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FIR-VUV Ellipsometry on $B_xGa_{1-x}As$ and GaN_yAs_{1-y}

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Motivation

- GaN_yAs_{1-y} and $B_xGa_{1-x}As$ differ fundamentally in their bonding properties, i. e., B-As is almost purily covalent whereas Ga-N-bond has large ionic contribution
- → Influence of ionicities on bandstructure and phonon properties
- $In_xGa_{1-x}N_yAs_{1-y}$ and $B_xGa_{1-x-z}In_zAs$ as new materials for 1.3-1.55 µm laser diodes and solar cells
- Effect of hydrogen on bandstructure of $In_xGa_{1-x}N_yAs_{1-y}$?

Conclusion

$B_xGa_{1-x}As$

- a_0^{BAs} = 4.777 Å → Δa/a ≈ 16%
- Ionicity of the B-As bond: f_i^{BAs} = 0.002
- → BAs-like phonon could not be detected using IR ellipsometry or IR transmission due to low ionicity of B-As-bond
- BAs-phonon is Raman-active
- Perturbation potential of B in GaAs mainly due to strain
- → Weaker than perturbation potential of N in GaAs
- → Small bowing parameters of all detected critical-point transitions (E_0, E_1, $E_1+\Delta_1$, E_0', E_2 and E_1')
- → $B_xGa_{1-x}As$ behaves like a „normal alloy"!

GaN_yAs_{1-y}

- $a_0^{\beta\text{-}GaN}$ = 4.52 Å → Δa/a ≈ 20%
- Ionicity of the Ga-N bond: f_i^{GaN} = 0.500
- → GaN-like phonon is infrared-active (high ionicity of Ga-N-bond)
- Strong, shortranging perturbation potential of N in GaAs due to strain and the large ionicity of the Ga-N bond
- → Drastic redshift of E_g with increasing *y*
- Redshift can be neutralized by Hydrogen implantation
- Moderate shift of E_1, $E_1+\Delta_1$, E_0', E_2 and E_1' with *y* → perturbation of the band-structure concentrated on the Γ- point of the Brillouin zone
- → GaN_yAs_{1-y} does not behave like a „normal alloy"!

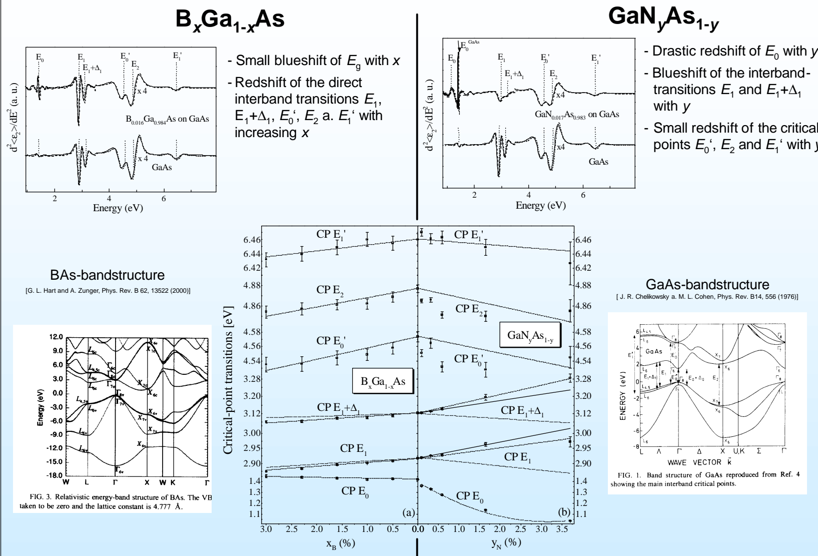
Bandstructure of $B_xGa_{1-x}As$ and GaN_yAs_{1-y}

$B_xGa_{1-x}As$

- Small blueshift of E_g with *x*
- Redshift of the direct interband transitions E_1, $E_1+\Delta_1$, E_0', E_2 a. E_1' with increasing *x*

GaN_yAs_{1-y}

- Drastic redshift of E_0 with *y*
- Blueshift of the interband-transitions E_1 and $E_1+\Delta_1$ with *y*
- Small redshift of the critical points E_0', E_2 and E_1' with *y*

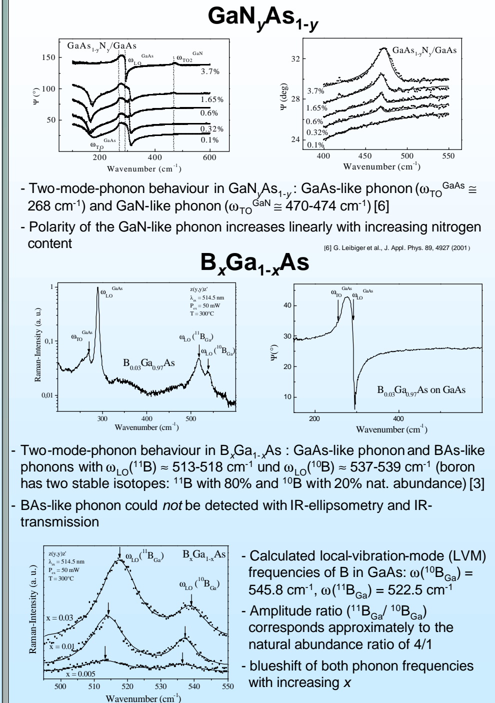


- Small blueshift of E_0 and redshift of E_0', E_2, a. E_1' with *x* can be described by small bowing coefficients of *b* ~ 0.7, 1.6, 1.4, and 0.9 eV, respectively [3]
- → Influence of B on the $B_xGa_{1-x}As$ bandstructure is rather small

- Dramatic redshift of E_0 with *y* [4]
- Blueshift of E_1 and $E_1+\Delta_1$ can be explained by the effects of biaxial strain and alloying [5]
- For the critical points (CP's) E_1, $E_1+\Delta_1$, E_0', E_2 and E_1', we obtain small Bowing parameters [3]
- → N-induced perturbation of the bandstructure is concentrated on the Γ-point of the Brillouin zone

[3] G. Leibiger *et al.*, Phys. Rev B **67**, 195205 (2003); [4] T. Mattila *et al.*, Phys. Rev. B **60**, R11245 (1999); [5] G. Leibiger *et al.*, Appl. Phys. Lett. **77**, 1650 (2000)

GaN- and BAs-like Phonons



GaN_yAs_{1-y}

- Two-mode-phonon behaviour in GaN_yAs_{1-y}: GaAs-like phonon (ω_{TO}^{GaAs} ≅ 268 cm^{-1}) and GaN-like phonon (ω_{TO}^{GaN} ≅ 470-474 cm^{-1}) [6]
- Polarity of the GaN-like phonon increases linearly with increasing nitrogen content

[6] G. Leibiger et al., J. Appl. Phys. 89, 4927 (2001)

$B_xGa_{1-x}As$

- Two-mode-phonon behaviour in $B_xGa_{1-x}As$: GaAs-like phonon and BAs-like phonons with $\omega_{LO}(^{11}B)$ ≈ 513-518 cm^{-1} und $\omega_{LO}(^{10}B)$ ≈ 537-539 cm^{-1} (boron has two stable isotopes: ^{11}B with 80% and ^{10}B with 20% nat. abundance) [3]
- BAs-like phonon could *not* be detected with IR-ellipsometry and IR-transmission

- Calculated local-vibration-mode (LVM) frequencies of B in GaAs: $\omega(^{10}B_{Ga})$ = 545.8 cm^{-1}, $\omega(^{11}B_{Ga})$ = 522.5 cm^{-1}
- Amplitude ratio ($^{11}B_{Ga}$/ $^{10}B_{Ga}$) corresponds approximately to the natural abundance ratio of 4/1
- blueshift of both phonon frequencies with increasing *x*

Ionicities of the bonds

	B (2s)²(2p)¹ 2.01, 0.853 Å	C	N (2s)²(2p)³ 3.07, 0.719 Å
	Al	Si	P
	Ga (4s)²(4p)¹ 1.82, 1.225 Å	Ge	As (4s)²(4p)³ 2.20, 1.225 Å
	In	Sn	Sb

Electro-negativity; Electronegativity; Tetrahedric radius

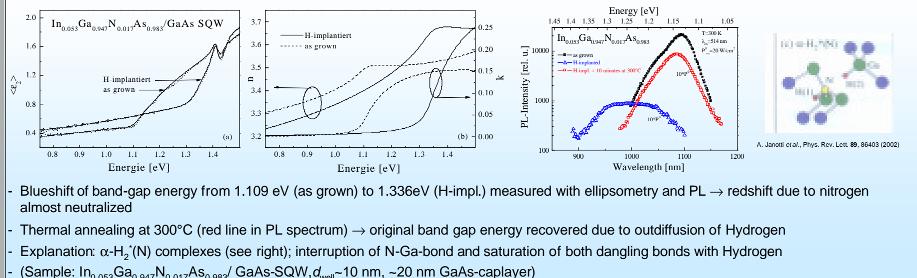
- Phillips/Van Vechten model: $E_g^2 = E_h^2 + C^2$ (E_g band gap, *C* ionic and E_h homopolar contribution to E_g) [7,8]
- → Ionicity of a bond: $f_i \equiv C^2/E_g^2$ [7,8]

B-As	Ga-As	Ga-N
f_i = 0.002	f_i = 0.310	f_i = 0.500

® **B-As bond is almost purely covalent, whereas the Ga-N bond has a large ionic contribution**

[7] J. A. Van Vechten, Phys. Rev. 187, 1007 (1969).
[8] J. C. Phillips, *Bonds and Bands in Semiconductors*, Academic Press, New York 1973.

Hydrogen Implantation in $In_xGa_{1-x}N_yAs_{1-y}$



- Blueshift of band-gap energy from 1.109 eV (as grown) to 1.336eV (H-impl.) measured with ellipsometry and PL → redshift due to nitrogen almost neutralized
- Thermal annealing at 300°C (red line in PL spectrum) → original band gap energy recovered due to outdiffusion of Hydrogen
- Explanation: α-H_2^*(N) complexes (see right); interruption of N-Ga-bond and saturation of both dangling bonds with Hydrogen
- (Sample: $In_{0.053}Ga_{0.947}N_{0.017}As_{0.983}$/ GaAs-SQW, d_{well}~10 nm, ~20 nm GaAs-caplayer)

Samples

MOVPE (metalorganic vapor-phase epitaxy)

- GaN_yAs_{1-y}: *y* = 0...3.7%, T_G = 525 °C, Precursor: TBAs, DMHy, TMGa
- $B_xGa_{1-x}As$: *x* = 0...3%, T_G = 550-600 °C, Precursor: AsH_3, TEB, TMGa

$B_xGa_{1-x}As/GaN_yAs_{1-y}$, d ~ 300 - 500 nm
GaAs buffer, d ~ 200 nm
(001) GaAs substrate

Experiment

- **Ellipsometry:** far- and mid-ir range (100 cm^{-1} ≤ ω ≤ 600 cm^{-1}) and near-ir-VUV range (0.75 eV ≤ *E* ≤ 8 eV), *T* = 300 K
- **Raman:** Dilor XY 800 in macroconfiguration; λ_{ex} = 514.5 nm, P_{ex} = 50 mW, backscattering-configuration z(y,y)z', *T* = 300 K
- **Photoluminescence (PL):** λ_{ex} = 514.5, *T* = 300 K
- **H-Implantation:** Kaufman-source, E_{ion}~300eV, T_{sample}~ 300°C, dosis ~4.4·10^{17} Ions/cm^2

Model Dielectric Function

- **Polar phonons:** $\epsilon^{(PP)}(w) = \epsilon_\infty \prod_{i=1}^{l} \frac{w_{LOi}^2 - w^2 - iwg_{LOi}}{w_{TOi}^2 - w^2 - iwg_{TOi}}$ here: no anharmonic interaction: $\gamma_{LO} = \gamma_{TO}$
  F. Gervais and B. Piriou, J. Phys. C **7**, 2374 (1974); D. W. Berreman and F. C. Unterwald, Phys. Rev. **174**, 791 (1968)
- **Free carriers:** $\epsilon^{(FC)}(\omega) = -\epsilon_\infty \frac{\omega_p^2}{\omega(\omega + i\gamma_p)}$ with $\omega_p = \sqrt{\frac{Ne^2}{\epsilon_\infty \epsilon_0 m^*}}$
  P. Drude, Wied. Ann. **39**, 481 (1890)
- **Valence electrons**[1,2]: Interband transitions E_0, E_1, $E_1+\Delta_1$, E_0', E_2, E_1'

E_0, $E_0+\Delta_0$: $\epsilon^{E0,\Delta0}(E) = A_j E_j^{-1.5}\left(c_j^{-2}\left[2-(1+c_j)^{0.5}-(1-c_j)^{0.5}\right]\right)$ with $c_j = (E + i\Gamma_j)/E_j$

E_1, $E_1+\Delta_1$: $\epsilon^{E1,\Delta1}(E) = -A_i c_i^{-2} \ln(1-c_i^2)$ plus: excitonic contributions to E_1 and $E_1+\Delta_1$ due to Lorentzian lineshapes

E_0', E_2, E_1': Damped harmonic oscillators

[1] S. Adachi, *Physical Properties of III-V Semiconductor Compounds* (Wiley, New York 1992); [2] C. W. Higginbotham *et al.*, Phys. Rev. **184**, 821 (1969)

Acknowledgement

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