their approximations. In particular, they predict that the Schottky barrier is independent of the metal, contrary to several experimental findings. Also, they do not predict any flexibility in modifying heterojunction band lineups, contrary to our present findings.

Recently, Mönch demonstrated that *both* defect states and induced gap states must be taken into account while explaining interfaces between silicon and different metals.[9] Furthermore, he found that the effects of these factors must be corrected by Schottky-like terms, determined by the metal work function and by semiconductor electron affinities. Similarly, Tersoff used a Schottky-like correction to explain the discrepancy between the theoretical midgap-energy predictions and the observed correlations between heterojunctions band lineups and Au Schottky barriers.[10] Without Schottky-like corrections, the midgap-energy valence band discontinuity is

$$\Delta E_V = E_M^1 - E_M^2 , \tag{1}$$

where $E_M^i$ is the midgap energy relative to the valence-band maximum (VBM) of semiconductor $i$. With a Schottky-like correction term, and using Cardona and Christensen's framework,[8] we have instead

$$\Delta E_V = E_M^1 - E_M^2 + S[(\chi^1 + E_G^1 - E_M^1) - (\chi^2 + E_G^2 - E_M^2)] , \tag{2}$$

where $\chi^i$ ($i = 1,2$) is the electron affinity and $E_G^i$ is the optical energy gap. $S$ is the so-called "pinning strength parameter." In first approximation, $S$ is proportional to $1/\epsilon_\infty$, the reciprocal of the optical dielectric constant of the interface.

We tested these ideas by studying the modifications of heterojunction band lineups induced by metal intralayers, starting from submonolayer thicknesses and up to thicknesses corresponding to "back-to-back Schottky barrier" configurations. The main results were the following. First, the metal intralayers do modify the band lineups. This fact alone demonstrates that neither the unified defect model nor the midgap energy theories are sufficient to describe interface properties without some kind of correction. Second, the observed changes can be understood, at least qualitatively, by introducing a Schottky-like correction such as that of Eq. (2). Third, the changes saturate for submonolayer thicknesses of the intralayer, and therefore the Schottky correction is present even before the establishment of true metal-semiconductor interfaces. Fourth, the intralayer thickness at which the changes saturate is correlated to the establishment of interface chemical bonds between the Al atoms and the anion atoms of the binary semiconductor substrate.

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The band lineups and their changes were studies with photoemission techniques, at the Wisconsin–General Motors beamline of the Wisconsin Synchrotron Radiation Center. The details of the experimental procedure for measuring band lineups and intralayer-induced changes have been discussed in Refs. 11 and 12. Briefly, substrate and overlayer valence band maxima were determined by linear extrapolation of the leading edges of the corresponding photoemission spectra. The difference between these maxima gives $\Delta E_v$, except for the intralayer-induced change in the substrate band bending. This change was derived from the energy shifts of core-level peaks.[11,12]

The novel part of the present experiments was the study of the changes as a function of the intralayer thickness, which required a complete set of band-lineup measurements for each thickness value. Figure 1 shows the measured valence band discontinuity for the Ge/ZnSe(110) heterojunction as a function of the thickness of the Al intralayer. The Ge/ZnSe(110) heterojunction is one of the prototypical lattice matched heterojunctions. Without an intralayer (0 Å of Al), we measure $\Delta E_V = 1.44 \pm 0.1$ eV. The valence band discontinuity increases rapidly with the Al intralayer thickness. The horizontal arrow shows the value obtained for a thick (64 Å) intralayer, corresponding to an increase of approximately 0.3 eV. This value was obtained by taking the difference of the two Schottky barrier heights for the two sides of the intralayer. In turn, the Schottky barrier heights were measured from the photoemission spectra. Thus the horizontal arrow corresponds by definition to a back-to-back Schottky barrier configuration. We see, however, that the saturation value is reached well before having a true metallic intralayer. In fact, the data suggest saturation at submonolayer thickness, where the monolayer thickness is defined as "one intralayer atom per ZnSe surface atom."

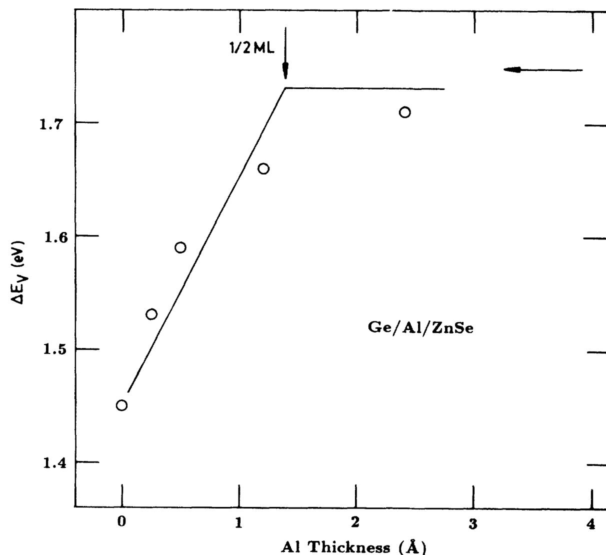


FIG. 1. Ge/ZnSe(110) valence-band discontinuity as a function of Al intralayer thickness. The horizontal arrow marks the value for back-to-back Schottky barriers. Saturation occurs for submonolayer intralayer thicknesses, as emphasized by the solid line that was drawn assuming saturation at $\frac{1}{2}$ monolayer.

Core-level photoemission spectra indicate that for thin intralayers the Al is highly reacted with the Se of the substrate, and is not metallic. Without Ge, the Al $2p$ core-level emission is broad with a shoulder to lower binding energy. The centroid of the broad emission has approximately 2.3 eV higher binding energy than the $\frac{3}{2}$ component of the spin-orbit split metallic doublet. An increase in binding energy of this magnitude from the metallic level is consistent with the formation of reacted Al-Se species, since the Se should take electric charge from the Al. In fact, the formation of $Al_2O_3$ increases the binding energy of the Al $2p$ core level by 2.7 eV.[13,14] Therefore, the 2.3 eV binding energy increase here suggests the formation of $Al_2Se_3$. The shoulder emission most likely results from the formation of a metastable selenide, such as AlSe. The deposition of 1.2-Å Ge onto the Al film removes the shoulder emission completely. The Ge may either assist in the formation of $Al_2Se_3$ or bind to the Al of the metastable Al-Se compounds. Further increase in Ge coverage does not produce an additional change in the chemical status of Al.

The data in Fig. 1 suggest that the band lineup changes saturate at coverages between $\frac{1}{3}$ and $\frac{1}{2}$ monolayer, consistent with the engagement of all Se surface atoms in chemical bonds with Al. The solid line was drawn assuming saturation at $\frac{1}{2}$ monolayer and a linear relation between band lineup change and number of Se atoms bound to Al. The actual saturation is expected somewhere between the $\frac{1}{2}$ monolayer value corresponding to the AlSe phase, and the $\frac{1}{3}$ monolayer value for $Al_2Se_3$.

Figure 2 is the equivalent of Fig. 1 in the case of Al intralayers at the Ge/CdS(10$\bar{1}$0) interface. Without the intralayer, we measure $\Delta E_V = 1.75 \pm 0.1$ eV, in good agreement with the results of previous experiments. Once again, $\Delta E_V$ changes rapidly with the intralayer thickness, and the value at less than one monolayer is indistinguishable, within the experimental uncertainty, from that given by a back-to-back Schottky barriers configuration, 2.0 eV (horizontal arrow). The binding energy of the Al $2p$ core level for the 2.4-Å film is $\sim 2.5$ eV below the metallic level, and suggests the formation of $Al_2S_3$.[15] The sharpness of the Al $2p$ emission suggests that the Al exists in only one chemical environment. The Ge layers do not affect the line shape of the emission, suggesting that the Al is very strongly bonded to the substrate. As in Fig. 1, the data indicate that saturation occurs at $\frac{1}{3}$ to $\frac{1}{2}$ monolayer coverage.

Figure 3 shows the results for another lattice-matched heterojunction. Si/GaP(110). The Al intralayers do not cause a measurable change in the value of the valence-band discontinuity from the value $\Delta E_V = 1.10 - 0.15 = 0.95$ eV, even when the back-to-back Schottky barrier configuration is reached (horizontal arrow). The core-level photoemission spectra show again that the Al reacts strongly with the substrate, and does not exhibit metallic behavior. The core-level emission shows two unresolved components separated by 1 eV, with the shallower one centered $\sim 0.9$ eV below the metallic level. The Ga $3d$

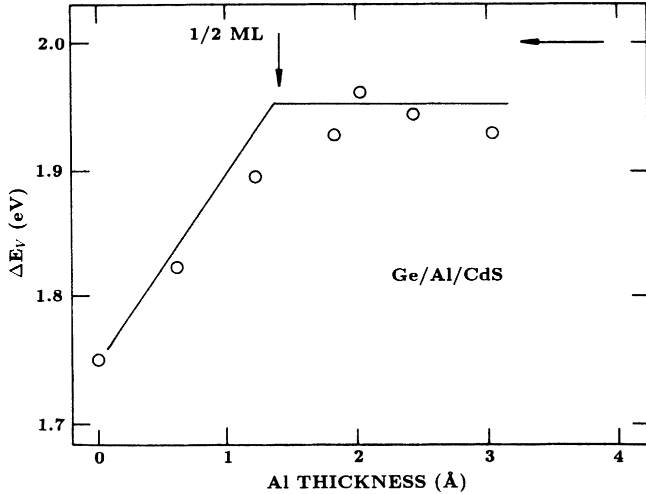


FIG. 2. The equivalent of Fig. 1, in the case of Ge/CdS($10\bar{1}0$) with Al intralayers.

core-level emission gives evidence for a strong Al-Ga exchange reaction. The Al forms AlP with the substrate and frees Ga.

As already mentioned, the observed band discontinuity changes cannot be explained by "pure" versions of the unified defect model and of the midgap-energy theories, without including Schottky corrections. We will consider now the effects of such corrections, using the midgap-energy framework, by analyzing how the Schottky-like term of Eq. (2) changes in the presence of an Al intralayer. Consider, first, the back-to-back Schottky barriers case. The valence-band discontinuity in this case is simply the difference between the two Schottky barriers (assuming $p$-type semiconductors): $\Delta E_V(\infty)=\phi_B^1-\phi_B^2$. Each Schottky barrier is given by

$$\phi_B^i=E_M^i+S^i(\chi^i+E_G^i-E_M^i-\psi^{\mathrm{Al}}) , \tag{3}$$

where $i$ labels the semiconductors and $\psi^{\mathrm{Al}}$ is the Al work function. Note that $\phi_B^i \to E_M^i$ as $S^i \to 0$, and that $\phi_B^i$ goes to the Schottky model expression as $S^i \to 1$. These are the limits for infinite screening and no screening. As we have seen, $S^i$ increases linearly with the reciprocal of the optical dielectric constant, and therefore must increase linearly with $E_M^i$, $S^i=aE_M^i+b$; thus

$$\Delta E_V(\infty)=\Delta E_V(0)(1+K) , \tag{4}$$

where $\Delta E_V(0)$ is the discontinuity with no intralayer, and we have assumed that $S$ for the heterojunction interface (without intralayer) is equal to the average of $S^1$ and $S^2$ for the individual Schottky barriers. Note that $K$ is nearly independent of the semiconductor, and given by

$$K=\frac{a}{2}[(\chi^1-E_G^1-\psi^{\mathrm{Al}})-E_M^1+(\chi^2+E_G^2-\psi^{\mathrm{Al}})-E_M^2] . \tag{5}$$

The sign of $a$ is positive, so that the sign of $K$ is fixed mainly by the magnitude of the metal work function $\psi^{\mathrm{Al}}$.

We estimate that $a \sim 0.07$ by using the values of $\epsilon_\infty$ and $E_M$ from Ref. 8. Then, by using the parameters of Table I taken from Refs. 8, 16, and 17, and $\psi^{\mathrm{Al}}=4.2$ eV, we find $K=0.06$, 0.04, and 0.06 for Ge/Al/ZnSe, Ge/Al/CdS, and Si/Al/GaP. The corresponding changes in the valence-band discontinuity derived from Eq. (4) are 0.09, 0.07, and 0.05 eV. Thus this very simple approach correctly predicts the sign of the changes, and the fact that the change for the last interface is smaller than for the first two. Even quantitatively, the predicted magnitudes are remarkably accurate, considering the many approximations, e.g., in the $S$ parameters and in their relation to the optical dielectric constant.

This approach also explains the observed correlation between Au Schottky barriers and valence-band discontinuities.[2] In fact, Tersoff[10] noted that this correlation is given directly by Eq. (4). In the case of Au Schottky barriers, he argued that $K<0$, in qualitative agreement with the experimental results of Ref. 2.

This simple model is based on a back-to-back Schottky barrier configuration. However, Figs. 1 and 3 show that the changes in the band lineup saturate well before reaching a metallic Al intralayer. This is an interesting experimental fact. Note that the changes predicted by Eq. (4) arise from the fact that in Eq. (2) we used an average value for the pinning strength parameter, while separate values for the two Schottky barriers. Thus the data imply that even for intralayers thicknesses of the order of 1 monolayer or less the screening on the two sides of the intralayer is substantially different from that of the intralayer-free heterojunction. In general, they also indicate that the Schottky-like corrections, although calculated using the work function of metallic Al, really describe localized effects. The correlation between saturation thickness and formation of Al-anion bonds suggests that

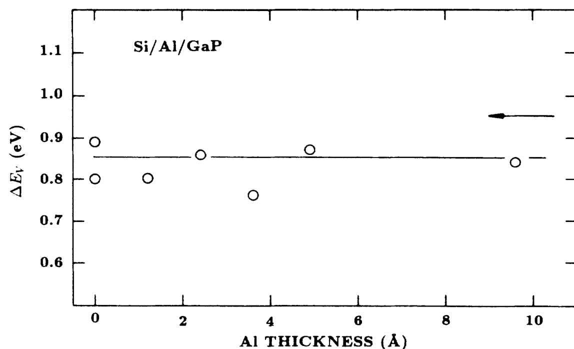


FIG. 3. The equivalent of Fig. 1, in the case of Si/GaP(110) with Al intralayers.

TABLE I. Parameters used to estimate the Schottky-term, derived from Refs. 8 and 17.

| Material | $\chi$ (eV) | $E_G$ (eV) | $E_M$ (eV) |
|---|---|---|---|
| ZnSe | 4.1 | 2.7 | 1.4 |
| CdS | 3.9 | 2.4 | 1.7[a] |
| GaP | 3.6 | 2.3 | 0.7 |
| Ge | 4.1 | 0.7 | 0.0 |
| Si | 4.0 | 1.1 | 0.2 |

[a]See Ref. 19.

the latter play an important role in the Schottky-like correction. The picture emerging from these considerations is closely related to that of the Freeouf-Woodall effective work function model, in which the Schottky term is determined by the work function of local interface species.[17] In this case, however, the Schottky-like term is a correction rather than providing a complete explanation for the interface behavior. We also note that Perfetti *et al.* attempted to calculate directly the effects of the local dipoles due to the interface chemical bonds.[18] Using a simplified model based on Sanderson's rule, they achieved remarkable accuracy in a number of cases, although this approach does not explain the present data for Si/GaP.

In summary, we find that Schottky-like corrections are necessary to explain not only Schottky barrier heights, but also heterojunction band discontinuities. A simplified treatment of such corrections provides a qualitative explanation of both the present data and of the observed correlations between Schottky barriers and heterojunctions. However, the present data also show that the intralayer-induced band lineup changes saturate before the intralayer is thick enough to have truly metallic Al. Specifically, the saturation occurs for an intralayer thickness sufficient to engage all surface anion atoms in bonds with intralayer atoms. This last fact indicates that the Schottky correction should be interpreted as the description of localized phenomena, as it is done by the effective-work-function model.

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