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Band offsets, defects, and dipole layers in semiconductor heterojunctions

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The role of defects in heterojunctions was investigated. The density of such defects required to pin the Fermi level or to affect the band offset was estimated using simple electrostatic considerations. We conclude that it is very unlikely that defects play any role in determining the band offsets, but they might affect the Fermi-level position at the interface.

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I. INTRODUCTION

Experiments performed on clean, cleaved surfaces of III-V semiconductors have demonstrated that the Fermi level at the surface is pinned by deposition of very thin coverages (submonolayer to several atomic layers) of either metal,¹⁻⁹ semiconductor,¹⁰⁻¹² or oxygen^{1,2,4,8,13-17} atoms. The fact that the Fermi-level position at the surface was almost the same for very different adatoms, as well as the fact that clean, cleaved III-V semiconductors do not have surface states in the gap,^{2,18-21} led Spicer *et al.*^{4,22-24} to propose the unified defect model. According to that model, chargeable native defects are formed upon deposition of minute quantities of adatoms (being either metal, semiconductor or oxygen atoms), and these defects may determine the position of the Fermi level at III-V semiconductor interfaces.

The unified defect model of Spicer *et al.*, which explains the position of the Fermi level at semiconductor interfaces in the limit of very thin coverages and is successful in predicting some interfacial properties, is currently used in the literature to predict the behavior of semiconductor interfaces when the coverage, either metallic or semiconducting, is thick. For example, it was predicted that in a metal-semiconductor interface, the Fermi level would be pinned at the various defect levels,^{3,9,25} and that this pinning position would depend on the semiconductor type²⁶ but not on the metal work function. Other researchers have applied the unified defect model to semiconductor heterojunctions and have predicted that the defect levels might pin the Fermi level at the interface.²⁶

In this paper we examine the role defects might play in determining band offsets and the position of the Fermi level at semiconductor heterojunctions. In a recent paper,²⁷ we have argued that the Fermi-level-pinning mechanism for very thin metallic coverages of semiconductor surfaces is different from the mechanism of Fermi-level pinning at the interface between two bulk materials, the main difference between the two cases being the source of charge that balances the charge captured on the surface defects. In the case of very thin coverage, this source must be the depletion charge in the bulk semiconductor. Therefore, only surface acceptors can be charged on bulk *n*-type semiconductors, and only surface donors can be charged on bulk *p*-type semiconductors, even if both surface acceptors and surface donors are present in both cases. This will result in pinning of

the Fermi level at the surface-acceptor level on *n*-type and at the surface-donor level on *p*-type semiconductors. The density of defects required to pin the Fermi level is comparable to the total depletion charge, which is of the order of 10^{12} cm^{-2} for a doping concentration of 10^{17} cm^{-3} in most wide-band-gap semiconductors. Such a low defect density can be formed by a submonolayer coverage of the semiconductor. It was also argued that if the defect density will be further increased, the two "pinned" Fermi-level positions would move and eventually merge.²⁸ The "pinning" at submonolayer coverage is, therefore, not complete.

In contrast to the case of very thin coverages, a defect concentration of 10^{12} cm^{-2} was shown²⁸ to be approximately two orders of magnitude too low to pin the Fermi level at a macroscopic metal-semiconductor junction. In this paper we shall investigate the effect of defects on semiconductor heterojunctions for both thin and thick coverages and contrast it with our previous papers concerning a metal-semiconductor interface.^{27,28} We shall show that the effect of defects in a bulk heterojunction is, qualitatively, very similar to the case of a submonolayer coverage. (This was implicitly assumed by Kroemer²⁹ in his treatment of interface charges in heterojunctions.) Quantitatively, we shall show that a defect concentration of 10^{12} cm^{-2} is also too low to pin the Fermi-level at the interface between two semiconductors, although it does have an effect on the Fermi-level position, which is more pronounced at semiconductor heterojunctions than at metal-semiconductor interfaces. A defect density of at least an order of magnitude more will be shown to be required to pin the Fermi level in a heterojunction.

We would like at this point to clarify the meaning of "Fermi-level pinning". This term means that the position of the Fermi level at the interface, relative to the band edges, is independent of some external conditions. The degree of this independence however, is important to our discussion. The experiments leading to the unified defect model show that the Fermi level at the surfaces of III-IV semiconductors is "pinned" by submonolayer coverages. The word pinned is used in this context to mean that the curve of Fermi-level position versus coverage, flattens out and reaches some "final" position at submonolayer coverages. There are, however, differences of about 0.1 eV between these "final" Fermi-level positions as measured on surfaces covered with different adatoms, as well as differences of about 0.2 eV

between the final Fermi-level positions measured on n - and p -type semiconductors covered with the same adatom.²⁶ Moreover, more recent experiments using a thicker coverage of metallic atoms^{30,31} demonstrate that this final Fermi-level position is not final and can still move about when the coverage becomes thicker. It appears, therefore, that enough defects are created at the surface to affect significantly the Fermi level but not quite to pin it. In our paper we shall reserve the term "pinning" to the case in which the Fermi-level position at the interface is determined by the defects but not by the bulk doping.

In our calculations, we assume that interface defects have no effect on the band offsets. To justify this assumption, we note that the interface defects would have to form a dipole layer in order to affect the band offsets; a single layer of trapped charge cannot abruptly change the potential, only its slope. Therefore, three conditions have to be satisfied if the defects form a dipole layer which affects the band offsets. First, both donor- and acceptor-type defects should be present at the interface. Second, the layer of donors should be separated from the layer of acceptors by some distance. This requirement is different from the case of a metal-semiconductor interface, in which the metal is guaranteed to supply charges of the opposite sign by screening. A reasonable value for this separation is several angstroms. It cannot be smaller than one atomic layer separation, and, on the other hand, it cannot be larger than a few tens of angstroms, since the band offset is abrupt. The third condition that has to be satisfied is that the defect density would be high enough. We can estimate the charge density required to affect the band offset by 0.1 V using the parallel-plate-capacitor formula:

$$\Delta\phi = \frac{\sigma \cdot d}{\epsilon\epsilon_0}.$$

For a separation of $d = 5 \text{ \AA}$ between the defect donors and acceptors, and assuming a dielectric constant on the order of 10, one obtains a defect density of approximately $\sigma = 10^{13} \text{ cm}^{-2}$. This defect density seems to be very high, especially when one considers the fact that this density of $\sigma = 10^{13} \text{ cm}^{-2}$ counts only those defects which participate in this narrow dipole layer, that is, only those defects which are separated by several angstroms from a layer of defects charged with the opposite sign. We must conclude, therefore, that it is very unlikely that interface defects determine the band offsets or have a significant influence on them. Some experimental evidence supports this assumption.^{32,33}

This paper is organized in the following way. In Sec. II, we discuss the theoretical methods. In Sec. III, we present the results based on our calculations. The conclusions of this paper are given in Sec. IV.

II. THEORETICAL METHODS

The schematic of our model is given in Fig. 1. Our model consists of two bulk semiconductors (infinitely thick) extending from $x = 0$ to either side. The interface at $x = 0$ is assumed to be abrupt. The band discontinuities at the interface

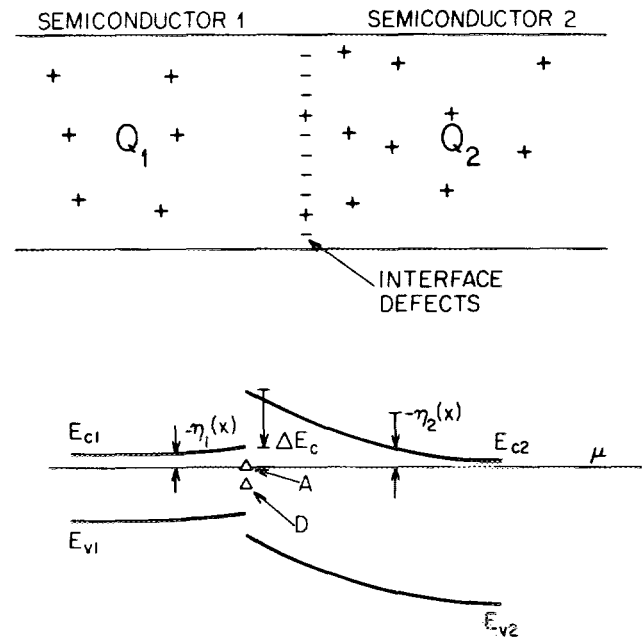


FIG. 1. The geometry and energy levels of our heterojunction model. We assume a very thin defect layer between the two bulk semiconductors, containing both defect donors and defect acceptors. The ionization energies of these defects relative to the band edges of the two semiconductors are denoted by "D" and "A", respectively. We assume that the band offset (denoted by ΔE_c) is independent of the defects.

are prescribed, and the interface contains a layer of defects (both donors and acceptors) with prescribed densities and ionization energies.

The calculation of the Fermi level at the interface is based on conservation of charge. It uses a property of semi-infinite semiconductors, namely, that the Fermi-level position at the surface ($x = 0$) determines the total charge per unit area in the semi-infinite semiconductor. Thus, if $\eta(x)$ denotes the position of the Fermi level relative to the conduction band edge,

$$\eta(x) = \mu - E_c(x), \quad (2.1)$$

and $Q(x)$ denotes the total number of charges per unit area between x and ∞ ,

$$Q(x) = \int_x^\infty (p - n + N_d^+ - N_a^-) dx, \quad (2.2)$$

then Poisson's equation relates $\eta(x)$ to $Q(x)$:

$$\begin{aligned} \frac{d\eta}{dx} &= \frac{q^2}{\epsilon\epsilon_0} Q(x), \\ \frac{dQ}{dx} &= n(\eta) - p(\eta) + N_a^-(\eta) - N_d^+(\eta). \end{aligned} \quad (2.3)$$

Here, q is the electron charge (taken positive), ϵ is the dielectric constant of the semiconductor, n and p are the densities of the electrons in the conduction band and holes in the valence band, and N_d^+ and N_a^- are the densities of ionized donors and acceptors, respectively. Expressions for n , p , N_d^+ , and N_a^- can be found in textbooks on the physics of semiconductors³⁴ and are not repeated here.

Dividing the two equations in Eq. (2.3) by each other, integrating from $\eta(\infty)$ to η and taking the square root, we obtain:

$$Q(\eta) = \pm \sqrt{\frac{2\epsilon\epsilon_0}{q^2} \int_{\eta(\infty)}^{\eta} [n(\eta') - p(\eta') - N_d^-(\eta') + N_a^+(\eta')] d\eta'}. \quad (2.4)$$

Equation (2.4) relates the Fermi-level position at the interface (η) to the total number of charges per unit area $Q(\eta)$. The sign in front of the square root in Eq. (2.4) is positive if $\eta(0) < \eta(\infty)$, negative otherwise. $\eta(\infty)$, the bulk Fermi-level position, is calculated from the local-charge-neutrality condition:

$$n(\eta) - p(\eta) + N_a^-(\eta) - N_d^+(\eta) = 0. \quad (2.5)$$

Now, we can put the interface together. Given $\eta_1(0)$, the Fermi-level position at the interface, relative to the conduction-band edge of semiconductor 1, we obtain $\eta_2(0)$, the Fermi-level position at the interface relative to the conduction-band edge of semiconductor 2, from the band discontinuity (which is an input to this model)

$$\eta_2(0) - \eta_1(0) = -\Delta E_c. \quad (2.6)$$

From $\eta_1(0)$ and $\eta_2(0)$, we obtain the total number of charges per unit area in the two bulk semiconductors, Q_1 and Q_2 using Eq. (2.4). Finally, the Fermi-level position at the interface determines the fraction of ionized interface defects. This fraction multiplied by the density of these defects gives the number of ionized defects per unit area Q_{sa}^- and Q_{sa}^+ .

$$Q_{sa}^+ = \frac{\sigma_d}{1 + g_d \exp\left(\frac{\mu - E_{sd}}{kT}\right)},$$

$$Q_{sa}^- = \frac{\sigma_a}{1 + g_a \exp\left(\frac{E_{sa} - \mu}{kT}\right)}. \quad (2.7)$$

Here, σ_d and σ_a are the densities, g_d and g_a are the degeneracy factors, and E_{sd} and E_{sa} are the ionization energies of interface donors and acceptors, respectively.

The Fermi-level position at the interface is now determined by an overall charge-neutrality condition:

$$Q_1 + Q_2 + Q_{sa}^+ - Q_{sa}^- = 0. \quad (2.8)$$

In the case shown in Fig. 1, both semiconductors are n type. Therefore, the depletion regions on both sides of the interface (Q_1 and Q_2) are positively charged. The Fermi level (μ) at the interface approximately equals the defect acceptor level ("A"), and, therefore, approximately half the defect acceptors will be negatively charged and balance the depletion charge. Since the Fermi level at the interface is above the defect-donor level ("D"), most of the defect donors will remain neutral.

III. RESULTS

A. Submonolayer coverage

The case of submonolayer coverage was treated before.^{26,27} The model for treating this case assumes that the adatoms cannot contribute any significant amount of charge, and their only role is the creation of defects. Therefore, one might assume $Q_2 = 0$ in Eq. (2.8), and that the charge due to the surface states balances the substrate depletion charge. Figure 2 shows the resulting Fermi-level position at the interface as a function of surface-defect density for both n - and p -type semiconductors. We assume that both

defect donors and defect acceptors are present at the interface at the same concentration. The shape of both curves is in good qualitative agreement with experimental results (compare to Figs. 3 and 8 in Mönch²⁶).

We should observe here that our assumption about the relative abundance of defect acceptors and defect donors is not restrictive in any way. If we assume any other fixed ratio of defect acceptors to defect donors, there will be a corresponding change in the horizontal scale of the two curves in Fig. 2. By comparing the curves of Fig. 2 with experimental results (for example, the point of maximum curvature), we may conclude that both defect donors and defect acceptors are present, and their concentration is of the same order of magnitude though not necessarily equal.

The curves in Fig. 2 seem to stabilize at a defect density on the order of 10^{12} cm^{-2} . (In fact, these two curves have some small but nonzero slope at that density, and they slowly approach each other). This defect density corresponds to a doping concentration of 10^{17} cm^{-3} and scales like the square root of the doping. Moreover, the pinning positions for n - and p -type semiconductors are substantially different and determined essentially by the defect-donor level for a p -type semiconductor and by the defect-acceptor level for an n -type semiconductor. One should be aware of the fact that this behavior is typical for the case of very thin coverage. A thick coverage of either a metal or a semiconductor can contribute a significant amount of charge to the system. In other words, Q_2 in Eq. (2.8) cannot be neglected, and as a result, the behavior of the Fermi-level position at the interface might be different. This difference in behavior between thin and thick

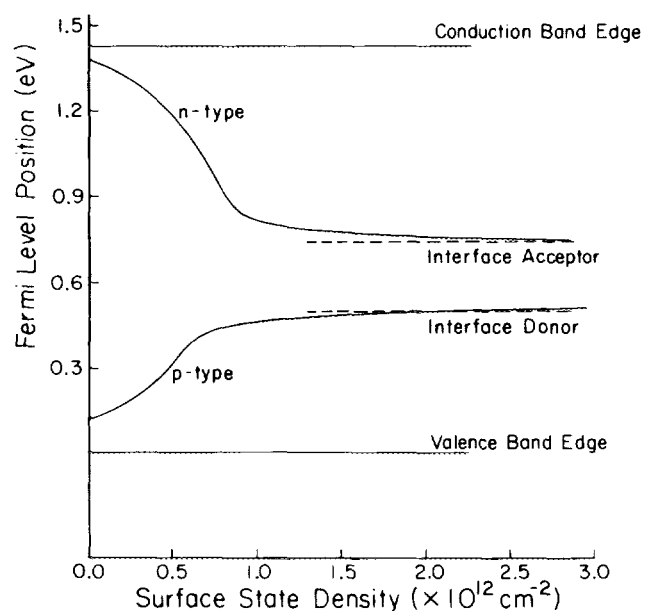


FIG. 2. The position of the Fermi level at the surface as a function of defect concentration for GaAs. The positions of the defect levels (either acceptors or donors) are shown by arrows. The density axis refers to either the defect donors or the defect acceptors.

coverage was treated in another paper for the case of a metal-semiconductor interface.²⁸ In the case of a metal-semiconductor interface, the charge contributed by the metal can be substantially higher than that contributed by the semiconductor ($Q_2 \gg Q_1$). As a result, the behavior of thick coverages was shown to be qualitatively different than that of a thin coverage. We now treat the case of a thick semiconductor coverage, i.e., a bulk heterojunction. Here, the charge contributed by both bulk materials is of the same order of magnitude. Therefore, one expects a similar behavior between thin and thick coverages, with some quantitative changes due to the presence of another bulk material.

B. Thick coverage

In our calculations, we have used the Ge/GaAs junction as a typical heterostructure. The band offset was chosen to be^{35,36}

$$\Delta E_c = 0.54 \text{ eV.}$$

This band offset is not the only one appearing in the literature. Other possible values for ΔE_c are 0.4^{11,12} and 0.13–0.28³². The interface-defect levels in this model correspond to the GaAs defect levels.²² Their energies are given by

$$E_c(\text{GaAs}) - E_{sd} = 0.93 \text{ eV,}$$

$$E_{sa} - E_v(\text{GaAs}) = 0.68 \text{ eV.}$$

Our choice of band offsets and defect levels, though somewhat arbitrary, is reasonable, but more importantly, our conclusions based on these calculations do not depend on this particular choice.

In Fig. 3, we show the band bending in the ideal Ge–GaAs heterostructure (ideal meaning that there are no interface defects or that the defect density is smaller than 10^{11} cm^{-2}). We show four different cases corresponding to either *n*- or *p*-type GaAs on either *n*- or *p*-type germanium. The doping concentration (either donors or acceptors) is 10^{17} cm^{-2} in all

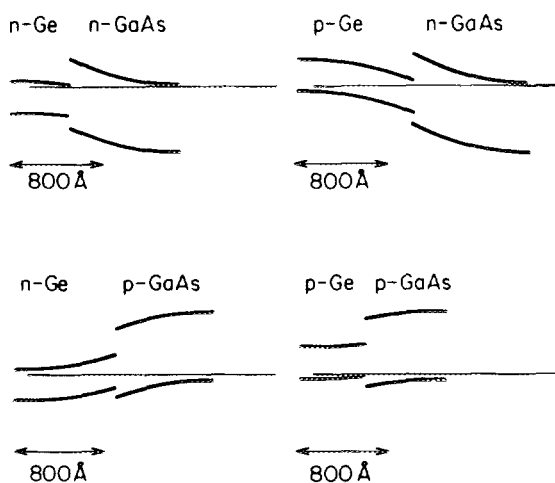


FIG. 3. The energy levels near the interface of a Ge–GaAs heterojunction with very few interface defects (less than 10^{11} cm^{-2}). The four band structures shown are the four combinations of either *n*- or *p*-type GaAs on either *n*- or *p*-type germanium. The doping concentration is 10^{17} cm^{-3} on both sides of the interface. The band offsets correspond to Ref. 36. The Fermi-level position can be moved throughout the germanium gap by changing the doping.

four cases. The important feature of the ideal heterojunction is that the Fermi-level position can be moved all the way across the germanium band gap by changing the doping. In fact, with the right doping concentration, the Fermi level can be anywhere in the gap without any band bending in either the germanium or the GaAs.

In Fig. 4, we show the result of introducing interface defects. The defect density in this figure is 10^{13} cm^{-2} , half of them donors and the other half acceptors. One can see that the possible range of the Fermi-level position at the interface decreases substantially as a result of this high defect density. The Fermi-level position at the interface as a function of defect density is shown in Fig. 5. The four curves correspond to the four combinations of either *n*- or *p*-type germanium on either *n*- or *p*-type GaAs. The doping in all four cases is 10^{17} cm^{-3} . One can divide Fig. 5 into three regions. For a defect density below 10^{12} cm^{-2} , the Fermi-level position at the interface is determined by the doping of the bulk semiconductors; the defect density is too small to have any effect. For a defect density of 10^{14} cm^{-2} or more, the Fermi-level position is determined by the interface defects. Between these two regions, that is, for a defect density in the range 10^{12} – 10^{14} cm^{-2} , the Fermi-level position is determined both by the bulk doping and by the defects.

It is interesting to compare the case of a thick coverage, described above, to either the thin coverage, described in the previous subsection, or to the case of a thick metallic coverage.^{27,28} The behavior of the Fermi-level position at the interface in Fig. 5 (representing a thick semiconductor coverage) is similar to the one shown in Fig. 2 (thin coverage). In both cases, the Fermi-level position shifts from being determined by the bulk to being determined by the interface defects at a defect density of 10^{12} – 10^{13} cm^{-2} (in the case of a bulk heterojunction, approximately twice as many defects are required to have the same effect). At that defect density, the bulk

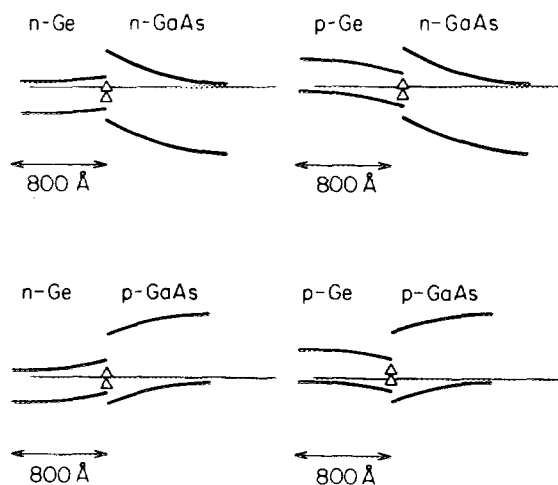


FIG. 4. The energy levels near the interface of a Ge–GaAs heterojunction with a high concentration of interface defects (10^{13} cm^{-2} , half of them donors and half acceptors). All the semiconductor parameters are the same as in Fig. 3. The interface-defect levels were taken from Ref. 22. The Fermi level is not quite pinned at the interface, i.e., it can be slightly moved, depending on the doping, but the range of this movement is very limited due to the high concentration of interface defects.

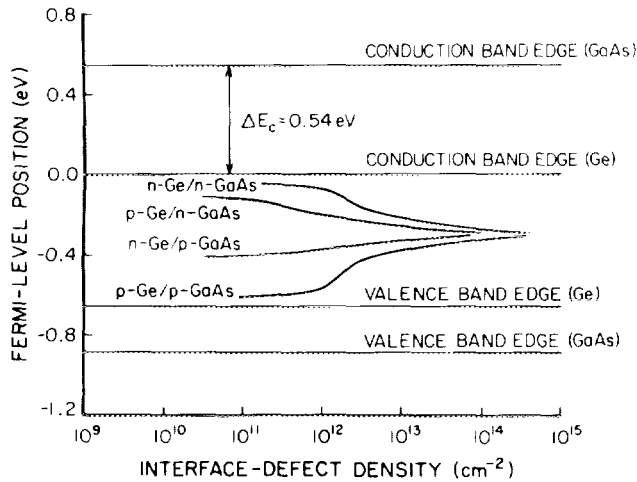


FIG. 5. The Fermi-level position at the interface of a Ge-GaAs heterojunction as a function of interface-defect density (50% acceptors and 50% donors). The semiconductor parameters (doping, bands offset, and defect levels) are the same as in Figs. 3 and 4.

doping still has some influence on the position of the Fermi level, namely, it determines on which defect level it will be pinned. Only when the defect density becomes substantially higher, does the influence of the bulk doping on the Fermi-level position vanish. This behavior should be contrasted with that of a bulk metal-semiconductor interface, in which the effect of the defects is very small below 10^{14} cm^{-2} , and the Fermi-level position is independent of the semiconductor doping.

IV. SUMMARY AND CONCLUSIONS

The effect of interface defects on semiconductor heterojunctions was investigated. It was shown that a defect density of approximately 10^{12} cm^{-2} (which is formed at submonolayer coverages) can affect the Fermi-level position at the interface of bulk heterojunctions. This defect density is comparable to the depletion charge in the bulk semiconductors. It was also shown that a much higher density 10^{13} – 10^{14} cm^{-2} is required to pin the Fermi level in a bulk semiconductor heterojunction (compared to approximately 10^{14} cm^{-2} in the case of a metal-semiconductor interface²⁸). When such a high density of defects is present, the defect charge is much higher than the bulk depletion charge. The experimental evidence supporting the unified defect model does not show the existence of such a high defect density.

An even stronger statement can be made regarding the effect (or lack thereof) of interface defects on band offsets. We have argued that if the defects affect the band offsets, then they have to satisfy three conditions. Firstly, there should be both defect donors and defect acceptors near the interface. Secondly, the layer of defect donors should be physically separated from the layer of defect acceptors by several angstroms. Thirdly, it requires a large density of such defects (so large, in fact, that it will affect the Fermi-level position even more, thus making the interface undesirable from a device point of view). In view of these requirements, we can

say that it is unlikely that interface defects determine the band offsets, or have a significant effect on them.

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