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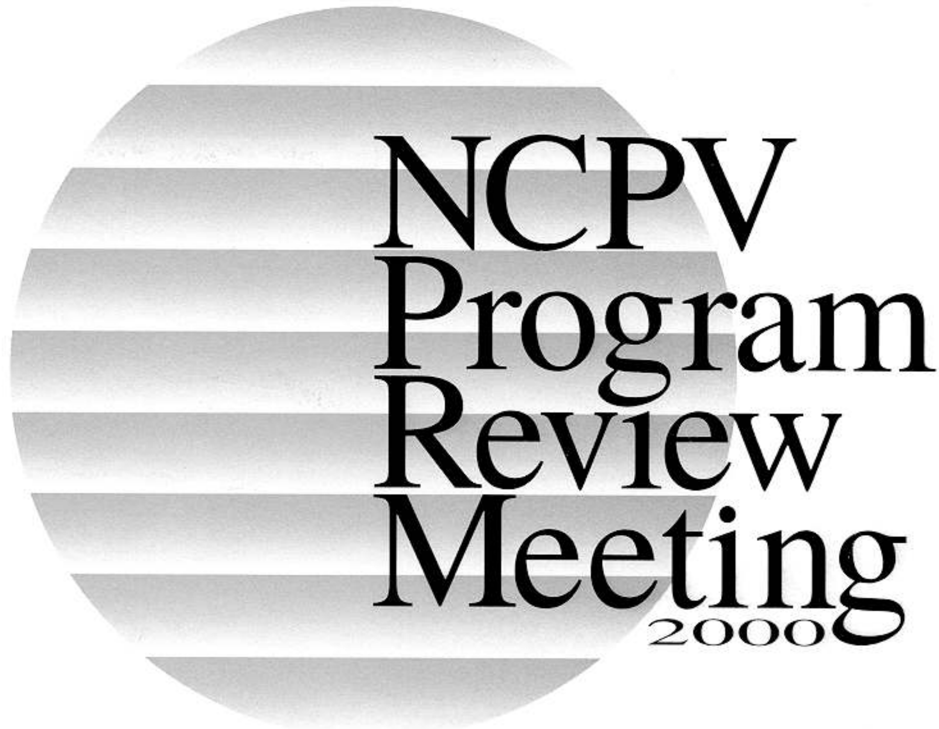

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BAs–GaAs Semiconductor Alloys as a Photovoltaic Alternative to Nitride Alloys

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ABSTRACT

Nitrogen alloyed III–V semiconductor compounds have been intensely studied in recent years due to unusual effects caused by nitrogen alloying. These effects are exploited in band gap engineering for specific applications such as solar cells and blue lasers. However, alloying with *boron* instead of nitrogen may offer similar effects while mitigating the difficulties associated with nitride semiconductors. Using the full-potential linearized augmented planewave implementation of density functional theory within the local density approximation, we have studied* BAs as well as boron alloying in GaAs. We find that BAs is unusual with respect typical III–V semiconductors in that it resembles Si, not III–Vs: it has an indirect gap; has the *p*-like conduction band below the *s*-like state; and the valence density is distributed equally on the 2 atoms in the cell. We find in this first theoretical study of BAs–GaAs alloys that the band gap bowing of $B_xGa_{1-x}As$ is much smaller than in $GaAs_{1-x}N_x$ and the bulk mixing enthalpy for boron in GaAs is significantly lower than for nitrogen. We conclude that boron alloying presents new opportunities in band gap engineering.

1. Introduction

Nitrogen alloying of semiconductors leads to unusual effects such as (i) localization of states near the conduction band minimum (CBM) (ii) giant band gap bowing, and (iii) composition dependent bowing. By exploiting these effects, the properties of an alloy (band gap, etc.) can be tuned for specific applications. However, there are also difficulties associated with nitride alloys such as poor transport, limited solubility, etc.

Boron alloying of GaAs has been proposed. [1–5] Both boron and nitrogen form exceptionally strong bonds in the alloys and cause large size mismatches. In the case of boron, however, the size mismatch is slightly less severe and the bonding somewhat weaker. Also the B–As bonds are very covalent whereas the Ga–N bonds have a strong ionic component. Until now, how these similarities and differences between nitrogen and boron would affect the properties of semiconductor alloys was an open question. Historically, the difficulty in fabricating boron alloys experimentally[2] and the computational burden of modeling dilute alloys have made studies of boron semiconductor alloys difficult. However, the development of advanced experimental techniques for fabricating nitride alloys (which can be applied to boron alloys) and significant advances in computational approaches have now made the study of boron alloys easily accessible. We have examined a typical III–V boron alloyed semiconductor, BAs, and have studied the effects of boron alloying in GaAs. Our results are as follows:

2. Zinc-blende BAs

BAs has an indirect band gap of ~1.6 eV near the X point, and the direct band gap is ~4.2 eV (as calculated by the GW method; reliable measurements do not exist).[6] The band structure of BAs is unusual compared to "conventional" III–V materials in that the Γ_{15c} *p*-like conduction state is *below* the *s*-like Γ_{1c} state. As a result of this reversal of conduction band states and the indirect gap, the band structure of BAs closely resembles that of silicon. The similarity to silicon is due in part to the very covalent nature of the bonding in BAs which results from the very similar electronegativities of boron and arsenic. Consequently the cation and anion states mix very strongly at the valence band maximum (VBM), the anion/cation distinction becomes blurred, and BAs resembles a covalent IV–IV semiconductor like silicon rather than a typical III–V semiconductor.

3. BAs–GaAs band offsets

Figure 1 shows our calculated band offsets for the group III–As family including BAs. Despite the much smaller bond length of BAs, its VBM is significantly higher than that of AlAs and close to that of GaAs. In contrast, in the Ga–group V family, the VBM of GaN lies more than 2.0 eV below that of GaAs and more than 1.5 eV below that of GaP. The height of the VBM in BAs results from the strong mixing of boron and arsenic *p* states at the VBM. This feature which is unusual compared to other III–Vs draws the VBM up towards the *p* orbital energy of boron. Notice the very small predicted band offsets in BAs–GaAs.

4. Band gap bowing in $B_xGa_{1-x}As$

The band gap bowing for $GaAs_{1-x}N_x$ alloys is very large, and even for relatively small concentrations of nitrogen, the bowing is composition-dependent, varying between ~10 to ~20 eV. Surprisingly, our calculations show that, unlike $GaAs_{1-x}N_x$, the bowing of $B_xGa_{1-x}As$ alloys is relatively small

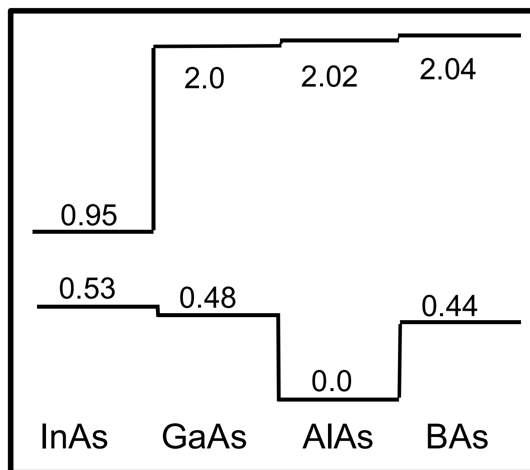

Figure 1. Valence and conduction band offsets for the group III–As family. The VBMs are calculated while the CBMs are determined from the minimum measured band gap (indirect near X for BAs and AlAs; direct for GaAs and InAs).

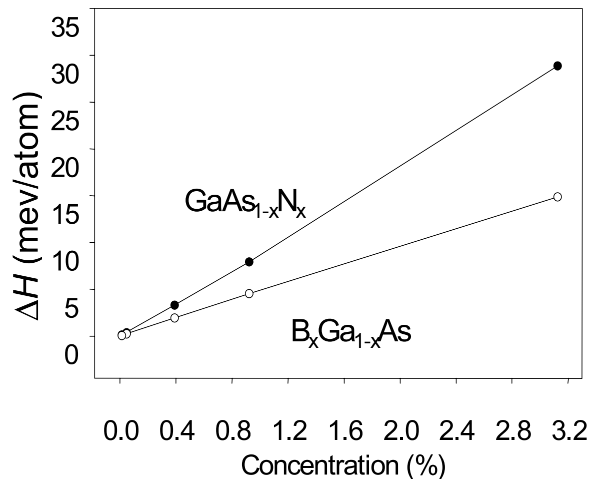

Figure 2. Mixing enthalpy of boron and nitrogen in GaAs as a function of concentration

(~3 eV) and fairly composition independent, in agreement with the experimental results of Ref. 5. This is somewhat unexpected given that both boron and nitrogen cause large size mismatches and both form very strong bonds with their neighbors. Nitrogen alloying very strongly perturbs the electronic structure of GaAs whereas the effects of boron alloying are much more "gentle."

5. Bulk mixing enthalpy of $B_xGa_{1-x}As$

The calculated bulk mixing enthalpy of $GaAs_{1-x}N_x$ versus $B_xGa_{1-x}As$ (Fig. 2) is also unexpected. The mixing enthalpies are much higher (~60%) for the $GaAs_{1-x}N_x$ alloy. If the differences in the bulk mixing enthalpies are indicative of the differences in the solubilities for boron and nitrogen alloying of GaAs, we can conclude that the boron containing alloy can be grown with a larger composition range than the nitride alloy.

6. Wavefunction localization in $B_xGa_{1-x}As$

An unusual feature of the nitride alloys is the localization of wavefunctions Ψ for states in or below the conduction band. In a 3% BAs–GaAs alloy (see Figure 3 below), Ψ^2 for the valence band maximum is completely delocalized and has a strong As *p*-like character. On the other hand, the CBM is "semi-localized", i.e. it is strongly localized near the boron atom but extended at longer distances. Similarly, the state just above the CBM is also localized around the boron atom and some of the gallium atoms.

7. Conclusions

Despite the fact that boron and nitrogen are both small, first row atoms that have a tendency to form strong bonds in compounds, their effects on III–V alloys show very pronounced differences. (i) The band gap bowing is large and composition-dependent for $GaAs_{1-x}N_x$ but relatively small and composition-independent for $B_xGa_{1-x}As$, and (ii) the bulk mixing enthalpy of boron in GaAs is much smaller than for nitrogen. Despite these differences, both alloys share the feature of wavefunction localization. Two implications of this study are immediately obvious. (i) Boron alloys may allow larger composition ranges than the nitrides, and (ii) the boron alloys offer new opportunities in band gap engineering.

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[*] Details of the calculations are given in our paper " BAs and Boron III–V Alloys," G. L. W. Hart and A. Zunger, to be published (2000).

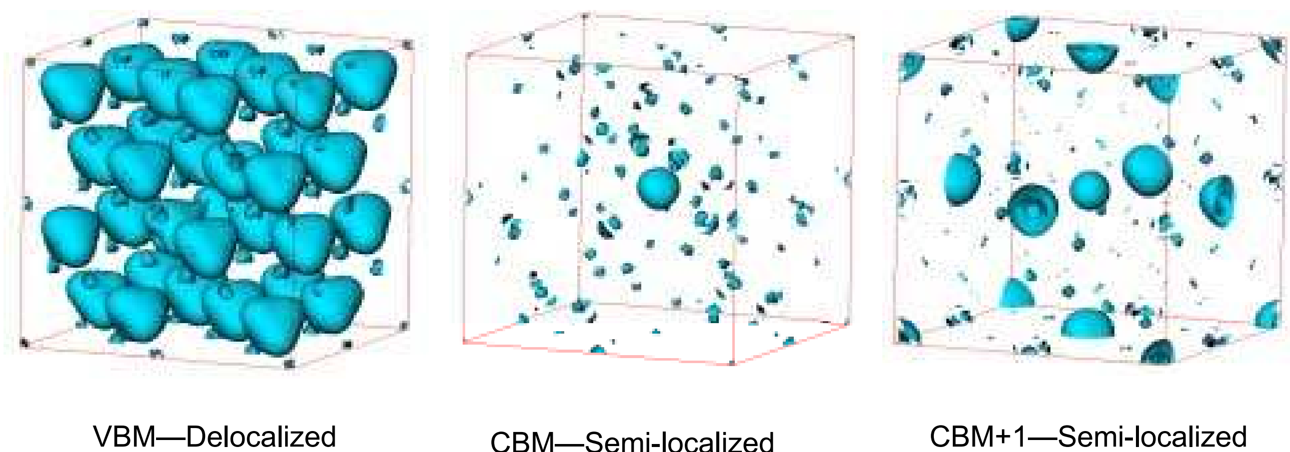

Figure 3. Isosurface plots of the square of the wavefunction for the VBM, CBM, and the first state above the CBM. The VBM is completely delocalized with As *p*-like character. In contrast, the first state states in the conduction bands shows effects of localization.