Double-dangling-bond defects and band bending at the GaAs (110) surface

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We note that contact-potential measurements which have shown band bending at the nonpolar GaAs surface can be interpreted with a simple model for cleavage defects at the surface. We find that defects with two dangling bonds at the surface produce both filled and empty defect states in the gap. This result then supports experimental work indicating that band bending at GaAs(110) is defect related.

Currently the best experimental evidence indicates that no surface states exist in the gap at the GaAs (110) surface. Although contact-potential measurements have led to a variety of conclusions regarding this question,[1,2] it is generally accepted that the lack of reproducibility in these experiments is attributable to cleavage defects at the (110) surface. Photoemission studies have similarly yielded conflicting evidence concerning the problem, with the most recent and generally accepted conclusion that band-gap states do not occur at GaAs(110).[3-5] In this paper we theoretically examine the electronic structure of a class of cleavage defects and relate our results to the experimental measurements.

The most compelling evidence that defect-related midgap Fermi-level pinning occurs at GaAs(110) is provided by the contact-potential measurements of Huijser and VanLaar.[2] Their results are presented schematically in Fig. 1. In a series of cleaves of doped GaAs crystals, the experimenters obtained surfaces with regions of varying quality. Generally, in part, a macroscopically "good" cleave with a mirror like finish would be obtained, and over some parts of the surface the crystal would appear broken, with macroscopically visible tears, steps, and cracks (indicated by the shaded region in Fig. 1). The experiment consisted of measuring the variations in the contact potential across such a surface. Typical results are shown in the figure. For an n-type sample, the Fermi level on the "clean" fraction of the surface was found to occur just below the conduction-band minimum. However, in the defective region, the Fermi level was found to drop into the gap, typically by ~0.3 eV. Similarly, for p-type materials, the Fermi level in the good "good" cleavage region occurred just above the valence-band maximum, and in the defective area moved into the gap by about 0.2 – 0.3 eV. This experiment indicates the presence of filled and empty defect-induced surface bands in the lower and upper gap, respectively.

DOUBLE-DANGLING-BOND DEFECTS

In order to approach theoretically this topic, we note that, first of all, the (110) surface is the natural stable cleavage plane for a heteropolar zinc-blende semiconductor. This is because the surface is nonpolar and the Fermi level is easily stabilized in a 1×1 reconstructed configuration.[6] By contrast, the polar (100) and (111) surfaces are extremely unstable, can be prepared only by argon bombardment,[7] or extremely carefully controlled molecular-beam epitaxy,[8] and exhibit complicated

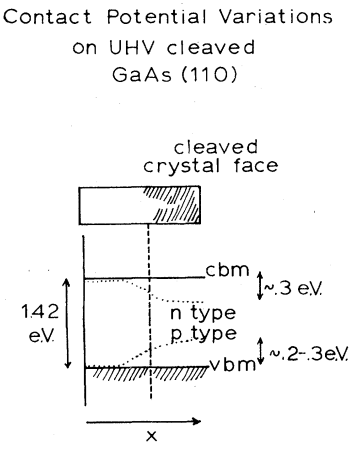

FIG. 1. Experimental band-bending measurements at defective GaAs(110) cleaves. The top rectangle schematically shows a typical cleave of aGaAs ingot, with the shaded region representing the defective area. For defect-free areas the Fermi levels are found at the valence-band maximum and conduction-band minimum for p- and n-type samples, respectively. In the defective areas the Fermi levels move several tenths of a volt deeper into the gap.

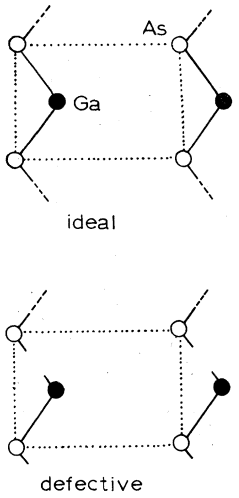

FIG. 2. Top: Geometry in the ideal GaAs (110) surface unit cell. Bottom: By breaking one bond in each unit cell (as shown), the defective surface is modeled.

long-range reconstructed (i.e., 4×2, 2×8, etc.) surfaces which are attributed to Fermi level instabilities in partially filled dangling-bond states.[9]

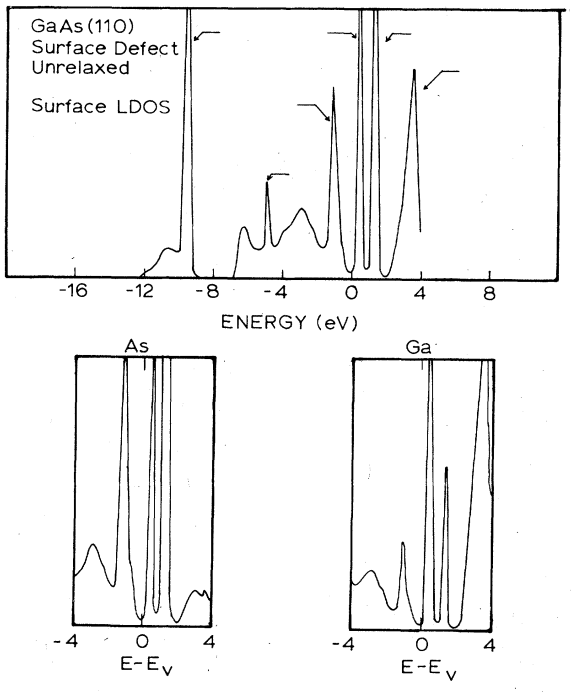

FIG. 3. Surface local density of states obtained for the unrelaxed defective surface shown in the lower panel in Fig. 2. The arrows indicate defect-induced surface states. In the lower two panels the surface density of states near the gap is projected separately onto the surface anion and cation.

Thus we are strongly led to suspect that when steps and cracks appear on cleaved GaAs(110), the crystal is trying to break along two different natural [i.e., (110)] planes, rather than exposing polar surfaces.

If we assume this is true, we then note that the intersection of the two (110) surface planes will result, at the edge, in the breaking of an "in the surface" bond, as well as the usual dangling-bond states. We are then led to investigate the electronic structure of such double-dangling bond defects to understand Fermi-level pinning near such defects.

To do this, we have artificially constructed a GaAs (110) surface posessing double-dangling-bond defects. The construction is shown in Fig. 2. In the top half of this figure we show the ideal-surface unit cell, with the characteristic GaAs zig-zag chains. To model the defective surface atom and one nearest neighbor as shown in the lower half of Fig. 2. The density of states at this artificial surface layer will then yield information about the double-dangling-bond defects.

The results from such a calculation are presented in Fig. 3. These calculations are performed on a semi-infinite solid terminated on a (110) plane using an effective-field method discussed in detail elsewhere.[10] The top panel shows the surface density of states near the defective layer. The lower two panels separately project the surface spectra near the gap separately onto the As and Ga. In the upper panel we call attention to distinct localized features, indicated by arrows, which are characteristic of such defects. We obtain a very localized surface s state on the anion near -10 eV, and a strong state shared between Ga s-like and As p-like surface orbitals near -5 eV. Near the band gap we obtain four distinct surface features, two of which occur within the gap. The lower two panels indicate that the situation is further complicated, as the lower band-gap state is filled but strongly localized on the cation, and the empty upper band-gap state is As derived.

The number, energies, and characterizations of the surface states near the gap may be directly understood from simple chemical arguments about the dehybridization that will occur at such a defect. For simplicity let us concentrate only on an As with two dangling bonds. As we have seen from Ref. 10, the state characteristic of a free As "dangling bond" occurs near the valence-band edge. If two noninteracting As dangling bonds are present, there will be two degenerate states at this energy given by the dashed line in Fig. 4. However, two As dangling bonds on the same atom will interact, splitting into a symmetric combination or an "sp"-like hybrid at lower en-

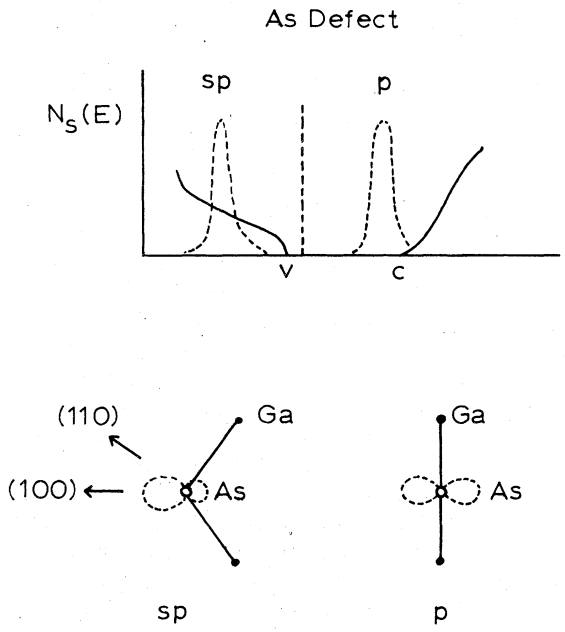

FIG. 4. Rehybridization of As dangling-bond states (dashed line) into sp-like and p-like surface-defect bands (dashed curves). The charge density associated with the lower sp-like band is shown in the lower left-hand diagram. The virtual charge density associated with the upper p-like state is directed out of this plane and is shown in the lower right-hand diagram.

ergy and a pure p state directed transverse to the sp hybrid at higher energies. These states are indicated by the dashed bands in Fig. 4. The charge densities associated with these states are given schematically in the lower half of Fig. 4. The solid lines represent the two intact bonds on a double-dangling-bond As. The lower filled sp-like state is directed in the plane of the intact bonds, and along the mutual double-dangling-bond direction. The p-like defect state is directed out of the plane, and we can see its virtual charge profile by looking down the [100] direction as shown on the right-hand side of Fig. 9.

With this insight we can easily understand the electronic spectrum near the band gap in Fig. 3. Each surface As and Ga possesses two dangling bonds and dehybridizes as detailed in the last paragraph. This gives rise to a filled As-like sp derived state below the valence-band maximum, a filled Ga-derived sp-like state in the lower band gap, and empty As-derived "transverse-p" state in the upper half of the band gap, and an empty Ga-derived transverse-p state above the conduction-band minimum. In all these states the character is somewhat shared because of interactions in the surface plane which we have ignored in these simple chemical arguments.

An intriguing aspect of these defects is that they are characterized by filled Ga-derived dangling-bond states. The presence of such states is uncharacteristic of the defect-free ideal surface. This is an important observation, because the absence of electrons in Ga dangling-bond orbitals reduces in part the chemical reactivity of Ga at a GaAs (110) surface.[11,12] We see that Ga atoms *at steps and edges* contain charge in states which are dangling-bond-like in character, and hence should readily react with adsorbates. Second, we see that the Fermi level for an intrinsic sample with such a surface falls in a gap; there are no partially filled dangling-bond "bands" at such steps as there are on polar surfaces. Third, we should point out that for Ga or As stabilized (100) surfaces in the 1×1 geometry (a theoretical construction),[9] the same sort of dehybridization occurs and has been discussed elsewhere.

Before turning to an interpretation of the contact-potential measurements using this model, it is important to establish the influence of the exact atomic geometry on these defect states. For the defect-free surface we saw that a physically motivated relaxation pushed surface states out of the gap. Here it is hardly likely that a defective surface would retain the unrelaxed configuration. Following the arguments of Ref. 10, we expect the surface As with two intact bonds to reduce the angle between these bonds from the 109° tetrahedral angle closer to the 90° bond angle expected from the elemental chemistry of As. Similarly we would expect the Ga bond angle to increase. As an example of a possible distortion, we consider the case where the surface-defect As (Ga) atoms are displaced outward (inward) along a line bisecting the angle between the intact bonds. Minimizing bond-length distortions, the As defect bond angle decreases to 99° while the Ga bond angle becomes very wide. In this geometry, the defective surface density of states is given in Fig. 5. We see that the two band-gap surface features persist. The surface feature above the conduction-band minimum has split somewhat, and there is an enhancement of states at −3 eV. These latter states are localized in the As "back bonds" and indicate strained back bonds in this geometry. Finally, there is an enhancement of As s-derived features at −9 eV. It is interesting that this model geometry assumes only slight atomic distortion from the buckled relaxation discussed in Ref. 10.

We have used the results of this calculation to construct a theoretical ultraviolet photoemission spectrum[11] from a surface characterized by a large fraction (unity) of these defects. The re-

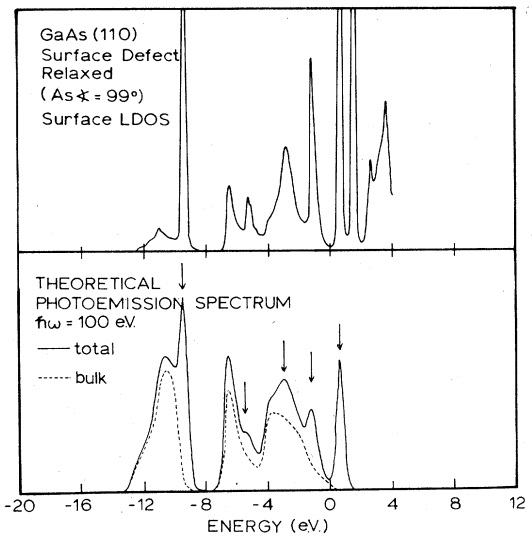

FIG. 5. Surface density of states of the relaxed defective surface discussed in the text is given in the top panel. Correcting for matrix elements and the finite escape lengths of emitted photoelectrons, we obtain the theoretical soft-x-ray photoemission spectrum in the lower panel. Arrows depict defect-induced features in the spectrum.

sults of this calculation are shown in the lower panel of Fig. 5. We have assumed valence wave functions which retain the core behavior of the atomic wave functions; we have assumed a plane-wave final state, and take the finite escape length of the emitted photoelectrons into account in this calculation.[11] The ultraviolet photoemission spectra show features near −9, −5, −3, −1, and 1 eV which are directly attributable to the presence of these surface defects. These features, if experimentally observed, would provide strong evidence for the existence of such double-dangling-bond defects at the surface. It is recognized, however, that such an experiment would be difficult to controllably perform.

Finally, we return to the band-bending measurements of Huijser and VanLaar[2] discussed at the beginning of this paper. The results are easily understandable in light of this model. We obtain theoretically both filled and empty defect-derived bands in the gap. We would then attribute the movement of the Fermi level for n-type samples to the trapping of donor electrons in the traverse-p As-derived defect states. Threshold for these states is several tenths of a volt below the conduction-band minimum. Similarly, Fermi-level pinning on p-type surfaces is due to the trapping of holes in the filled sp-like-hybird Ga-derived defect band. The upper edge of this band lies about 0.6 eV above the valence-band maximum.

Note that we do not require a large density of these defect states on the surface; 10^{12}–10^{13} states cm^2 are sufficient to pin the Fermi level. We should point out that, as noted in Ref. 10, in the ideal geometry the defect-free GaAs (110) surface possesses both filled and empty band-gap surface states. Hence any tendency of the (110) buckled relaxation to be quenched on defective surface would provide band-gap states which would similarly influence the position of the Fermi level. We should remark that such a tendency seems unlikely, as it has been recently shown theoretically that the buckled reconstruction is a direct consequence of only the coordination numbers of As and Ga on the surface,[13] which are only changed at *the defect site*. In addition, the occurrence of steps, edges, and surface vacancies cause double-dangling-bond defects to exist in abundance, and these are sufficient to interpret the available experimental data. Finally it is established that double-dangling-bond defects occur at homopolar semiconductor surfaces, where their presence is not required by the tendency of the solid to break along nonpolar planes.

In summary, we have constructed a simple model for cleavage defects at the GaAs(110) which appears to be consistent with contact-potential measurements at this surface. We find that the dehybridization of orbitals on sites in which the coordination number is reduced to two produces filled and empty "defect states" in the gap. These states are rather insensitive to reasonable relaxations near the defect site and would induce band bending at the nonpolar surfaces of a doped GaAs sample.

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