Band-gap Bowing Effects in $B_xGa_{1-x}As$ Alloys

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Photo-modulation spectroscopy studies of the transitions at the Γ point of the Brillouin zone of thin films of $B_xGa_{1-x}As$ alloys grown by metalorganic chemical vapor deposition are presented. A very small increase of the fundamental band gap is found in samples with B content up to 3%. Under hydrostatic pressure, the band gap increases at a rate almost identical to the pressure dependence of the GaAs band gap. In contrast to the case of N incorporation at similar concentrations into GaAs, the experimental results show that B incorporation does not cause large modifications of the conduction band structure in $B_xGa_{1-x}As$ alloys.

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Highly mismatched semiconductor alloys (HMAs) in which one of the constituent elements is replaced by an element with highly dissimilar properties are attracting much attention. These new alloys exhibit a range of unexpected fundamental physical properties with the promise of novel device applications.[1] It has been found that the substitution of the group V element in group III-V compounds with small amounts of nitrogen leads to dramatic changes of the electronic properties. The most significant of which are a large reduction of the fundamental band gap and a change in the effective electron mass.[2-6] For example, a 0.18 eV reduction of the band gap has been observed in GaN_xAs_{1-x} at x=0.01.[6] Furthermore, a new extra optical transition E_+ from the valence band to the conduction band at the Γ point has been found.[7,8] Similarly striking effects have been observed in other group III-N-V alloys[9,10] as well as in group II-VI alloys in which Te anions are partially replaced with more electronegative Se, S, or O atoms.[11,12]

Two distinctly different theoretical explanations have been proposed to explain the properties of HMAs. In the band structure calculations based on the Local Density Approximation (LDA) the unusual properties of GaNAs alloys are attributed to interaction between Γ, L, and X conduction-band minima resulting from a breaking of the crystal symmetry by the substitution N for As atoms. On the other hand the band anticrossing (BAC) explains the properties of all highly mismatched alloys in terms of an interaction between localized states introduced by highly electronegative atoms and the extended states of the conduction band. So far, all highly mismatched alloys have been formed by alloying on the anion sites. Drawing on the similarity between boron and nitrogen as small, electronegative atoms it has been speculated that substituting metallic Ga in GaAs with more electronegative B to form $B_xGa_{1-x}As$ would produce effects similar to incorporating nitrogen into GaAs. However, a recent experimental study of $B_xGa_{1-x}As$ with *x* up to about 2-4% found that alloying boron with GaAs does not

induce any significant change in the fundamental band gap.[13] A subsequent theoretical LDA study supported this finding of a small and normal band gap bowing in $B_xGa_{1-x}As$ alloys.[14]

Recently, a theoretical study based on quantum molecular dynamics calculations using standard pseudopotentials was performed to explore the electronic structure of GaAs:B alloys.[15] While this study suggested that the relatively small effect of boron on the band structure as opposed to nitrogen is caused by the difference in the substitution sites, it predicted that the pressure dependence of the band gap for GaAs:B should be considerably weaker than in GaAs and nonlinear. In addition, a new optical transition at about 0.5 eV above the band gap, similar to the E_+ transition observed in GaN_xAs_{1-x} alloys, is predicted.

In order to test these theoretical predictions we have studied the optical transitions from the valence band to the conduction band at the Γ point in a few $B_xGa_{1-x}As$ alloy samples to determine the change of fundamental band gap as a function of boron mole fraction. The effect of hydrostatic pressure on the optical transitions in these $B_xGa_{1-x}As$ samples has also been examined. We show in this letter that alloying a small amount of BAs with GaAs produces only small modifications of the band structures and that $B_xGa_{1-x}As$ behaves just like conventional III-V alloys.

The $B_xGa_{1-x}As$ samples used in this study were grown by metalorganic chemical vapor deposition (MOCVD). Before the growth of BGaAs, a 0.1-μm thick $Ga_{0.5}In_{0.5}P$ etch-stop layer was deposited on a Si-doped GaAs substrate. The BGaAs layer thicknesses are around 1.1 μm. The boron composition was estimated from the peak splitting of double-crystal X-ray diffraction rocking curves measured in the (004) reflection. Secondary Ion Mass Spectroscopy (SIMS) using 8.0 keV O_2^+ primary ions with detection of positive secondary ions was also used to determine

the boron content. Detailed discussions of the sample preparation, X-ray measurements, and the related experimental uncertainties have been reported in Ref. 13.

Photomodulation spectroscopic measurements were carried out to measure the band gap energy of the $B_xGa_{1-x}As$ samples at room temperature (295 K). Quasimonochromatic light from a halogen tungsten lamp dispersed by a 0.5 m monochromator was focused on the samples as a probe beam. A chopped HeCd laser beam (4420 Å) provided the photomodulation. The photo-modulated reflection or transmission signals were detected by Si photodiode using a phase-sensitive lock-in amplification system. Application of pressure was accomplished by mounting small sample chips with sizes of ~200×200 μm^2 into gasketed diamond anvil cells. The applied pressures were determined by the standard method of monitoring the shift of ruby R1 line.

Figure 1 shows PR spectra recorded with a few $B_xGa_{1-x}As$ samples with different boron compositions ranging from under 1% to 3.0-5.6%. The derivative-like spectral lineshapes arise from the differential changes in the reflection due to photomodulation. The PR spectral features correspond to the optical transitions associated with the energy gap of the samples. The transition energies listed in the figure were determined by fitting PR spectral features to the lineshape functional form of three-dimension interband transitions.[16,17] In agreement with previous experimental studies, the band gap of $B_xGa_{1-x}As$ as measured by PR is found to only slightly increase with the B concentration; the largest increase observed is only 14 meV. So far there is very limited information related to the electronic band structure of BAs. While early experimental results reported a 1.46-eV direct gap,[18] the most recent theoretical calculations predict an indirect band-gap (~1.9 eV) material with 5.5-eV direct gap at the Γ point.[14] Even, when the uncertainties in the B content and in the BAs gap are considered, the results are

consistent with the range of bowing parameters estimated previously (1.6 – 2.3 eV)[13]; these values are an order of magnitude smaller than those derived for the GaAsN system.

The inset of Fig. 1 shows the PR spectrum of the sample with 3-5.6% boron content taken over a wide energy range from 1.30 to 2.35 eV. The spectrum exhibits only two expected spectral features related to transitions from the top of valence band to the bottom of the conduction band (E_0 transition) and to transitions between the spin-orbit split-off band and the conduction-band minimum ($E_0+\Delta_0$ transition) for their 0.34-eV energy separation. The theoretically predicted[15] disorder-activated Γ_V-L_C transition (~E_0+0.5 eV) similar to the E_+ transition found in GaNAs alloys was not observed.

To further demonstrate that alloying a small amount of BAs with GaAs does not induce a significant modification of the conduction band structure, we have measured band-gap transition energies as a function of applied hydrostatic pressure for three different samples: GaAs, $B_xGa_{1-x}As$ ($x=1.2\sim2.3\%$), and $B_xGa_{1-x-y}In_yAs$ ($x=1.2\sim2.3\%$, $y=4\%$). It is well known that alloying a few percent InAs with GaAs reduces the band-gap energy but does not affect its pressure dependence.[19] Figure 2 displays photomodulated transmission (PT) spectra of the $B_xGa_{1-x-y}In_yAs$ sample at several selected pressures. The optical transition from the top of the valence band to the bottom of the conduction band (Γ_V-Γ_C) shifts toward higher energy as the direct band gap of the alloy sample increases. At pressures above 50 kbar, the PT spectral feature broadens and the signal intensity decreases drastically as a result of the pressure induced Γ-X crossover. The PT spectral feature associated with the Γ-transition eventually disappears at the pressures around 65-70 kbar as the indirect absorption of the Γ_V-X_C and Γ_V-L_C of the GaAs substrate becomes correspondingly stronger.

The pressure-induced energy shifts of the optical transition related to the direct band gap are plotted in Fig. 3 for all the samples. Data obtained previously for the fundamental band gap (E_-) of $GaN_{0.03}As_{0.97}$ is also plotted for comparison. The solid lines in Fig. 3 for the boron containing samples are least-square fits to the experimental data using a quadratic pressure-dependent fit function:

$$E(P)=E(0)+aP+bP^2, \quad (1)$$

where the energy E is in eV and the pressure P is in kbar. The pressure coefficients derived from the best fit to the experimental data are listed in Table I. It is clear that for the boron-containing alloy samples the pressure dependence of the band gap is nearly identical to that of GaAs and does not exhibit any significant nonlinear effect. This type of pressure dependence is commonly observed for conventional group III-V semiconductors. These experimental results do no support recent calculations based on the local density approximation (LDA)[15] that predict a much weaker pressure dependence similar to that observed in GaN_xAs_{1-x} alloys.

The pronounced difference in the pressure dependence of the energy gap of $GaN_{0.03}As_{0.97}$ has been understood in terms of an anticrossing interaction between localized N states and the extended Γ states of the conduction band of the host semiconductor matrix.[6,20,21] The interaction splits the conduction into two subbands (E_- and E_+). The downward shift of the lower E_- subband relative to the top of the valence band is responsible for the reduction of the fundamental band gap and the transition from the valence band to the E_+ upper subband account for the high-energy edge. Application of high pressure gradually changes the character of the E_- subband edge from extended-like to localized-like that results in a much weaker but highly nonlinear pressure dependent behavior in GaNAs. The absence of any significant band anticrossing effects in $B_xGa_{1-x}As$ alloys indicates that the localized B level is located very high

above the conduction band edge. This is consistent with the much smaller electronegativity of B compared with N atoms. Also it demonstrates that because of much smaller electronegativities of column-II and III elements, band anticrossing effects are not expected to play a significant role at cation sites in group II-VI or III-V alloys.

In conclusion, we have studied the effect of boron on the electronic band structure of $B_xGa_{1-x}As$ alloys by investigating the optical transitions associated with the Γ point at the conduction- and the valence-band edges, as well as the effect of hydrostatic pressure on the transitions. We have found that alloying BAs in a few atomic percent with GaAs forms a conventional III-V alloy. It does not have the anomalous characteristics such as large band-gap reduction within a small alloy composition as that are observed in highly mismatched III-N-V alloys. The pressure dependence of its band gap closely follows that of GaAs. Our experimental results do not confirm a theoretically predicted weak pressure dependence of the band gap or the existence of an additional strong transition at about 0.5 eV above the fundamental band-gap transition.

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Table I. Pressure coefficients for the fundamental band gap of $B_xGa_{1-x}As$ epilayer samples

	$E(0)$ (eV)	$a = dE/dP$ (meV/kbar)	$b = d^2E/dP^2$ (meV/kbar^2)
GaAs	1.421	11.5	0.029
$B_{0.012}Ga_{0.988}As$	1.420	11.0	0.023
$B_{0.02}Ga_{0.94}In_{0.04}As$	1.350	11.1	0.027

Figure Captions :

Figure 1. PR spectra taken with several $B_xGa_{1-x}As$ samples at 295 K. The inset is a PR spectrum taken over a wide energy range from 1.3 to 2.35 eV for the sample with a boron concentration of 3~5.6%.

Figure 2. Optical transition associated with the band gap of a $B_xGa_{1-x-y}In_yAs$ sample measured by photomodulated transmission at selected pressures. The arrows mark the spectral features related to the transitions from the top of the valence band to the Γ- and X-conduction bands.

Figure 3. The energy of optical transitions associated with the direct band gaps of $B_xGa_{1-x}As$ and BGaInAs samples as a function of pressure. The results from a $GaN_{0.03}As_{0.97}$ sample are also plotted for comparison.

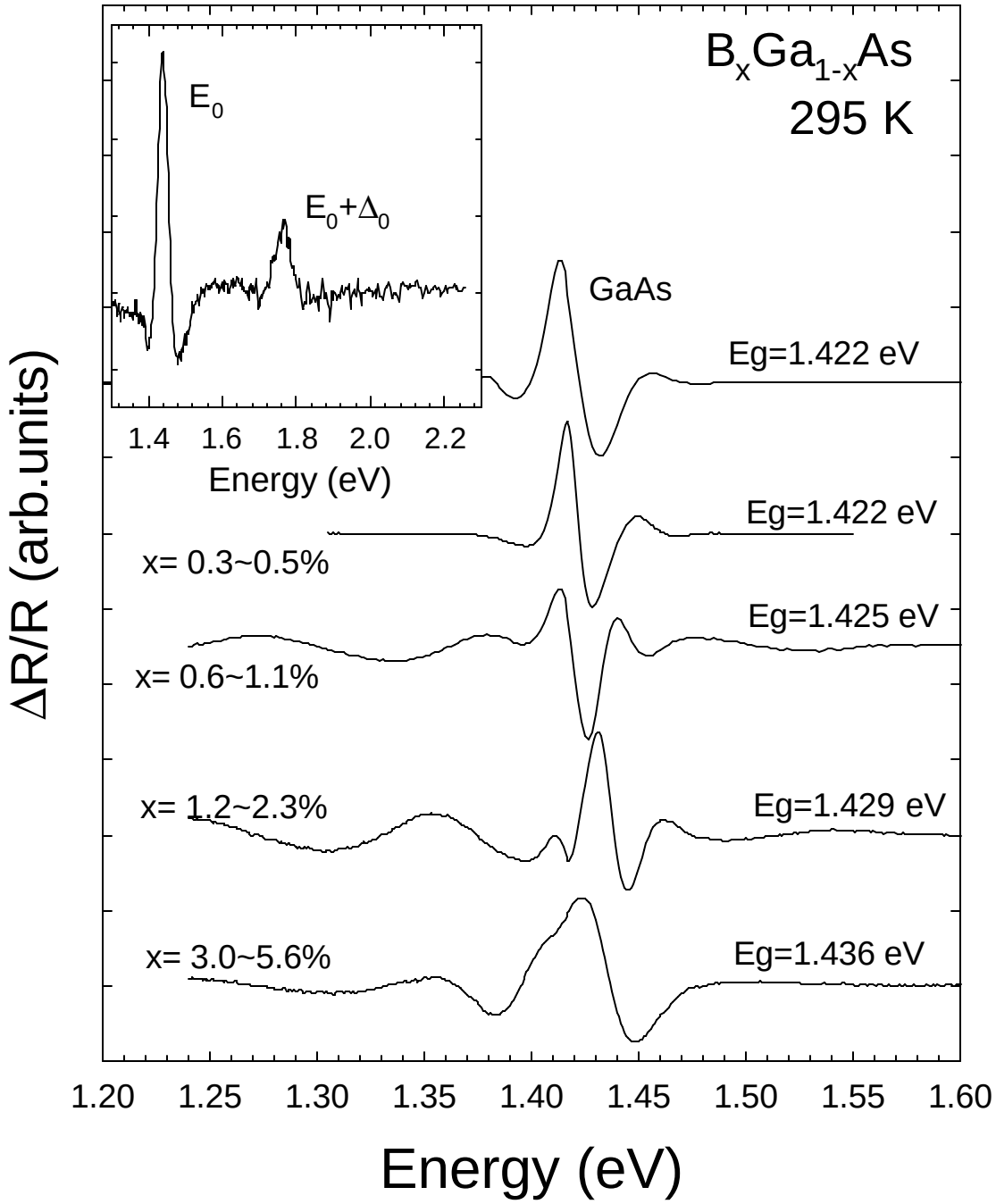
B$_x$Ga$_{1-x}$As
295 K
E$_0$
E$_0$+Δ$_0$
1.4 1.6 1.8 2.0 2.2
Energy (eV)
GaAs
Eg=1.422 eV
Eg=1.422 eV
x= 0.3~0.5%
Eg=1.425 eV
x= 0.6~1.1%
x= 1.2~2.3%
Eg=1.429 eV
x= 3.0~5.6%
Eg=1.436 eV
ΔR/R (arb.units)
1.20 1.25 1.30 1.35 1.40 1.45 1.50 1.55 1.60
Energy (eV)

Figure 1.

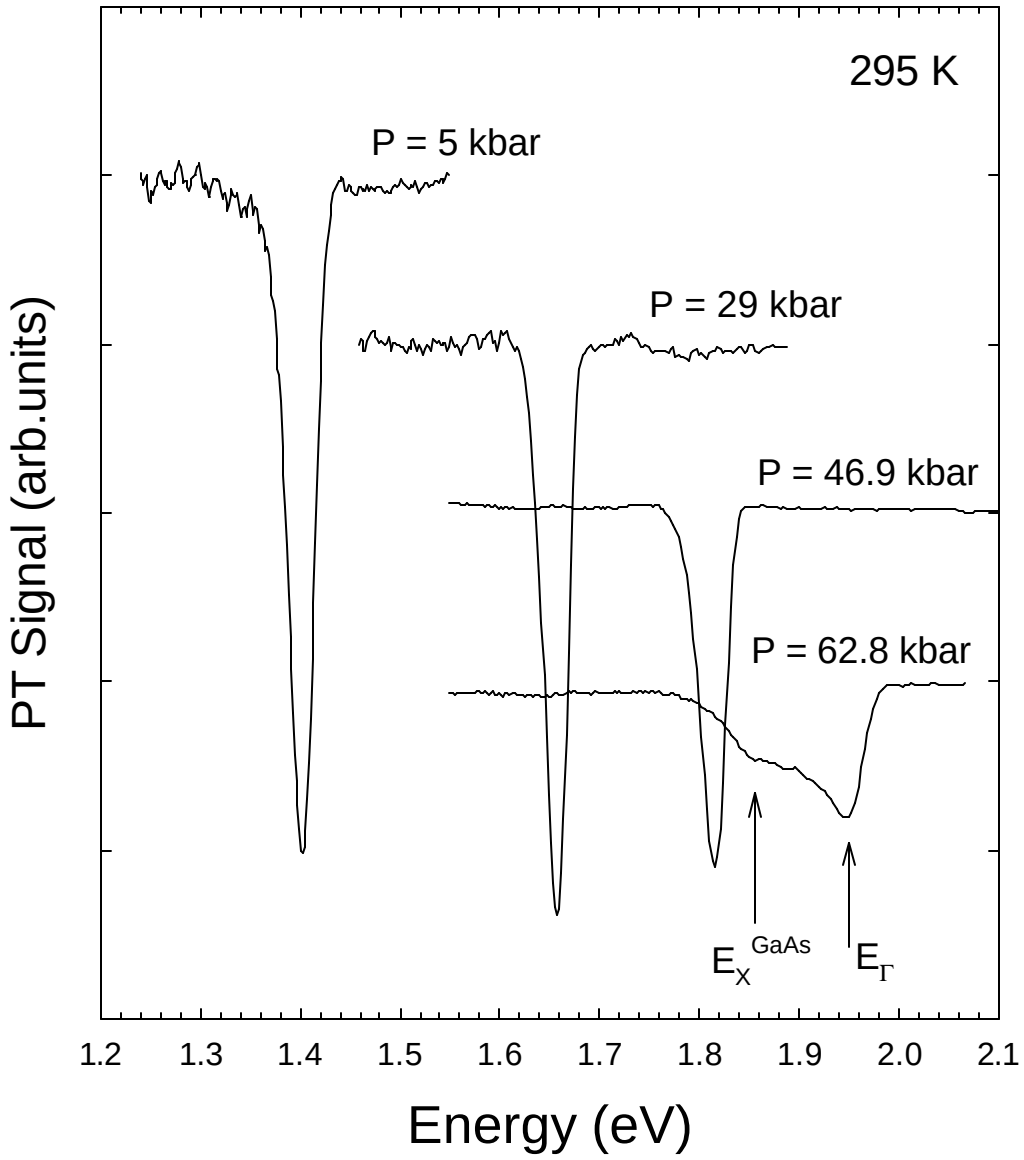
295 K
P = 5 kbar
P = 29 kbar
P = 46.9 kbar
P = 62.8 kbar
E_X^{GaAs}
E_Γ
PT Signal (arb.units)
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
Energy (eV)

Figure 2

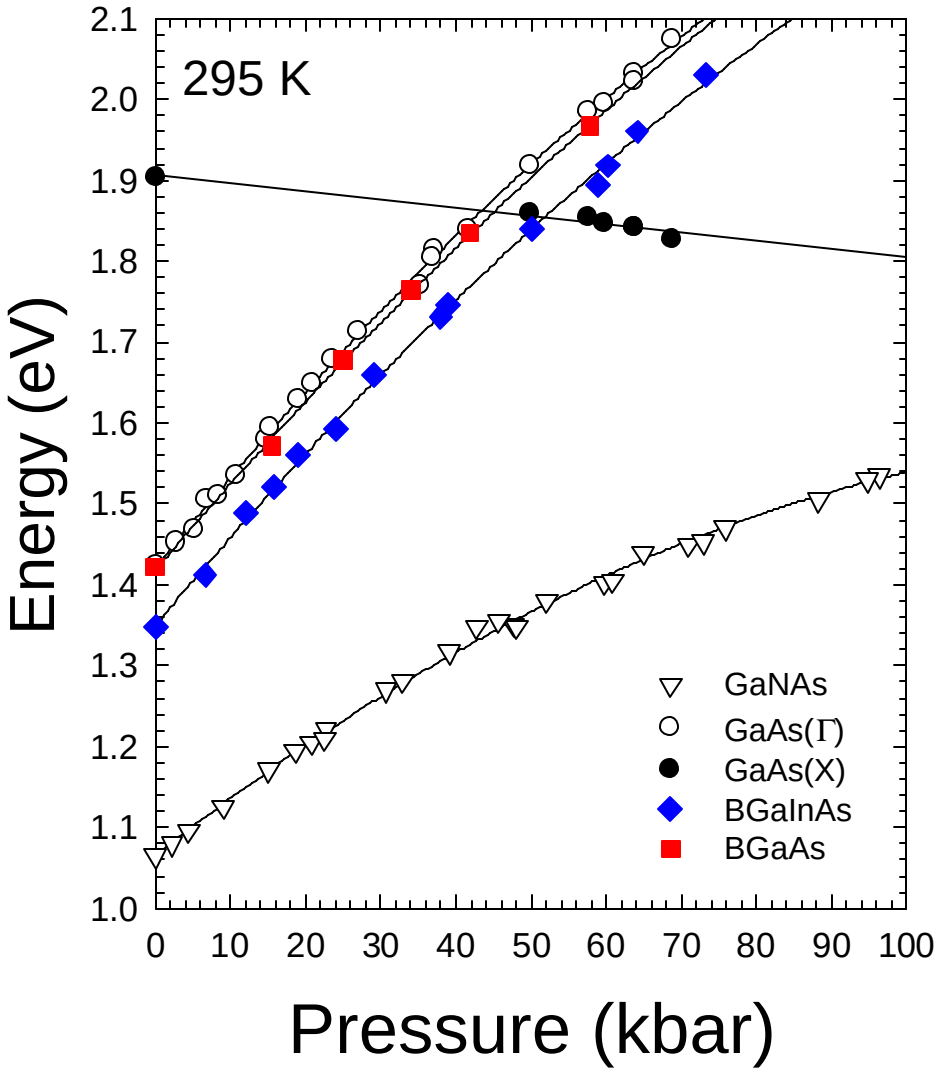
295 K
Energy (eV)
Pressure (kbar)
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0
10
20
30
40
50
60
70
80
90
100
GaNAs
GaAs(Γ)
GaAs(X)
BGaInAs
BGaAs

Figure 3