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Electronic structure of amorphous III-V and II-VI compound semiconductors and their defects

E. P. O'Reilly
Department of Physics, University of Surrey, Guildford, GU2 5XH, Surrey, United Kingdom

J. Robertson
Central Electricity Research Laboratories, Central Electricity Generating Board, Leatherhead, Surrey KT22 7SE, United Kingdom

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The local electronic structure of bulk and defect sites has been calculated for nine amorphous III-V compound semiconductors and for two amorphous II-VI compound semiconductors using the tight-binding recursion method. We find that structural disorder in a chemically ordered, tetrahedrally coordinated network causes a smoothing of the valence-band density of states, but little movement of the band edges, so that theoretically little change in the band gap is expected. Experimentally, the optical gap is found to close up and we attribute this to the presence of significant numbers of defect states at the band edges. The principal defects studied are undercoordinated atoms ("dangling bonds") and like-atom bonds ("wrong bonds"). In all III-V compounds we find that anion dangling bonds give rise to occupied acceptorlike states at or below the valence-band edge (E_v) and that cation dangling bonds produce empty donorlike states at or above the conduction-band edge (E_c). Isolated wrong bonds are found to introduce gap states in some of the compounds; usually anion wrong bonds introduce donor states near E_c while cation wrong bonds introduce acceptor states near E_v. Overall, a much lower density of states at the Fermi level E_F is expected for these compounds compared to *a*-Si, and this is indeed found experimentally. In the wider-gap compounds such as *a*-GaAs, we propose that clusters of wrong bonds are the most probable cause of mid-gap states, while in some cases like *a*-InP isolated cation wrong bonds may also be responsible. We argue that the dangling-bond concentration in these materials is intrinsically high, of order 1–5%, and that they are the predominant defect in annealed material. We also show that stoichiometry changes produce a combination of wrong bonds and trivalent sites of the excess species. This frequently leads to an increased density of mid-gap states, but E_F does not shift from mid-gap. We have also calculated the electronic structure of various hydrogen configurations and compared them to the photoemission spectra.

I. INTRODUCTION

The atomic and electronic structure of an amorphous semiconductor is conveniently described by drawing a distinction between bulk sites, which have normal bonding, and defect sites. Structural studies have established that the bulk sites in amorphous III-V compound semiconductors are tetrahedrally bonded with each atom having four unlike atoms as neighbors, as in the corresponding crystal.[1–4] Such chemical ordering requires that the bonding network possess only even-membered rings, as in the Connell-Temkin model.[5] There is less experimental information available about the defects, but *a priori* we expect two types of defects to predominate in these compound semiconductors:[6,7] threefold-coordinated sites ("dangling bonds"), as found in amorphous (*a*-) Si, and "wrong bonds" between like atoms. Because defects tend to introduce electron states in or around the optical-gap region and thereby dominate many electrical properties, it is particularly important to understand their behavior.

We examine the electronic structure of bulk sites and of a range of possible defects in the nine amorphous III-V compound semiconductors, and in amorphous ZnSe and ZnTe. By examining eleven semiconductors, we can identify trends in their behavior. The defects considered are relaxed and unrelaxed dangling bonds, isolated wrong bonds, and finally, certain defect complexes. We argue that for the well-annealed stoichiometric semiconductor, the predominant defects should be three-coordinated atoms and that these in general will give no states in the gap. Wrong-bonded atoms should be less common but have a greater effect on electronic properties, introducing gap states in many compounds. We then show that the predominant defects alter away from the stoichiometric composition, such that in, for example, As-rich *a*-Ga_xAs_{1-x} both As—As wrong bonds and As dangling bonds are found. This is of practical importance because the composition of III-V alloys depends strongly on preparation conditions (see e.g., Ref. 8) with the result that many of the samples studied to date are known to be off-stoichiometric.

The behavior of defects in amorphous III-V compounds is complicated by two effects. First, as these materials are not glasses but quenched from the vapor, their defect concentrations are often quite large (> 1%) and may depend strongly on the deposition and annealing conditions, as in

a-Si. A second complication is that their bulk bonding does not obey the $8-N$ rule.[6,7] This rule is followed by most covalent amorphous semiconductors. It states that an atom's coordination is given by $8-N$, where N is the valence number (but by N if $N<4$). Thus, while individually Ga and As have three and five valence electrons each, and so would both be expected to be trivalent, their tetravalence is possible only because the GaAs unit as a whole has eight electrons. This effect is particularly significant in the alloys. For instance, in an alloy where the $8-N$ rule is obeyed, like a-As_xSe_{1-x}, an excess of Se is accommodated as extra Se—Se bonds, without change of coordination number. In a-Ga_xAs_{1-x} however, its valence requirements cause an excess As to create both As—As bonds and trivalent As sites.

The motivation of much of the early work on amorphous III-V compounds was the identification of wrong bonds. Wrong bonds can be considered either as defects in the network, as here, or as the consequence of topological disorder within the bulk network. In a-Si, topological disorder creates five- and sevenfold rings in the random network. Similar topological disorder in amorphous III-V compounds would automatically require wrong bonds, and consequently much of the early work focused on this aspect. However, Connell and Temkin[5] were able to construct a random network containing only even-membered rings and so proved that an ideal chemically ordered network is possible. Evidence for wrong bonds has been sought, by analyses of the radial distribution functions (RDF's) (Refs. 1–4), by photoemission studies of the valence and core electron states,[9–11] by optical spectroscopy,[12–16] and by extended x-ray-absorption fine-structure (EXAFS) studies of the nearest-neighbor bonding.[17,18] EXAFS showed that few wrong bonds were present in a-GaAs but significant concentrations were found in a-GaP although these were attributed to "extrinsic" factors such as nonoptimum annealing conditions.[18]

Paramagnetic centers have been observed in amorphous III-V compounds but these were rarely assigned to specific centers. The exception is that the characteristic signature of the As antisite defect (an As atom with four As neighbors) has been found[19] in amorphous GaAs.

Dangling bonds attracted much less interest until recently. Dangling bonds are readily identified in a-Si by electron spin resonance (ESR), but we shall see that they are more difficult to detect in amorphous III-V compounds as they are most likely to be diamagnetic. Dangling bonds are also difficult to detect from analysis of the RDF's as their main effect is to cause only a small change in the average coordination, but some evidence for them can be found from photoemission, as we describe later.

The present paper is the first major theoretical study of amorphous III-V compound semiconductors. Preliminary results for the defects in a-GaAs were reported earlier.[7] Joannopoulos and Cohen[20] have studied some effects of homogeneous disorder and of arrays of defects using crystalline polytype models, but this method is unable to study the properties of isolated defects. Yndurain and Joannopoulos[21] studied some defect models using Bethe lattices and a highly simplified Hamiltonian but the results were not sufficiently quantitative for direct comparison with experiment.

The following section presents the calculational method, and Sec. III describes the results for bulk sites and the effects of homogeneous disorder. Section IV describes the bonding at defects while their calculated electronic structure is presented in Sec. V. Section VI discusses the results in the light of experiment.

II. THE CALCULATIONAL METHOD

The electronic structure at a particular site is calculated in the form of a local density of states (DOS) projected onto that site using the recursion method[22] and the tight-binding approximation. Calculations for bulk sites use the 238-atom Connell-Temkin model. Calculations for defects use larger clusters with the required defect at their center and with 256-1024 atom crystalline clusters attached to each bond of the defect site. The recursion method derives the local DOS from a continued fraction, terminated after 30 levels. The orbital character of any defect level can be found by examining the poles of the recursion continued fractions, as in earlier work[23] on defects in SiO_2.

The interactions between cation and anion sites are described by the sp^3s^* first neighbor Hamiltonian of Vogl *et al.*[24] This Hamiltonian describes well the valence and lower conduction bands of the crystals and it has been extensively employed in studies of their defect and surface states. Its parameters for GaAs are given in Table I for reference. Lannoo[25] has shown that defects tend to modi-

TABLE I. Tight-binding interactions, in eV [$V(sp)=V(\text{Ga } s, \text{As } p)$].

	$V(ss)$	$V(sp)$	$V(ps)$	$V(p\sigma)$	$V(p\pi)$	$V(s^*p)$	$V(ps^*)$	d (Å)
Ga—As	-1.61	2.50	1.94	3.03	-0.78	2.08	2.10	2.45
Ga—Ga	-2.0	2.1		2.2	-0.67	2.0		2.46
As—As	-1.42	2.1		3.10	-0.79	1.8		2.49
As—H	-2.8	3.0						
Ga—H	-2.3	2.4						
Ga—Ga (in bridge)	-1.4	1.6		2.0	-0.5			
	$E(s)$	$E(p)$	$E(s^*)$					
Ga	-2.66	3.67	6.74					
As	-8.34	1.04	8.59					
H	-4.8							

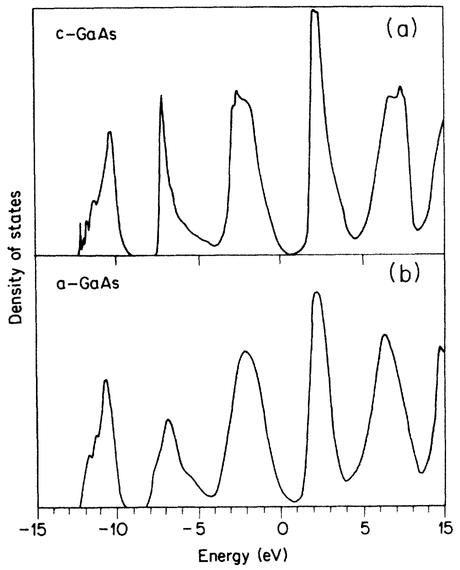

FIG. 1. Calculated density of states of (a) crystalline GaAs and (b) amorphous GaAs (using sp^3s^* Hamiltonian). The DOS in (b) is obtained by averaging the local DOS over six atoms in the Connell-Temkin (1974) model.

fy the interactions on adjacent bonds, so that defect calculations require careful parametrization. Thus, As-As interactions are not taken from Ga—As bonds, but from work[26] on c-As, and then adjusted slightly to place the A_1 level of the $\mathrm{As_{Ga}}$ antisite defect in c-GaAs at 0.65 eV above the valence-band edge, as suggested by experiment.[27] Ga—Ga bond interactions are taken from a fit[28] to the bands of c-GaSe. Interactions for other bonds between group-III atoms and between group-V atoms were found by scaling the Ga and As parameters by (bond length)$^{-2}$, respectively.

III. BULK ELECTRONIC STRUCTURE

Figure 1 compares the local DOS of c-GaAs with that averaged over six sites at the center of the Connell-Temkin model, representing bulk a-GaAs. The main features of the spectra are very similar. The filled valence bands lie between -12.5 and 0 eV. The lowest band from -12.5 to -9.9 eV is As s-like and is separated by an "ionicity" gap from the higher bands. The next peak at -7.5 eV is composed largely of Ga s and some As p states. The large broad peak from -3 to 0 eV is composed of As p and some Ga p states. The conduction-band states above 1.55 eV are more Ga-like, as expected from ionicity. The gap is direct and the conduction-band minimum is a pure s-like Γ_1 state in all the crystalline compounds, except in GaP and the Al compounds where, like in Si, it is indirect and the minimum lies near the X point and has mixed s-p character.

We comment on three aspects of the calculated DOS of a-GaAs. Firstly, the DOS is much smoother than that of c-GaAs, particularly the p-like states around -2 eV. This is a general feature of the amorphous phases and is seen in the experimental valence-band spectra as measured by photoemission.[9,10,29,30] Secondly, the leading edge of the valence band is barely shifted in a-GaAs, unlike the recession found in a-Si. Finally, we also calculate that the conduction-band edge does not move much. The conduction-band minimum state being s-like is not directly affected by bond-angle disorder, because of the spherical symmetry of s states. However there is the possibility of an indirect effect via the variations in second-neighbor distances and interactions. We therefore checked the calculations including explicit second-neighbor interactions of similar magnitude to those of Osbourn and Smith,[31] and allowed them to vary with distance. However, we still found little shift, essentially because these Ga-Ga interactions are numerically quite small. A similar lack of movement was found for the equivalent Γ_2' state in a-Si.[32] As the X_1 conduction-band state is also insensitive to disorder,[32,33] we conclude that the bulk conduction edge will barely shift in both the direct and indirect gap compounds.

The experimental data on the movement of the band edges is rather contradictory. Photoemission[10,29] suggests that the valence-band edge of GaAs does not move when disordered, in agreement with Fig. 1(b). However the phosphorus $K\beta$ x-ray emission spectra suggests that the valence-band edges of a-GaP (Ref. 34) and a-InP (Ref. 11) have both receded. Meanwhile, x-ray absorption shows that the conduction-band edges of a-GaP and a-InP have not moved.[11,34] Thus, these experiments suggest that the gap is either unchanged or larger in the amorphous phases. In fact, direct optical measurement of the gap finds a decrease in all cases, sometimes dramatically. For example, the 1.55 eV gap of GaA shrinks to 1.1—1.2 eV in annealed a-GaAs (Refs. 12, 14, 16, 35, and 36), the 1.4 eV gap of c-InP shrinks to approximately 1.2 eV in a-InP (Ref. 16), and the 2.35 eV gap of c-GaP shrinks to 1.2—1.55 eV.[12] We attribute the gap shrinkage to the presence of dangling-bond defect states lying in the band tails, as discussed in Sec. VI.

IV. DEFECT CONFIGURATIONS

A. Occupancies

Defect behavior is significantly more complicated in a-GaAs than in a-Si, principally because of the breakdown of the $8-N$ rule. We first describe defect bonding, using Fig. 2, and then show how this also controls the defect concentrations away from stoichiometry.

Both Si and GaAs are sp^3-bonded solids. In Si, there are four valence electrons per atom, so that each atom contributes one electron to each of its four bonds, giving two electrons per bond. In GaAs, Ga has three valence electrons and As has five electrons, so that each site now contributes unequally to each bond, with Ga providing $\frac{3}{4}$ electrons and As providing $\frac{5}{4}$ electrons. These same contributions are retained at defect sites.

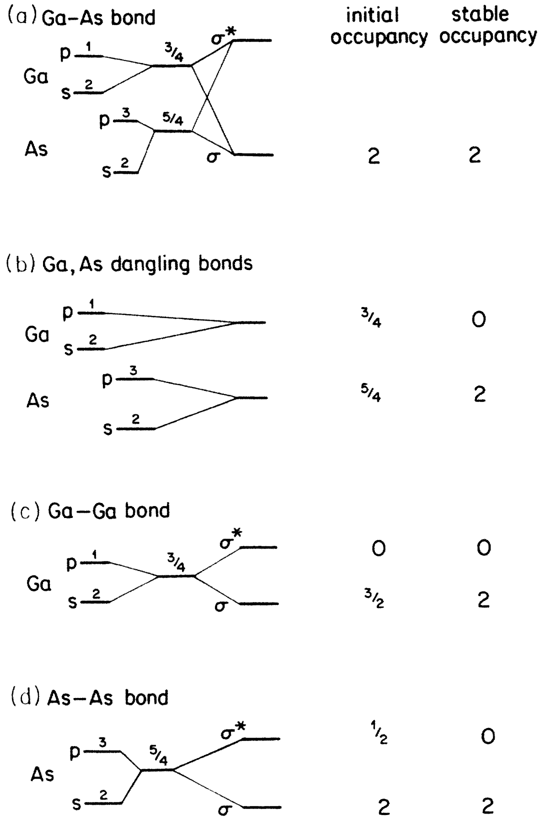

FIG. 2. Schematic diagram of bulk bonding (a) and of defect energy levels (b)–(d) in a-GaAs. For each energy level, the number in the first column indicates the formal occupancy of an *isolated* level, and the number in the second column indicates the preferred number of electrons in the level. (a) Each isolated As atom has two s and three p electrons, each Ga has two s and one p electron. On sp^3 hybridization, As has $\frac{5}{4}$ electrons on average per bond and Ga has $\frac{3}{4}$ electrons per bond, giving 2 electrons per Ga—As sp^3 bond. (b) An isolated As dangling bond has formally $\frac{5}{4}$ electrons and an isolated Ga dangling bond $\frac{3}{4}$ electrons; the preferred occupancies are 2 and 0, respectively. (c) An isolated Ga wrong bond has a formal occupancy of $\frac{3}{2}$ electrons. (d) An isolated As wrong bonds has $\frac{5}{2}$ electrons. In both cases the preferred occupancy is two electrons.

We now consider the formation of defects, as in Fig. 2. At a Si dangling-bond site, one sp^3 hybrid is nonbonding and contains one electron, when neutral. Two differences occur in a-GaAs. Firstly, the isolated neutral Ga dangling bond possesses only $\frac{3}{4}$ electrons in its defect level, while the As dangling bond possesses $\frac{5}{4}$ electrons, as shown in the first column in Fig. 2. Secondly, this Ga level lies at a higher energy than the As dangling-bond level. This favors a charge transfer tending to empty the Ga dangling-bond level into the As dangling-bond level [Fig. 2(b)]. Thus, the Ga dangling bond is a $\frac{3}{4}$ electron donor, as shown in Table II. Conversely the As dangling-bond level is a $\frac{3}{4}$ electron acceptor.

The wrong bonds are treated similarly. An As—As bond is formed by bringing together two As sp^3 hybrids, producing a bonding (σ) and an antibonding (σ^*) level. This bond has $\frac{5}{2}$ electrons associated with it when neutral, so $\frac{1}{2}$ electron must enter the high-lying σ^* state. Thus the As—As bond is a $\frac{1}{2}$ electron donor. Conversely, the Ga—Ga bond possesses only $\frac{3}{2}$ electrons and, needing $\frac{1}{2}$ electron to fill its σ level, it acts as a $\frac{1}{2}$ electron acceptor. Table II also shows the equivalent stoichiometries of the defects which are found by noting that a dangling bond is $\frac{1}{4}$ vacancy and a wrong bond is $\frac{1}{4}$ antisite.

B. Trivalence

The dangling bonds differ in one crucial respect from those of a-Si, in that the trivalent Ga and As configurations are just those expected from the $8-N$ rule.[6,7] Arsenic is normally trivalent with a doubly occupied nonbonding level and a bond angle of $\theta=97°$. Therefore by analogy, we expect the As dangling bond to relax from a bond angle of $\theta=109.5°$ towards $\theta=97°$, when its level is filled. Similarly, trivalent Ga normally has a bond angle of 120° and an empty nonbonding state. Thus, we expect the Ga dangling bond to relax towards $\theta=120°$ as its level empties. These relaxed configurations are just those found at the relaxed (110) surface of c-GaAs.

A consequence of relaxation is that the diamagnetic configurations of dangling bonds are much more probable than the half-filled configurations. Relaxation of the As dangling bond from 109° to 97° causes the dangling-bond

TABLE II. Chemical bonding, stable formal charge, and stoichiometry of some defects in a-GaAs. The lone pair electrons of As are indicated by two dots.

Site	Bonding	Formal charge	Equivalent As atom excess
Ga dangling bond	$\equiv$Ga	$+\frac{3}{4}$	$-\frac{1}{4}$
Ga wrong bond	$\equiv$Ga—Ga$\equiv$	$-\frac{1}{2}$	$-\frac{1}{2}$
As dangling bond	$\equiv$As:	$-\frac{3}{4}$	$\frac{1}{4}$
As wrong bond	$\equiv$As—As$\equiv$	$+\frac{1}{2}$	$\frac{1}{2}$
	$\equiv$As—H	$-\frac{3}{4}$	$\frac{1}{4}$
	$\equiv$Ga—H—Ga$\equiv$	$+\frac{1}{2}$	$-\frac{1}{2}$
	$=$As—As$=$	-1	1

level to change from sp^3 to more s-like character, and so it drops in energy. Thus, the filled s-like level tends to lie *below* the half-filled sp^3 level, which is a negative U ordering of states. As these levels tend to be below E_F, we believe that half-filled As dangling bonds are unlikely to be observed, except perhaps for severely distorted sites or under optical illumination. Complementary arguments apply to Ga dangling bonds which become more p-like as they empty.

C. Stoichiometry

Deviations in composition occur by the introduction of defects; the size of the deviation controls their total number, and the position of E_F controls their relative proportions. Using a-$Ga_{1-x}As_x$ as an example, we expect that an As excess is accommodated by some mixture of As—As bonds and As dangling bonds. From Table II, the As excess $(2x-1)$ is given by

$$\tfrac{1}{4}d_{As}+\tfrac{1}{2}w_{As}-\tfrac{1}{4}d_{Ga}-\tfrac{1}{2}w_{Ga}=2x-1 \ . \tag{1}$$

This simplifies to

$$\tfrac{1}{4}d_{As}+\tfrac{1}{2}w_{As}=2x-1 \ , \tag{2}$$

for $x>\frac{1}{2}$ because the Ga-site defects correspond to a Ga excess and are therefore quickly suppressed. Here d_{As} is the number of As dangling-bond sites and w_{As} is the number of As—As bonds, etc.

Because As—As bonds, etc., are donors or acceptors, any general combination of defects in a-GaAs will also create free carriers. In this case, from Table II, the net number of free electrons (n-p) generated is given by

$$\tfrac{1}{2}w_{As}-\tfrac{3}{4}d_{As}-\tfrac{1}{2}w_{Ga}+\tfrac{3}{4}d_{Ga}=n\text{-}p \ . \tag{3}$$

Now, Robertson[37] showed that most amorphous III-V compounds are highly compensated, so that the presence of free carriers will cause the spontaneous creation of the appropriate defects which will then trap the carriers and allow E_F to return to midgap. This is possible because the energy released by the compensation process (approximately equal to the band gap) exceeds the defect creation energy. Equation (3) now simplifies to

$$\tfrac{1}{2}w_{As}-\tfrac{3}{4}d_{As}=0 \tag{4}$$

for $x>\frac{1}{2}$. Combining (2) and (4), we find that an As excess is accommodated by the creation of three As—As wrong bonds for every two As dangling bonds. This generates the a-As structure at $x=1$; in other words the structure of As-rich a-$Ga_{1-x}As_x$ can be described as an alloy of the a-GaAs and a-As structures. Alternatively, from the III-V viewpoint a-$Ga_{1-x}As_x$ is "semi-insulating" because defects are present in a suitable combination. Interestingly, a closely related compensation process also occurs for point defects in bulk c-$Ga_{1-x}As_x$ and at the polar (111) surfaces of c-GaAs.[38]

The contrast with alloys which obey the $8-N$ rule like a-$As_{1-x}Se_x$ is instructive. In that case, wrong bonds (wb) are self-compensated, so that an As excess in the selenide involves only the addition of As—As bonds. In systems

TABLE III. Bond lengths (d) in Å, and gap states for various defect centers, in eV. d_{ac} refers to the anion-cation bond length. 109°, etc., refer to the bond angle at the dangling bond sites. $(wb)_2$ denotes a complex of two adjacent dangling bonds. All energies are referred to the valence-band top of the crystal.

	AlP	AlAs	AlSb	GaP	GaAs	GaSb	InP	InAs	InSb	ZnSe	ZnTe
d_{ac} (Å)	2.36	2.45	2.66	2.36	2.45	2.64	2.54	2.62	2.81	2.45	2.64
d_{aa} (Å)	2.23	2.49	2.65	2.23	2.49	2.65	2.23	2.49	2.65	2.34	2.78
d_{cc} (Å)	2.46	2.46	2.46	2.46	2.46	2.46	2.76	2.76	2.76		
E_g (eV)	2.5	2.3	1.88	2.35	1.55	0.78	1.41	0.43	0.23	2.68	2.56
Anion db, 109 °	0.32	0.15	0.25	0	−0.12	0	0	−0.1	−0.15	0.3	0.53
97°	−0.4	−0.42	−0.22	−0.52	−0.7	−0.45	−0.56	−0.8	−0.6	−0.45	−0.18
Cation db, 109°	2.21	1.99	1.42	2.04	1.45	0.84	1.89	1.36	0.82	3.3	3.0
120°	2.73	2.48	2.02	2.45	1.85	1.37	2.04	1.55	1.10	3.5	>3.0
Anion (wb)	2.30	1.86	1.41	1.98	1.45	0.76	1.70	1.15	0.75	2.4	2.5
Anion $(wb)_2$	2.1	1.5	1.1	1.75	1.2	0.5	1.45	0.85	0.4		
Anion antisite (A_1)	1.59	0.87	0.37	1.22	0.65	−0.06	0.95	0.23	−0.3		
Cation (wb)	0.14	−0.1	−0.35	0.09	−0.35	<0	0.57	0.21	−0.25		
Cation antisite (T_2)	0.6	0.2	−0.2	0.5	0.1	−0.35	1.0	0.6	0.0		

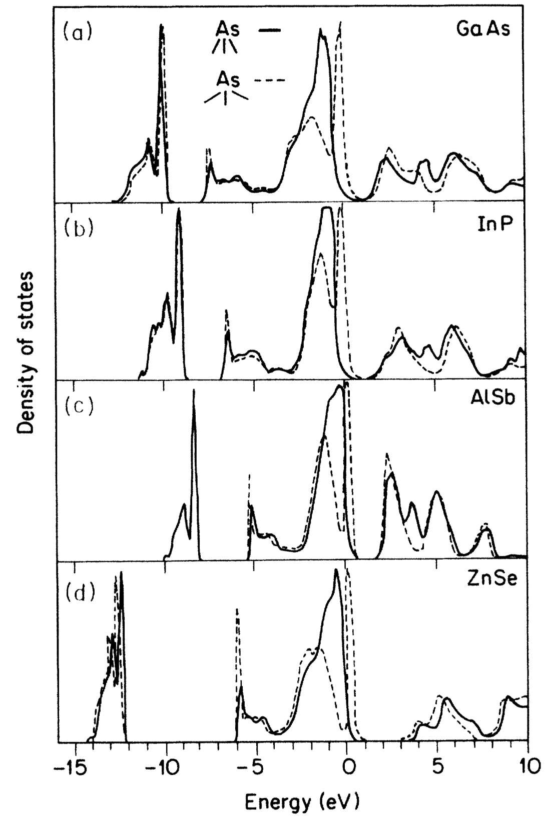

FIG. 3. The local DOS on an undercoordinated anion site for relaxed ($\theta=97°$; solid lines) and unrelaxed ($\theta=109°$; dashed lines) dangling-bond configurations. In this and Figs. 4–6: (a) GaAs, (b) InP, (c) AlSb, (d) ZnSe.

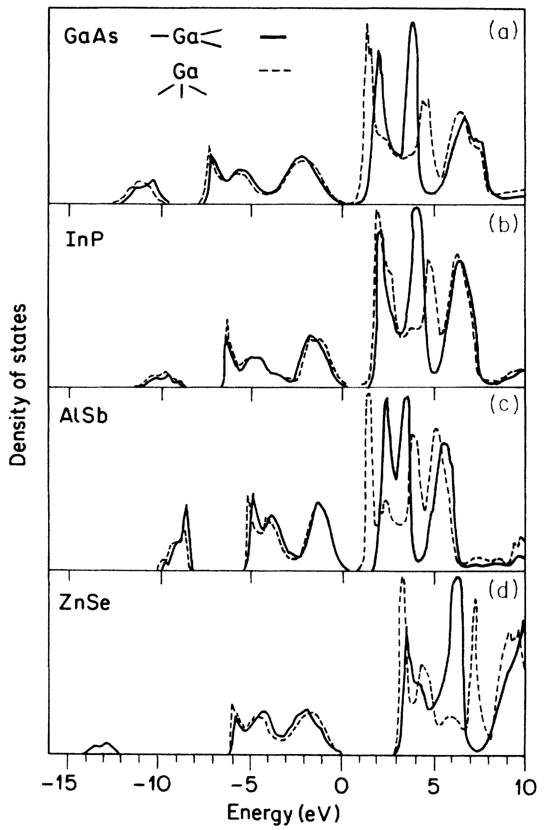

FIG. 4. The local DOS on an undercoordinated cation site for relaxed ($\theta=120°$; solid lines) and unrelaxed ($\theta=109°$; dashed lines) dangling-bond configurations.

not obeying the $8-N$ rule like a-$\mathrm{Ga}_{1-x}\mathrm{As}_x$, a combination of defects is found, but in both cases E_F remains at midgap.

V. ELECTRONIC STRUCTURE OF DEFECTS

A. Anion dangling bond

The density of states at an unrelaxed singly occupied anion dangling bond ($\theta=109°$) is shown in Fig. 3 for GaAs, InP, AlSb, and ZnSe. A dangling-bond state is found near the valence-band edge (Table III). This state lies above the valence-band edge for the Zn and Al compounds and close to or below the edge in the Ga and In compounds. It has strong p character with some s admixture. There is also a strong s resonance at the top of the lowest valence band.

The bond angle relaxes towards 90° for the doubly occupied dangling bond. By $\theta=97°$ (the three-coordinated As angle), the gap state has relaxed into the valence band for all the semiconductors studied (Fig. 4 and Table III). Thus, singly occupied anion dangling bonds can give p-like gap states in some of these compounds but doubly occupied dangling bonds always give a valence-band resonance.

B. Cation dangling bond

The unrelaxed cation dangling bond with $\theta=109°$ gives a defect state close to the conduction-band edge (Fig. 4, Table III). This state lies in the gap for Al and Ga dangling bonds and above the edge for Zn and In dangling bonds. The singly occupied state is of predominantly s-like character, with a significant p admixture, being 34% s-like and 18% p-like in GaAs. The main p-like resonance is found higher in the conduction band.

When the site relaxes to a planar configuration ($\theta=120°$), its symmetry changes from C_{3v} to D_{3h}. The s orbital of a_1 symmetry now decouples from the p orbital which is now a $p\pi$ orbital and of b_1 symmetry. The bonding now becomes sp^2-like and the defect state moves up and out of the gap, giving an s-like antibonding resonance at the bottom of the conduction band. The p-like state shifts down in energy due to the sp decoupling but remains high in the conduction band. This p state is the true dangling-bond level.

The behavior of the cation dangling bond complements that of the anion dangling bond. When singly occupied, it gives a gap state in some of the compounds, but when empty it always relaxes to give a band resonance.

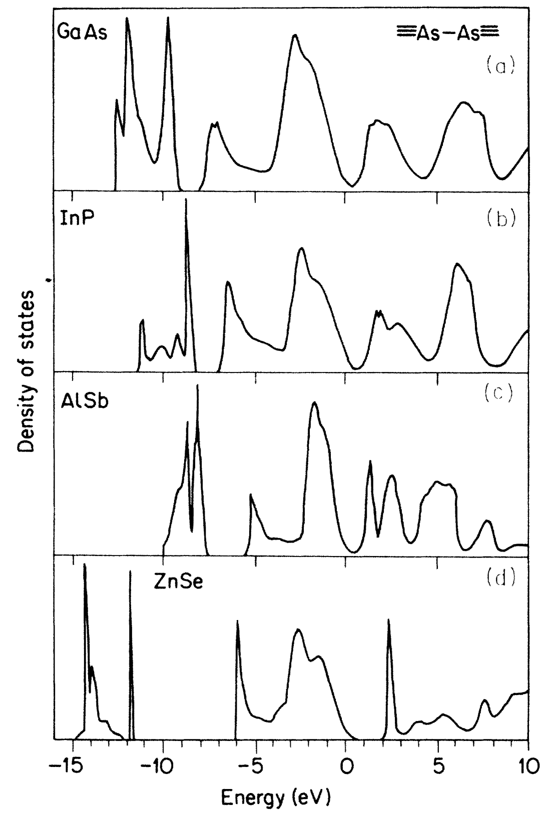

FIG. 5. The local DOS for an isolated anion-anion wrong bond.

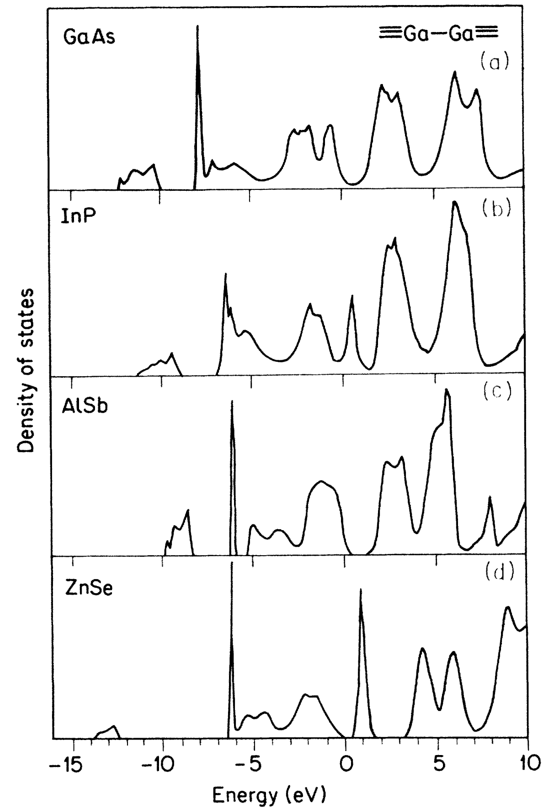

FIG. 6. The local DOS for an isolated cation-cation wrong bond.

C. Anion wrong bonds

We first consider isolated wrong bonds between two four-coordinated anions and then examine the effects of clustering. An isolated anion wrong bond introduces a pronounced splitting of the anion s band, giving an s resonance or bound state at the band bottom and an s antibonding level at its top (Fig. 5). More critically, many of the wrong bonds give a gap state (Table III). This state is an antibonding level, pulled down from the conduction band, as shown schematically in Fig. 2. For GaAs, this state has 8% s and 11% p character on each wrong-bond site, i.e., it is 38% localized in the bond. We find a gap state for all Al and Ga compounds and for ZnSe. The In-based compounds give a conduction-band resonance and the ZnTe level is at the conduction-band edge. The corresponding σ-like resonance is seen in the downward shift in weight of the valence p band.

D. Cation wrong bonds

The behavior of the cation wrong bond is in many respects complementary to that of the anion wrong bond. An isolated wrong bond produces a strong s-like state or resonance around -7 to -8 eV, at the bottom of the cation s band in III-V compounds (Fig. 6). Many of the wrong bonds give a gap state, due to a bonding level raised above the valence-band edge (cf. Fig. 2). The gap state is found in the two II-VI compounds and in the three phosphides, i.e., the semiconductors with the most electronegative anions in which the bulk valence band lies deepest. This state has 4% s and 21% p character on each site in GaP, so it is localized 50% in the bond. For the remaining semiconductors, a $p\sigma$-like resonance is found near the top of the valence band. The character and position of states associated with both cation and anion wrong bonds is similar to that deduced by Joannopoulos and Cohen.[20]

E. Wrong-bond complexes

Defect complexes are studied for two reasons: They are the probable cause of mid-gap states in a-GaAs, and they are likely to occur away from stoichiometry because of the large defect concentrations.

The antisite consists of a tetravalent site surrounded by four wrong bonds. The anion antisite is calculated to produce a deep gap state in all compounds except InSb and GaSb. The gap state is a symmetric a_1 combination of the four wrong-bond σ^* states. In a-GaAs, this lies at approximately 0.65 eV [Fig. 7(c)], a t_2 resonance lies at -3 eV, another a_1 state is bound below the Ga s band at about -8.5 eV and there is finally an enhancement of the lowest As s band at -13 eV (cf. Refs. 39 and 40). Tetrahedral anion sites with two or three wrong bonds are also found to have gap states; the state of the single wrong bond moves downward through the gap as the number of

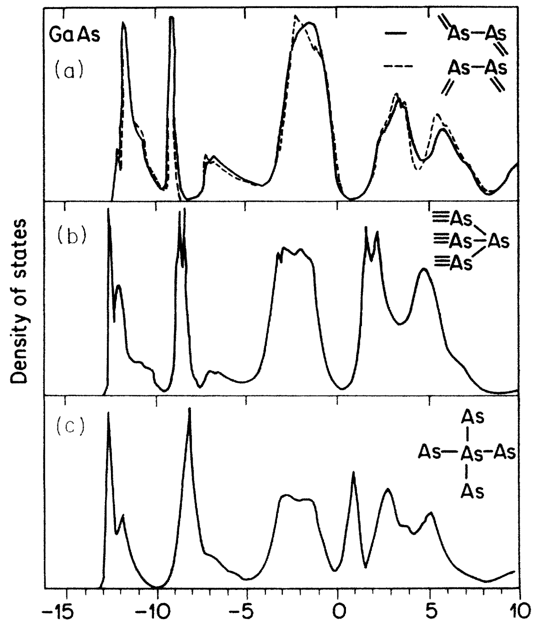

FIG. 7. (a) The local DOS for an isolated wrong bond between two trivalent As sites: solid line, *trans* configuration; dotted line, *cis*. (b) For an ≡As site with three As—As wrong bonds. (c) The local DOS for a As$_{\mathrm{Ga}}$ antisite in GaAs.

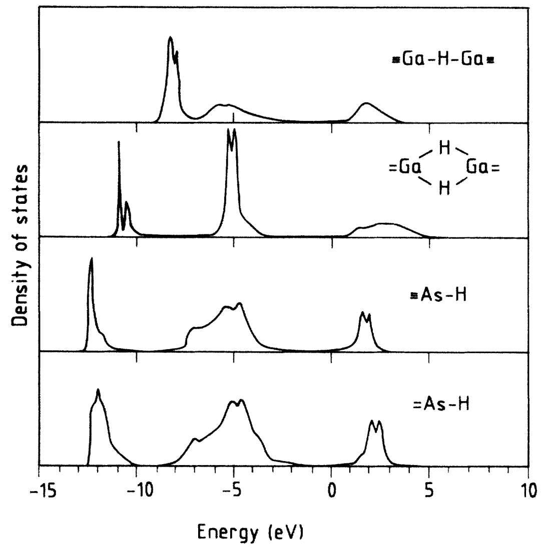

FIG. 8. The local DOS for various hydrogen centers; ≡Ga—H—Ga≡, =GaH$_2$Ga=, ≡AsH, and ≡AsH.

wrong bonds in the complex increases, and has passed into the valence band for the antisite in GaSb and InSb. Previous calculations[41] with the sp^3s^* Hamiltonian have found that anion antisites give gap states except in InSb and InAs; these compounds are exceptional largely because of their rather narrow gaps; InAs being 0.37 eV and InSb being 0.25 eV.

Clearly, wrong bonds can also occur between trivalent sites, so we have also studied the single As—As bond between two trivalent sites [Fig. 7(a)] and the case of three As—As bonds meeting at one trivalent As site [Fig. 7(b)]. Interestingly, neither configuration is found to give a gap state. This suggests that, in the various possible defect complexes, trivalent As is not, itself, a cause of gap states.

A comparison of the DOS of the trivalent and tetravalent wrong bonds is instructive. The trivalent wrong bond can have two extreme configurations, either *cis* or *trans*, according to its dihedral angle but their DOS is rather similar [Fig. 7(a)]. As in the tetrahedral case (Fig. 6) the As—As bond causes a splitting of the As *s* band. Now however, the As *p* band has more weight at smaller binding energies, due to the more *p*-like character of the As—As σ state. It is this greater *p* character which raises the As—As σ^* state out of the gap into the conduction band.

F. Hydrogen-related states

Hydrogenated amorphous III-V compounds have been prepared by a number of groups.[42,43,29] In *a*-GaAs:H hydrogen is found to bond preferentially to Ga in the form of Ga—H—Ga bridges, and monovalently with As in the form of As—H units.[44] However this has not completely specified the two hydrogen configurations. We have therefore calculated the local electronic structure of two GaH configurations (≡Ga—H—Ga≡ and =GaH$_2$Ga=) and two AsH configurations (≡As-H, =As—H), as shown in Fig. 8. The interaction parameters are given in Table I. We see that the ≡GaHGa≡ bridge gives a single peak in the lower valence band, just below the Ga *s* band, while the =GaH$_2$Ga= double bridge gives two peaks in the lower valence band. The two AsH configurations are found to have similar spectra on their hydrogens, a sharp peak in the lower As *s* band around −12 eV, and a broad peak in the next band centered on −5 eV due to interactions with As *p* states.

The valence band DOS of *a*-GaAs:H has been measured by ultraviolet photoemission by Karcher *et al.*,[29,30] and shows hydrogen related peaks at −7 and −14 eV. We concur with their assignment of these peaks to GaH and AsH features, respectively. The presence of only one peak around −7 eV suggests that hydrogen occurs as single ≡GaHGa≡ rather than double bridges. This peak position is relatively insensitive to the bridging angle, so we cannot comment on whether the bridge is bent, as inferred by infrared.[44] The calculated position of the As—H peak is higher than that found experimentally. Its insensitivity to the As coordination prevents us from discriminating between =AsH and ≡AsH.

VI. DISCUSSION

A. Wrong bonds

Wrong bonds have frequently been considered to be the most probable defects in amorphous III-V compounds for energetic and topological reasons. One expects that replacing a heteropolar bond by a homopolar bond is unlikely to cost more than losing the bond altogether, and this is confirmed by recent total energy calculations for antisites and vacancies in *c*-GaAs.[38] Consequently, there have been many attempts to identify features due to wrong bonds in amorphous III-V compound semiconductors and to place limits on their concentrations. An obvious upper limit of 12% on their concentrations can be set by assuming that the fraction of odd-membered rings in *a*-GaAs is not larger than in the Polk model of *a*-Si.[3] Dixmier *et al.*[3] then carefully analyzed the peak positions of the structure factors of annealed *a*-GaAs, *a*-GaP, *a*-GaSb, and *a*-InP and concluded that an even-membered ring network was strongly favored, so reduced limits of perhaps $\lesssim 5\%$ can be inferred from this result. Recent EXAFS measurements by the same group[18] found little evidence of wrong bonds in *a*-GaAs, in agreement with this, but found significant Ga—Ga bonding in their *a*-GaP samples, which they attributed to lack of annealing. In principle, photoemission from the valence band and core levels ought to reveal effects due to wrong bonds. Any homopolar bonding reduces the atomic charges on the atoms involved and this might be detectable from a shift of core-level energies. Such broadening has been observed in *a*-Si, where bond angle distortions cause charge fluctuation, and in *a*-Si:H where the finite polarity of the Si—H bond causes charge fluctuations.[45] However, earlier measurements by Shevchik *et al.*[9] and more recent work by Ley[30] have failed to detect broadening attributable to wrong bonds. In the valence band DOS, Shevchik *et al.*[9] assigned small peaks in *a*-GaSb and *a*-GaAs near -9 eV to possible wrong bonds, while Karcher *et al.*[29] also observed this peak in GaAs during its recrystallization, together with another peak at -14.5 eV and assigned them to Ga—Ga and As—As wrong bonds, respectively. Our calculations suggest that both peaks are perhaps too deep to be assigned to wrong bonds in a homogeneous GaAs network and perhaps might be due to crystallites. We have therefore concluded that no experimental technique to date can put a quantitative estimate on the proportion of isolated wrong bonds in the amorphous III-V compounds.

B. Dangling bonds

We now propose a slightly unusual model for the nature of gap states in *a*-GaAs. Usually, deep gap states in amorphous semiconductors are due to dangling bonds. In *a*-GaAs, from our calculations, we propose that simple isolated centers such as dangling bonds and wrong bonds can only introduce states at or near the band edges, while any states observed deeper in the gap are most likely to be due to defect clusters of various forms. Furthermore, we propose that dangling bonds are present in large concentrations (3—4 %) but are diamagnetic.

Two arguments favor a high proportion of trivalent sites in amorphous III-V compounds. Firstly, trivalent sites satisfy the atom's normal-valence requirements and can assume a relaxed, diamagnetic configuration. Secondly, trivalent sites are favorable for relieving strain in the random network. Phillips[46] has proposed that networks with mean coordinations greater than 2.4 are "overconstrained" so that instead of the network being homogeneous and fully-bonded, it possesses a fraction of intrinsically broken bonds to relieve the strain. A fraction of 3—4 % is expected in *a*-Si, most of which then reconstruct into weak bonds. As amorphous III-V compounds are also tetrahedral networks, a similar fraction of intrinsic dangling bonds is expected, but these will now relax rather than reconstruct; as discussed in Sec. IV B. Thus, we propose that amorphous III-V compounds possess about 2% diamagnetic dangling bonds of each species. In contrast, the presence of wrong bonds leaves the mean coordination unaltered and so they are only able to relieve strain indirectly by allowing a greater variety of ring statistics. Thus, we argue that the wrong-bond concentration is essentially extrinsic and, in particular, the intrinsic concentration is likely to be below the 3—4 % expected for dangling bonds.

C. The nature of mid-gap and band tail states

As isolated dangling bonds and wrong bonds are calculated to introduce only band-edge states or band resonances, we expect a much lower density of states at the Fermi level, $N(E_F)$, than in *a*-Si. This is indeed found experimentally. E_F usually lies near midgap. At low temperatures the conductivity follows an approximate $T^{-1/4}$ dependence in many compounds (GaAs, InP, GaP, AlSb, GaSb, InSb), indicating variable range hopping through states near E_F.[12,14,16,47,48] When annealed, the conductivity changes over to a T^{-1} law in most cases, indicating that conduction is by hopping through states away from E_F.[14,16] Indeed, even in the $T^{-1/4}$ regime, the thermopower is large for all compounds except *a*-InP, implying that conduction occurs through states somewhat away from E_F.[47] These various results suggest an upper limit of order 10^{18} cm^{-3}eV^{-1} for $N(E_F)$ for most compounds.

Evidence for the presence of large defect concentrations at the band edges is found in the photoemission and optical spectra. A change in the defect density just below E_v has been seen by ultraviolet photoemission during recrystallization.[29] Theye *et al.*[35] noted that annealing did not sharpen the optical absorption edge in *a*-GaAs, as it does in *a*-Ge. They suggested that annealing in *a*-Ge sharpens the edge because it allows the network to relax, but that the edge is controlled by defects in *a*-GaAs which do not anneal out and so its slope does not change. The defect nature of the band tails perhaps also accounts for the much smaller pressure coefficient of the gap in *a*-GaAs compared to *c*-GaAs,[36] as it is well known that deep levels like dangling bonds have a rather small pressure coefficient because they contain components from many bands, and do not usually follow the bulk band edges.[49]

Paramagnetic states with concentrations of order 10^{18} cm^{-3} have been observed in *a*-GaAs, *a*-InP, and *a*-GaP by ESR.[50,51] Three signals with $g=1.94$, 2.05, and 2.07 were observed in *a*-GaAs. Hydrogenation decreases the $g=2.07$ signal, and this has been tentatively assigned to an As dangling bond.[50] Our results caution against such an identification, as they suggest that such a singly occupied level when E_F lies as high as $E_v+0.6$ eV in *a*-GaAs would require a severly distorted trivalent As site with its bond angles increased to approximately 115°, which is opposite to the usual direction of relaxation for such a site.

Our results suggest that paramagnetic states near midgap should be assigned to clusters of wrong bonds. For example, the characteristic signature of the As_{Ga} has been observed[19] in some samples of *a*-GaAs in concentration of approximately 3×10^{17} cm^{-3}. However, in contrast to *a*-GaAs, our results (Table III) suggest that isolated wrong bonds are possible deep states in *a*-InP.

When wrong bonds are present in large concentrations, as often occurs in *a*-GaP, they do cause pronounced narrowing of the optical gap.[12]

D. Hydrogenation

Hydrogenation is not as effective in the III-V compounds as in *a*-Si at reducing the gap state density.[42,43] The simplest reason suggested by our results is that hydrogen passivates *a*-Si by tying off dangling bonds, but cannot passivate the wrong-bond clusters which form the problematic mid-gap states in amorphous III-V compounds. However, this argument must be treated with caution, as hydrogen has recently been found to passivate fully bonded centers,[52,53] and even the As_{Ga}-related EL2 level in *c*-GaAs.[54] A second reason is that in all alloys, hydrogen tends to bond preferentially to one of the species, e.g., Si in *a*-Si_xGe_{1-x}:H and Ga in *a*-GaAs:H. Infra-red spectroscopy shows that most of the hydrogen forms three-center Ga—H—Ga bridges with Ga, reminiscent of the three-center bonds in boron hydrides.[44] Thus, while *a*-GaAs begins with fewer intrinsic mid-gap states than *a*-Si, after hydrogenation, *a*-Si:H is better than *a*-GaAs:H, and indeed rectification has not yet been observed in *a*-GaAs:H Schottky diodes.[42]

Experimentally, in photoemission,[29] hydrogenation does not produce the large erosion of the valence-band edge of *a*-GaAs that it does in *a*-Si. One might assume that this is because the valence edge is largely As *p*-like and that hydrogen bonds preferentially to Ga. However, there is still no erosion in *a*-GaAs:H containing 50% H, in which the -15 eV peak attributed to As—H bonds is very strong.[29,30] The reason why As—H bonds do not cause an erosion of the valence-band edge is unclear to us at present.

E. Doping

The interest in any semiconductor system is greatly increased if it can be doped. To date, doping has not been observed in *a*-GaAs:H. The two obvious possible reasons for this are a high density of gap states and a failure to produce substitutional sites. Clearly, the density of gap states is higher in *a*-GaAs:H than in *a*-Si:H but it is probably not so high as to ultimately prevent the observation of doping. Secondly, the fact that Ga and As already occupy four-fold sites, suggests that the formation of substutional sites is also not a crucial problem. Additionally, interstitial doping can always be used.

Recently, Robertson[37] proposed a more general reason why doping has not been observed, that dopants are strongly compensated in *a*-GaAs:H. Figure 9 compares the gap states of doped *a*-GaAs:H and *a*-Si:H. A donor would introduce a singly occupied level near E_c. Any As dangling bonds would introduce an acceptor level at E_v. If the donor electron were to fall into the defect level this releases a certain amount of energy. It was shown that in *a*-GaAs this energy would exceed the creation enthalpy of that defect.[37] Hence, such defects will be spontaneously created during the deposition process and they will act to compensate the donors. A similar process actually occurs in *a*-Si:H but there the energy balance is such that the compensation is incomplete and approximately 10% of the electrons are left in the band tails. The lower defect level causes the compensation to be essentially complete in *a*-GaAs:H. A similar compensation of donors could also be provided by the acceptor states of Ga—Ga wrong bonds. In fact, the nature of the compensating defect depends on whether there is an As or Ga excess. Equivalent arguments apply to *p*-type doping.

Dopant compensation is minimized in small gap semiconductors, where the energy gained through compensation is less. This suggests that the *a*-GaSb and *a*-InSb systems should be studied. In narrow gap amorphous semiconductors, there is always the problem that the density of states in the midgap will be high due to strongly overlapping band tails. Our calculations of bulk disorder in Sec. III suggest that the intrinsic width of the band tails in amorphous III-V compounds need not be large and might even be less than in *a*-Si:H due to their narrower dihedral angle distribution. Also, the dangling-bond and wrong-bond states may now be true band resonances in narrower gap amorphous III-V compounds, rather than often lying in the band tails, so this source of tailing may also be minimized. Thus there is still the possibility that doping might be observed in these systems.

F. Stoichiometry deviations

In off-stoichiometric samples with large excess of the group *V* element, the excess species appear to be largely incorporated in their preferred threefold coordination. A detailed study of *a*-Ga_xSb_{1-x} using Raman and electron diffraction confirmed the alloy picture for $x>0.5$. In this antimonide, alloying increases the conductivity and enhances the $T^{1/4}$ behavior at low temperatures.[12] This implies a substantial increase in gap states, consistent with the above model that alloying introduces 1 dangling bond and $\frac{3}{2}$ wrong bonds per excess atom. The gap states in

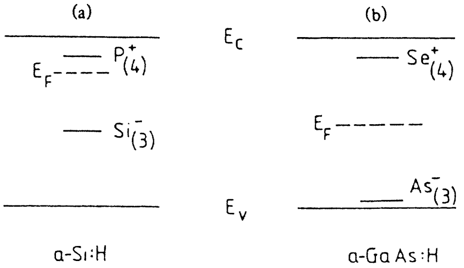

FIG. 9. Schematic gap states in doped *a*-Si:H and doped *a*-GaAs:H. The compensation is only partial in *a*-Si:H and E_F lies in the band tail, but the compensation is essentially complete in *a*-GaAs:H and now E_F is pinned in its intrinsic position, near midgap. The subscripts refer to the atomic coordinations.

these alloys are attributed to wrong-bond clusters. Our model of alloys is also supported by work on the *a*-$Ga_{0.4}As_{0.6}$ alloy where x-ray photoemission has found the characteristic splitting of the As *s* peak at -12 eV due to As—As bonds.[10]

Little work has been carried out an alloys containing an excess of the group III species. We expect these alloys to be dominated by group-III-related defects.

VII. CONCLUSIONS

We have examined a range of native defects in the amorphous III-V compounds and in *a*-ZnSe and *a*-ZnTe. We calculate that relaxed anion dangling bonds give a valence-band resonance and relaxed cation dangling bonds give conduction-band resonances in all cases. Either isolated wrong bonds and/or wrong-bond complexes give gap states in all the semiconductors studied. We argue that the predominant defects in stoichiometric amorphous III-V compounds are diamagnetic dangling-bond states. Thus high-quality amorphous III-V alloys have fewer intrinsic gap states than *a*-Si. We propose the study of the pressure dependence of the optical-absorption edge to reveal the presence of dangling-bond states in the band tails. Off-stoichiometry, we expect an alloy of the excess species and the stoichiometric III-V compound semiconductor. From the III-V-compound viewpoint, the alloying introduces a mixture of dangling-bond and wrong-bond defects associated with the excess species. The properties of III-V alloys then depend very sensitively on the preparation method and conditions.

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