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Polar heterojunction interfaces

W. A. Harrison,* E. A. Kraut, J. R. Waldrop, and R. W. Grant
Science Center, Rockwell International, Thousand Oaks, California 91360

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A study of heterojunction interface geometry based on our measured differences in $3d$ core-state binding energies for germanium and gallium at Ge-GaAs heterojunctions of different crystallographic orientations is reported. For the interfaces which have been studied, i.e., (110), (100) Ga, (100) As, (111) Ga, and $(\bar{1}\bar{1}\bar{1})$ As, orientation-dependent variations in dipole contributions to valence-band discontinuities of about 0.2 eV have been observed. From electrostatic considerations we deduce the simplest interface geometries consistent with the facts that the differences are small and no large charge accumulations can occur at the junction. An abrupt planar junction is allowed for the (110) interface, but the polar interfaces require at least two transition planes of atoms with compositions which are deduced from the two conditions above. The electrostatic calculations were based upon the differences in nuclear charge and are unaffected by the resulting polarization of the bonds if that polarization is described in an "electronegativity" approximation. In this approximation there would in fact be no dipole shift for the ideal geometries proposed. An improved treatment of the bond polarization based upon the bond-orbital model gives residual dipole shifts somewhat smaller than those observed, and in poor agreement with our measurements. Inclusion of lattice-distortion effects at the interface also fails to account for the observed dipole shifts. We conclude that the experimentally prepared junctions must contain deviations from the ideal atom arrangements. The number of these deviations required to account for the observed shifts is on the order of one for every fifteen interface atoms.

I. INTRODUCTION

It has been possible to understand the essential properties of heterojunctions without concern for the possibility of electrostatic dipole shifts at the interface. Band-edge discontinuities could be predicted from differences in experimental electron affinities[1] or theoretically from differences in bulk energy bands.[2] A direct estimate of the dipole for a Si-Ge junction,[2] a detailed treatment of the Ge-GaAs nonpolar (110) junction by Picket, Louie, and Cohen,[3] and general considerations of junctions by Frensley and Kroemer[4] all suggested that indeed the dipole effects should be small, at most on the scale of a few tenths of an eV.

If, however, there were no electrostatic dipole shifts at the interface, the band-edge discontinuities would necessarily be identical for any pair of materials, independent of the crystal orientation of the interface separating them. Thus a measure of differences for different crystal faces can give unambiguous evidence for dipole shifts and experimental distinction of dipole shifts from intrinsic band-energy differences associated with electron affinities. We analyze here a direct measurement of the differences in dipole shifts on different interfaces for Ge-GaAs heterojunctions,[5] and thus the first direct evidence of electrostatic dipole shifts.

To see what these measurements can tell us about the junction, we need a formulation of the electrostatic properties of the different junctions. This leads immediately to the fact that properties such as dipole shifts are extremely sensitive to the detailed geometry of the interface. Because details are not known experimentally, we use the experimental findings, with the electrostatic formulation, to learn about the geometry. We find that the analysis places rather stringent conditions on the geometries which must exist in the experimental systems.

In Sec. II, the experimental results concerning the measurement of the relative dipole shifts are briefly summarized. In Sec. III, we make a careful formulation of the electrostatics for (110), (100), and (111) interfaces, and include bond dipoles in a simple approximation, finding that the ideal planar geometry is not allowed for the polar interfaces. We then proceed to find the simplest geometry which *is* consistent with the experimental findings of only small shifts. Geometries are in fact found which give no shift at all and the problem becomes that of understanding the observed small shifts. Improvements in the calculation of electron redistribution, discussed in Sec. IV, do not account for them, nor do lattice distortions suggested by covalent radii, and discussed in Sec. V. In Sec. VI, we conclude that the experimentally prepared junctions must contain deviations from the proposed ideal-atom arrangements.

II. SUMMARY OF EXPERIMENTAL RESULTS FOR Ge-GaAs HETEROJUNCTIONS

For convenience, in this section we briefly summarize our experimental findings on the relative dipole shifts for Ge-GaAs heterojunctions with different crystallographic orientations. These results which employ x-ray photoelectron spectroscopy (XPS) as the primary measurement technique have now been reported.[5]

Substrates of GaAs with (100), (111), $(\bar{1}\bar{1}\bar{1})$, and (110) faces were cleaned within the XPS vacuum system by Ar^+-ion sputtering (750 eV) followed by annealing at about 575 °C to remove sputter damage. After annealing the surface, cleanliness was confirmed by XPS and the removal of sputter damage was assessed by low-energy electron diffraction (LEED). Very thin ($\approx$20 Å) epitaxial layers of Ge were grown within the XPS apparatus on heated ($\approx$425 °C) GaAs substrates by evaporative molecular beam epitaxy (MBE) techniques. Additional LEED measurements confirmed the epitaxy of the Ge overlayers. XPS was used to measure the differences in Ge-3*d* and Ga-3*d* core-level binding energies at Ge-GaAs heterojunctions with different crystallographic orientations. As discussed in Ref. 5, observed changes in core-level binding energies provide a direct measure of the crystallographic orientation dependence of interface dipoles and variations of band-gap discontinuities.

Measurements were carried out on eight different interfaces. In Table I we summarize the results. Additional experimental details may be found in Ref. 5.

III. THEORY OF THE DIPOLE SHIFT

We are concerned here with potentials arising from infinite arrays of charges, a type of problem known to be very tricky and even to lead to conditionally convergent answers in some cases. It is therefore absolutely essential to proceed with care and to be certain that we include the essential physical effects correctly. A model of the system may not be adequate; we must treat the system itself.

To do this we start with a plane (to become the junction plane) through a germanium crystal, with germanium atoms extending indefinitely on both sides. We imagine having solved for the electronic states in this system which by definition has no dipole shift across the junction. We will then "freeze" the electronic structure and imagine transferring protons between nuclei to the right of the junction such as to convert half of the nuclei to gallium (atomic number one less than germanium) and half to arsenic (atomic number one greater than germanium). This shift of protons (theoretical alchemy[6]) will of course produce an exactly calculable change in electrostatic potential and may produce an accumulation of nuclear charge at the interface or a dipole layer at the interface. [In fact, both occur at polar interfaces, (100) and (111).] We then allow the electronic system to relax, which if done sufficiently accurately would lead to a precise description of the true Ge-GaAs heterojunction with this particular set of germanium, gallium, and arsenic atom positions. The change in electronic structure can, of course, only be done approximately but the most important qualitative features can be obtained rigorously.

We begin with a discussion of the (110) interface, which provides a reference for the other interfaces. Shown in Fig. 1 is a Ge-GaAs (110) interface resulting from the transfer of protons,

TABLE I. Ge 3*d*–Ga 3*d* binding energy differences ΔE_B for various Ge-GaAs heterojunctions. All error limits are ±0.01 eV.

Substrate surface	(111) Ga	(100) Ga	(110)	(100) As	$(\bar{1}\bar{1}\bar{1})$ As
ΔE_B (eV)	10.27 10.31	10.22	10.20 10.21	10.17	10.11 10.10

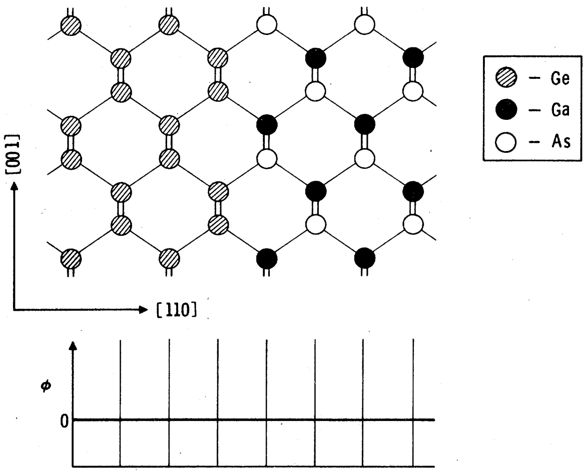

FIG. 1. A (110) heterojunction between Ge and GaAs. The crystal is viewed along the [$\bar{1}$10] direction with the [001] direction vertical. Note that every plane of atoms parallel to the junction is on the average neutral corresponding to a nonpolar junction. The symbols used to identify specific atoms are defined in this figure and are the same in all figures. All atoms are tetrahedrally bonded; the "double" bonds schematically illustrated in the figures are two tetrahedral bonds separated by the usual 109° tetrahedral bond angle and projected on to the plane of the figure.

with the electronic structure still frozen as in germanium. It is apparent from the figure that each plane of atoms parallel to the interface is still neutral on average. This corresponds to the transfer of protons parallel to the surface, perhaps downward in the figure. This also corresponds to no charge accumulation at the interface nor any electrostatic dipole layer. There are, of course, fluctuations in electrostatic potential along the interface, but the *potential* averaged over a plane parallel to the interface (which is equivalent to the potential at one point due to *charges* averaged over planes parallel to the surface) is unchanged. At a heterojunction interface, the terms dipole shift and charge accumulation are defined as a discontinuity in average potential and average potential slope, respectively. The average potential is defined as the potential averaged over a plane midway between adjacent atomic planes. We will return later to the relaxation of the electronic structure and see that its effect should be very small.

We turn next to a (100) interface shown in Fig. 2. Again, think of the electronic structure as frozen to be the same as in germanium. In this case each plane of atoms parallel to the interface is charged; this corresponds to proton transfer perpendicular to the interface. The consequences of this transfer may not be immediately obvious, but we may again understand them by averaging the charge distribution over planes parallel to the interface. We may readily integrate Poisson's equation from the germanium on the left, where we take the potential to be constant and zero through the junction. The result is illustrated at the bottom of Fig. 2. Upon crossing the first plane of negatively charged atoms the potential gradient becomes positive and constant, and then becomes zero again after crossing the first plane of positively charged atoms. Thus the potential in the GaAs contains an average gradient in addition to a fluctuating component; the average gradient may be thought of as coming from charge accumulation at the interface due to proton transfer, and therefore polarization density, perpendicular to the interface, and terminating at the interface. In any case, it is real and unambiguous and results in a potential which cannot be sustained in the real system because it leads to potential differences over a few atom distances which are greater than the band gap; spontaneous generation of carriers would immediately occur.

Let us turn to the redistribution of the electrons due to the redistribution of protons. We look first at the response to the fluctuating component of the potential, with the average potential gradient subtracted. This becomes just the fluctuating potential which would arise in a bulk crystal from converting the germanium nuclei to gallium and arsenic nuclei [for example, by transferring protons parallel to the surface of a slab with (110) surfaces]. The charge redistribution could be calculated rather reliably in a linear combination of atomic orbitals (LCAO) context and in the bond-orbital model[7] in particular, but the essential features are more easily understood in terms of an *electronegativity approximation*. In that approximation we assert that the added proton lowers the energy of the atomic states on the arsenic atom, the removed proton raises the energy on the gallium atom, and this effect polarizes the intervening bonds towards the arsenic. This will produce a dipole in the bond but *no net change in the charge of two in the bond*. Whatever charge is added to the arsenic is removed from the neighboring gallium atoms. This would follow from any nearest-neighbor (or higher-order neighbor) LCAO or Wannier-function calculation. It follows

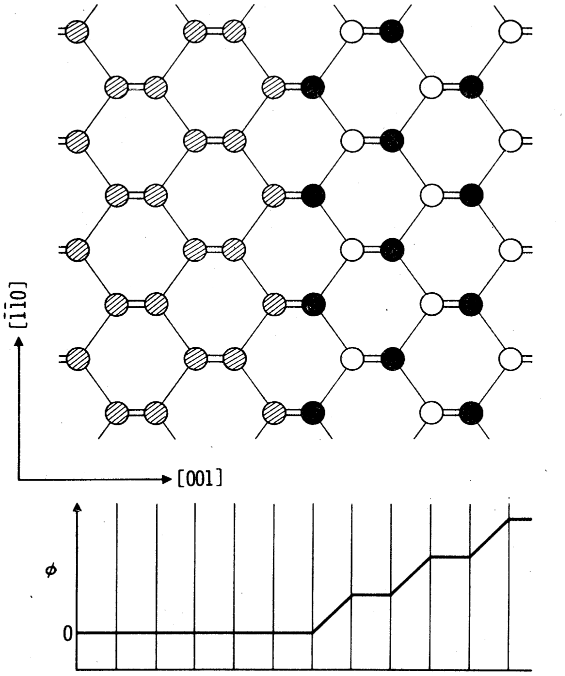

FIG. 2. A (001) heterojunction between Ge and GaAs, again viewed along the $[\bar{1}10]$ direction with the $[\bar{1}\bar{1}0]$ direction now vertical. Note that the first atomic plane to the right of the junction is entirely Ga [it is therefore called a (001) Ga junction] which, without bond polarization, is negatively charged. The potential averaged over planes parallel to the junction, is obtained by integrating Poisson's equation from left to right. A nonzero average electric field has arisen to the right of the junction due to charge accumulation. It is not eliminated by bond polarization although this will change the sign of the effective charge on the Ga (see Sec. IV).

that charge redistribution in the bonds at the interface cannot remove the charge accumulation which arose from the proton transfers.

We turn next to the average potential gradient, which has not been eliminated by the bond distortions. (In our construction this occurred in the GaAs, but it could as well have been in the Ge; it is the *difference* in gradients which is guaranteed by the electrostatic calculation.) This gradient will cause an additional polarization of each bond extending indefinitely to the right and therefore can cause a charge accumulation. This is just the dielectric polarization of GaAs and reduces the average field by a factor of the dielectric constant ϵ. We are left with an average potential gradient which may be readily calculated. The charge density in each plane is $2e/a^2$, where a is the cube edge, 5.65 Å for GaAs. The change in the potential gradient ($\nabla^2\phi = -4\pi\rho$) is 4π times this. To obtain the average gradient we divide by 2 and by the dielectric constant $\epsilon = 10.9$ for GaAs and multiply by e to obtain a change in electrostatic potential energy of

$$\delta E = 4\pi e^2/\epsilon a = 2.9 \text{ eV} \qquad (1)$$

for each distance a. This corresponds to a huge field and, as we indicated earlier, would raise the valence band maximum at one point above the conduction-band minimum a few atom distances away, thus producing instantaneous carriers (in this case, one electron per area a^2) and reducing the net charge at the interface to zero. This is exactly the result which Baraff, Appelbaum, and Hamann[8] obtained by detailed treatment of just this junction geometry. As Baraff[9] has emphasized, it is guaranteed by this geometry of the junction.

There is, however, no experimental evidence for such a huge free-carrier density or such a large qualitative difference in junctions prepared upon (100) faces rather than (110) faces. Indeed, it is almost inconceivable that a junction could be prepared with one electron per surface atom in an antibonding (conduction-band) state. We therefore postulate that the planar geometry must be modified to eliminate the excess charge; the planar geometry shown in Fig. 2 is not expected to occur in a real junction. We proceed to seek the simplest modification which is acceptable.

The geometry of Fig. 2 produced fields which corresponded to a deficit of one proton for every two surface atoms at the junction. In terms of our theoretical alchemy one proton must be added for every two surface atoms. Note that this could be done by adding a proton to half of the gallium atoms in the first gallium plane to the right of the junction in Fig. 2, converting them to germanium atoms, or it could be done by adding one to half of the last plane of germanium atoms to the left of the junction, converting them to arsenic atoms. There are innumerable other ways to add the protons, but these two are the simplest; the first is illustrated in Fig. 3.

We may again average the charges over atom planes, leaving the electrons frozen in the germanium electronic structure, and integrate Poisson's equation through the junction as indicated below in Fig. 3. The added protons have eliminated the average potential gradient in the GaAs and therefore produce an allowed geometry in this regard. However, this geometry has produced a shift in the average potential in the GaAs of $\delta = \pi e^2/2a\epsilon = 0.37$ eV. One way of seeing that there is a dipole shift here is to construct to the right of the GaAs shown in Fig. 3 the analogous junction with an extra half-plane of gallium atoms (so the entire system is neutral) and with germanium to the right; that is, to construct a GaAs slab surrounded by germanium. We then see that the potential in the germanium to the right is shifted with respect to that on the left by twice the value given above. This large dipole did not occur on the (110) junction illustrated in Fig. 1 and is not consistent with the much smaller differences

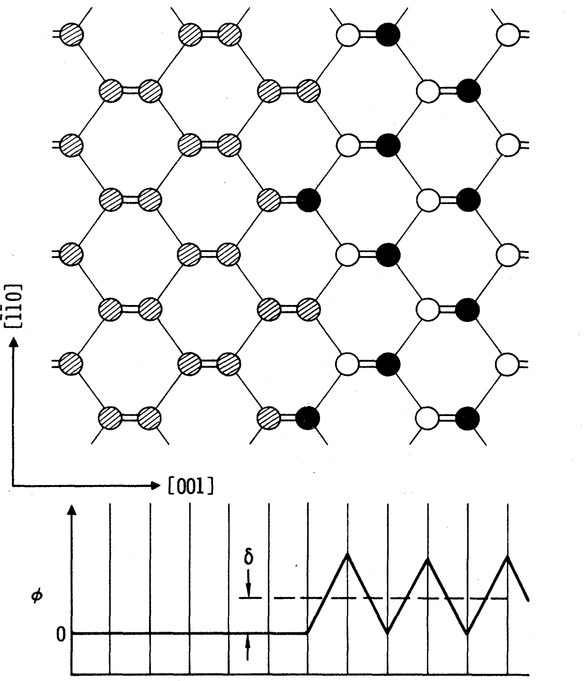

FIG. 3. A (001) heterojunction as in Fig. 2, but with $\frac{1}{2}$ of the Ga atoms in the junction plane replaced by Ge atoms. The average electric field in the GaAs has been eliminated but there is still a dipole shift δ much larger than is experimentally observed. The dipole shift is not eliminated by bond polarization.

in dipole shifts on different surfaces which are observed (Sec. II). We conclude that this geometry also is not correct; however, the redistribution of electronic charge must first be considered.

We approximated the redistribution in terms of an increased electronegativity on each arsenic atom which polarized neighboring bonds in proportion to the electronegativity difference with the neighboring atoms. We may do this atom by atom near the junction and see immediately that the dipoles induced to the right of each atom are just equal and opposite to those on the left; *no net dipole layer is introduced* and the shift in average potential remains. Thus the geometry of Fig. 3 must be modified.

It is interesting that this same result was obtained by Frensley and Kroemer[4] *who modeled the total charge distribution* at a polar inteface by just such an electronegativity model. They found no charge accumulation and no dipole shifts for geometries such as those of Figs. 2 and 3. We note that this model omits the very important difference in nuclear charges which is an essential feature of real junctions.

The conclusion of no net dipole layer would be modified slightly by a more realistic LCAO calculation. We will see in Sec. V that in the bond-orbital approximation,[7] the excess electronic charge on the arsenic is not extracted equally from the neighbors on the two sides. This does not modify our earlier conclusion concerning total-charge accumulations, but it does introduce dipole shifts of the order of a few hundreths of an eV for the geometries we have discussed. These are not large enough to cancel the 0.37 eV shift found above; thus we conclude that the (100) geometry, consisting of a single transition layer (the half-gallium layer of Fig. 3) does not occur.

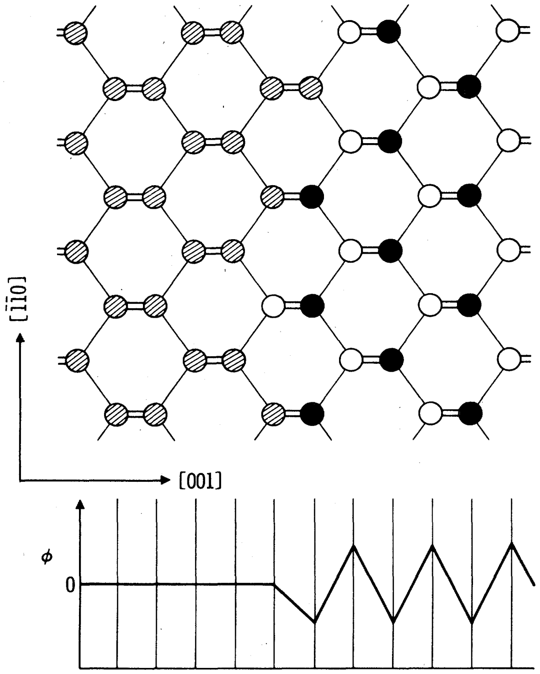

FIG. 4. A (001) heterojunction as in Figs. 2 and 3, but with two transition planes. The first is $\frac{1}{4}$ As, the second $\frac{3}{4}$ Ga with the remaining atoms Ge; it is appropriate to refer to it as a (100) $\frac{3}{4}$-Ga junction. This is the simplest junction geometry which eliminates both charge accumulation and dipole shift.

The simplest modification which eliminates the dipole shift requires two transition layers, a $\frac{3}{4}$-gallium layer and a $\frac{1}{4}$-arsenic layer as schematically illustrated in Fig. 4. It seems appropriate to think of this as a modification of a geometry with the last GaAs layer being gallium and we therefore refer to this as a (100) $\frac{3}{4}$-Ga surface. The integration of Poisson's equation, shown below, indicates that there is no dipole shift nor charge accumulation. The second alternative is a $\frac{3}{4}$-arsenic and $\frac{1}{4}$-gallium layer; it can be constructed by interchanging gallium and arsenic atoms in Fig. 4. We refer to it as the (100) $\frac{3}{4}$-As junction. Either type of junction can be grown on a given (100) surface of GaAs, which we will see is in contrast to the (111) surface. All other allowed alternatives involve more than two transition planes and will not be considered. It would be difficult to guess the precise pattern which occurs in a real junction although electrostatic energies are usually lowered by high-symmetry patterns. The geometries shown in Figs. 3–6 are only intended to illustrate the average composition of atom planes without specifying a two-dimensional symmetry pattern. The highest symmetry allowed for the (100) interface would be 1×4, but it is possible that a 2×4 pattern would have lower electrostatic energy.

It is fair to ask how such a pattern would arise experimentally. If it were possible to construct a planar junction, as in Fig. 2, with its sheet of compensating carriers, the chemical force derivable from the excess energy of electrons in antibonding states would cause diffusion of gallium atoms out of the junction or arsenic atoms in until there was no excess nuclear charge at the junction and no free carriers. In fact, a residual dipole would favor diffusion in such a way as to eliminate the dipole. It seems more likely, however, that the growth process itself produces a nonplanar junction such as that shown in Fig. 4 directly, as an interface of lowest energy.

We have applied this same analysis to the (111) junctions, requiring that in the electronegativity

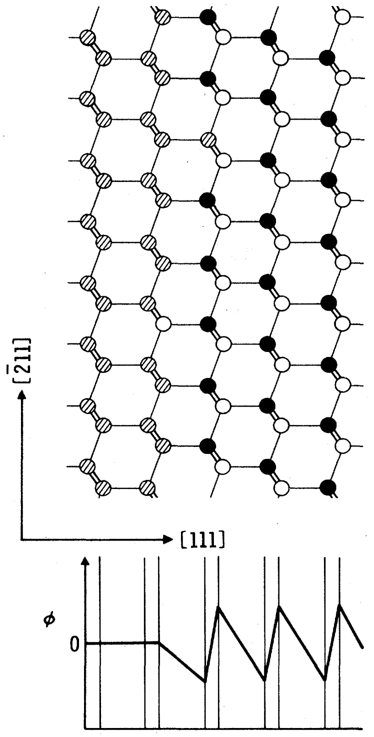

FIG. 5. A (111) heterojunction, viewed along the [01$\bar{1}$] direction, constructed on the (111) Ga face of GaAs. It is a two-transition-plane junction with the first plane $\frac{1}{8}$ As and the second plane $\frac{7}{8}$ Ga. We call it a (111)$\frac{7}{8}$-Ga junction. This is one of the two-plane geometries giving no charge accumulation nor dipole shift, as seen in the potential plot below. The other is shown in Fig. 6.

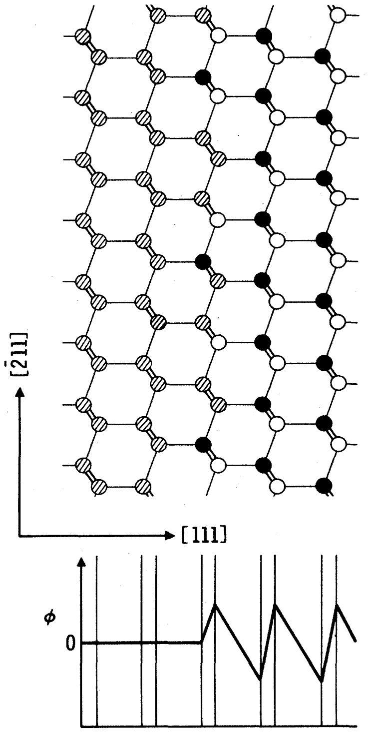

FIG. 6. The second two-transition-plane geometry for a heterojunction, on a (111) Ga face, such as that shown in Fig. 5; it gives no charge accumulation and no dipole shift. The first plane is $\frac{3}{8}$ Ga; the second is $\frac{5}{8}$ As. We call it a (111) $\frac{3}{8}$-Ga junction. The corresponding two allowed geometries on the (111) As face of GaAs are obtained by interchanging empty and full circles on Fig. 5 and here.

approximation there be no charge accumulation nor dipole shift at the junctions. In Fig. 5 we show a (111) interface. Note that along the [111] direction atomic planes are alternately connected by bonds parallel to the [111] direction and bonds (three times as many) inclined to that direction. Thus there are two distinct [111] directions and two crystallographically distinct (111) junctions; Fig. 5 illustrates the orientation with gallium atoms at the end of the parallel bonds away from the germanium. This is usually called the (111) Ga face since it is assumed that the crystal will terminate with the minimum number of bonds broken leading in this case to a Ga terminating plane. We find that for this crystallographic arrangement there are two kinds of interfaces with two transition planes which give no charge accumulation and no dipole shift in the electronegativity approximation. The interface shown in Fig. 5 terminates in a Ga plane, with $\frac{1}{8}$ of the gallium atoms replaced by germanium; the first germanium plane has $\frac{1}{8}$ of the Ge atoms replaced by As. We call it the (111) $\frac{7}{8}$-Ga geometry. The second alternative (with two transition planes) terminates the GaAs in a Ga plane with $\frac{5}{8}$ of the Ga atoms replaced by Ge with $\frac{3}{8}$ of the As atoms in the next GaAs plane replaced by Ge; it is shown in Fig. 6. Both Figs. 5 and 6 give allowed geometries for a heterojunction on the crystallographic (111) Ga face of the GaAs. The allowed geometry for a heterojunction on a (111) As face can be constructed by interchanging Ga and As atoms in Figs. 5 and 6.

This completes the specification of the simplest allowed interface geometries on the different crystallographic interfaces. They have been chosen to give no charge accumulation at the interface and, in the electronegativity approximation, no dipole shift.

IV. CORRECTIONS TO THE ELECTRONEGATIVITY APPROXIMATION

We have used only the smallness of the dipole shifts, not the actual values, to learn about the interface geometry. We wish also to see what can be learned from the shifts themselves. The ideal geometries proposed in Figs. 1 and 4–6, and the electronegativity model of the bond polarization have led to no dipole shift at all. Small dipole shifts may be expected to arise from corrections to the electronegativity model, from distortions of the lattice at the interface, and from deviations from the ideal arrangements of atoms we have proposed. These are discussed here and in Secs. V and VI.

We first improve on the electronegativity model by using the bond-orbital model.[7] Each bond is treated individually by using known parameters[6] to obtain the effective charge on each plane; Poisson's equation is then integrated over these effective charges, just as was done with the frozen-electron charges in Sec. III. It is interesting that bond polarization actually changes the sign of most effective charges but as we have seen this has only a small effect on the net dipole shift. The calculation is rather intricate because with two transition planes the effective charges on four planes are modified. We have carried the analysis through and will give here only the final resulting dipole contribution to ΔE_B. Enough details will be given in Sec.V to see exactly how the calculation was performed.

For the (110) interface shown in Fig. 1 a contribution of +0.02 eV is obtained. For the (100) $\frac{3}{4}$-Ga junction shown in Fig. 4 we also obtain +0.02 eV but for the (100) $\frac{3}{4}$-As interface obtained by interchanging Ga and As atoms in Fig. 4 we obtain 0.00 eV. Both the (111) $\frac{7}{8}$-Ga interface shown in Fig. 5 and the (111) $\frac{3}{8}$-Ga interface shown in Fig. 6 yield a contribution of −0.01 eV. The corresponding (111) $\frac{7}{8}$-As and (111) $\frac{3}{8}$-As interfaces yield 0.05 eV. By subtracting shifts from that for the (110) interface we may make a direct comparison with the experimental shifts. We find that the magnitudes of the relative shifts are about half of those observed but for both (111) faces they are just the opposite sign as those observed. It is not clear which of the two (100) geometries is to be associated with the gallium-rich and arsenic-rich surfaces.

V. EFFECT OF LATTICE DISTORTIONS

It is to be expected that the ideal germanium geometry will not continue through the junction. A table of covalent radii for tetrahedral systems[10] gives a value of 1.22 Å for Ge, a value of 1.26 Å for Ga, and a value of 1.18 Å for As. We see by summing radii that the GaAs bond length equals the Ge-Ge bond length, in accord with the good match in lattice constant but a Ge-Ga bond should be about 2% longer and the Ge-As bond 2% shorter. The effect of these distortions is included next.

For this aspect of the problem the electronegativity approximation is not adequate. It would imply that the effective charges on the atoms remain constant as the lattice is distorted while it is well known[6,7,11] that charge redistribution gives effects as large as the displacement of static charge. We therefore use the bond-orbital model,[6,7] discussed in Sec. IV, which is known to give a good account of both effects.[11]

The dipole associated with each bond has a contribution from the electron-charge distribution and from the difference in nuclear charge at the two ends of the bond. (A quarter of each nucleus is associated with each bond.) For a Ge-Ga bond, for example, the dipole is given by[6,7,11]

$$\vec{p} = \tfrac{1}{2}(\alpha_p - \tfrac{1}{4})e\vec{d}\,, \tag{2}$$

where $\vec{d}$ is the vector distance from the Ge to the Ga nucleus. (We have dropped a scale factor $\gamma = 1.4$ used in the earliest treatments.[11]) α_p is the polarity given by $V_3/(V_2^2+V_3^2)^{1/2}$ based upon a polar energy[6,7]

$$V_3 = \tfrac{1}{2}(\epsilon_p^{\rm Ga} - \epsilon_p^{\rm Ge}) \tag{3}$$

(with values 0.73 eV for Ge-Ga, 0.78 eV for As-Ge, and 1.51 eV for As-Ga) and a covalent energy given by

$$V_2 = 2.16\hbar^2/md^2 \tag{4}$$

(equal to 2.76 for all bonds if d is taken to be 2.44 Å for all). It is these dipoles, or more particularly effective atomic charges obtained by summing the dipoles from the four bonds directed at each atom, which were used in the calculation of the dipole shifts listed in Sec. IV. They were used to determine charge densities averaged over atomic planes. We then integrated Poisson's equation through the junction. The results included a reduction by a factor of the dielectric constant, as did the potential shifts in Eq. (1). This approximates the self-consistent response of the intervening bonds to the charge redistribution.

We are interested here in the change due to distortion. The change in magnitude of the dipole due to a change in bond length d is

$$\delta p = \tfrac{1}{2}ed\,\delta\alpha_p + \tfrac{1}{2}e(\alpha_p - \tfrac{1}{4})\,\delta d\,. \tag{5}$$

From Eq. (5) we see that

$$\delta\alpha_p = \frac{-V_3V_2\delta V_2}{(V_2^2+V_3^2)^{3/2}} = 2\alpha_p(1-\alpha_p^2)\,\frac{\delta d}{d} \tag{6}$$

and thus

$$\delta p = (-2\alpha_p^3 + 3\alpha_p - \tfrac{1}{4})\,e\delta d/2\,. \tag{7}$$

We will approximate the effect of distortion by this change in dipole for any Ge-Ga or Ge-As bond due to a change in bond length d computed from the covalent radii given above; i.e., +0.04 and −0.04 Å, respectively, for the Ge-Ga and Ge-As bonds. By using the expressions given above (with an appropriate V_3 for the Ge-As bond) we obtain a magnitude of δp of $0.24e\delta d$ for the Ge-Ga bond and $0.26e\delta d$ for the Ge-As bond.

In both cases the effect of the distortion is to transfer electrons to the germanium atom. Physically the reason for the same sign is that the increase of bond length for the Ge-Ga bond makes it more polar, increasing the difference in electronic charges, while the decrease of the Ge-As bond length makes it less polar, decreasing the difference in electronic charges. Since the Ge has excess charge in the first case and a deficit in the second, in both cases the transfer of electrons is to the germanium. The fact that the sign is the same, along with an almost equal magnitude, leads directly to the result that lattice distortions have little effect on our observed variation in dipole shifts for different crystallographic orientations.

We note first that if the difference between the $0.24e\delta d$ and $0.26e\delta d$ for the two bond types is neglected, any dipole shift arising from bond distortion will not be changed by interchanging gallium and arsenic atoms. Thus bond distortion in the (100) interface shown in Fig. 4 will lead to the same dipole shift as in the corresponding interface obtained with Ga and As atoms interchanged. Furthermore, a shift of the electrostatic energy in the germanium relative to that in the GaAs will be proportional to the number of Ge-Ga and Ge-As bonds per unit area of interface and this is the same in the allowed geometry of Fig. 4 as in the abrupt geometry of Fig. 2. (One fourth of the bonds to the right from the last full Ge layer are Ge-As bonds, $\frac{1}{2}$ from the next layer are Ge-Ga bonds, and $\frac{1}{4}$ from the next layer are Ge-As bonds. This is equivalent to having all Ge-Ga or Ge-As bonds in one layer.) The dipole shift is in fact independent of interface geometry. We obtain its magnitude by considering the abrupt geometry, multiplying the average change in bond dipole, $\delta p = 0.25e\delta d$, by the cosine of the angle it makes with the surface ($3^{-1/2}$), multiplying by 4π from Poisson's equation, multiplying by the bond density ($4/a^2$), and dividing by the dielectric constant to obtain

$$\delta E = 0.25(\delta d/d)4\pi e^2/\epsilon a = 0.012 \text{ eV}, \quad (8)$$

with the electron potential energy higher in the germanium than in the GaAs. In fact, the product of the bond-angle cosine and bond density is identical for the (110) and (111) surfaces so this model predicts the same dipole shift for all interfaces considered and therefore no contribution to the measured differences.

This model is rather crude but should give the principal effect of bond distortion. Since the shift obtained is small compared to the observed differences, and corrections to the model would be smaller, bond distortions cannot alone account for the observed differences in dipole shift.

VI. CONCLUSIONS

We conclude that the smallness of the differences in dipole shift on the different crystallographic faces is inconsistent with a structure containing less than two transition layers. With two or more layers a structure can be selected which in the simplest (electronegativity model) approximation gives no dipole differences at all. We found further that the leading corrections to this model for the ideal structure gave smaller dipole shifts than those observed and that their signs were not consistent with those of the experimental shifts. Finally, we considered the expected distortions of the lattice at the interface and found that the effects were small and independent of crystal orientation.

We therefore conclude that an explanation of the experimentally observed dipole shifts must be a deviation from the structures proposed in Figs. 4–6. The simplest kind of deviation would be an interchange of atom pairs. This shift of a single proton between adjacent planes, separated by $\frac{1}{4}a$, introduces a dipole of $\frac{1}{4}ea$. If the number of such displacements was a fraction x of the two interface atoms per area a^2, the dipole shift would be $4\pi e^2(a/4)(2x/a^2)/\epsilon = 2\pi e^2 x/\epsilon a$. To obtain a dipole shift of 0.1 eV, a value of $x = 0.07$ is required. We see no inconsistency of such a compositional mixing with our experimental results.

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*Permanent address: Applied Physics Dept., Stanford University, Stanford, Calif. 94305.

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