Optical Properties of $GaP_{1-y}N_y$

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Motivation

→ $GaP_{1-y}N_y$ as new material for light emitters/detectors in the visible spectral range

→ crossover from indirect to direct material theoretically predicted

→ strong decrease of the band-gap energy with increasing nitrogen concentration experimentally observed

Results

→ growth of $GaP_{1-y}N_y$ ($y < 0.03$) single layers and GaPN/GaP superlattice structures on GaP substrates with orientations (001), and (001) with 5° off towards [110]

→ increased N-incorporation on miscut substrates

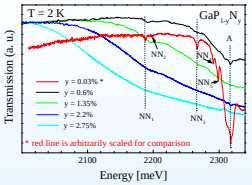
→ photoluminescence (PL): **redshift of PL-peak** with increasing y;disappearance of phonon-replicas for $y > 0.0135$ as possible hint for indirect to direct crossover

→ transmission (2K): redshift of N-induced absorption tail with y; absorption peaks due to excitons bound to NN-pairs

→ ellipsometry (MIR): detection of a GaP ($\omega_{TO1} \approx 366$ cm^{-1})- and a GaN ($\omega_{TO2} \approx 495$ cm^{-1})- like phonon; linear increase of the amplitude of the GaN-like phonon opens possibility to measure y independently

→ ellipsometry (NIR-VUV): detection of 6 critical point transitions at the Γ-point (E_0^{direct}, E_0'), and along the [111] (E_1, E_1') and [100] (E_2^1, E_2^2) directions (L- and X-bands, respectively): **blueshift of E_0^{direct}** and E_1 with y, and small y-dependence of all other detected CP's indicate that the direct Γ-, L- and X-transitions do not show the N-induced redshift of the absorption tail

Transmission (T = 2 K)



→ impurity limit ($y = 0.03\%$): sharp absorption peaks due to excitons bound to NN_i (i < 6, i...index of discrete N-N distances in GaP lattice) pairs

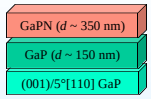
→ $y > 0.03\%$: NN_i-peaks become smaller and more broadened with increasing nitrogen concentration y

→ redshift of the absorption tail with increasing y

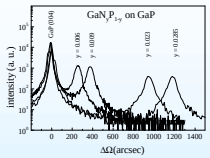
→ possible explanation:
- interaction between NN_i-pair states and formation of N-cluster with more than two N-atoms lead to increasing broadening and decreasing amplitude of NN_i-peaks, respectively
- redshift of absorption tail might be explained by a superposition of N-cluster states

Samples/Growth

→ GaPN single layers



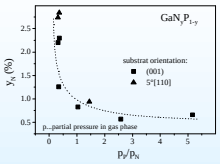
High-resolution x-ray diffraction



→ FWHM-values indicate good structural quality

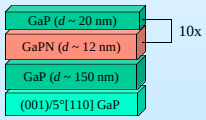
→ FWHM-values do not depend on substrate orientation

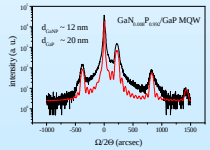
MOVPE



→ Precursors: phosphine; 1,1-DMHy; TMGa
→ p_{tot} = 50 mbar
→ f_{tot} = 7 l/min
→ T_G = 650°C
→ V/III = 50...300

→ GaPN/GaP MQW's



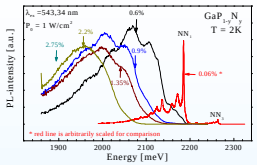


→ presence and shape of satellite peaks indicate relatively abrupt interfaces

→ increased N-incorporation on 5° towards [110] miscut compared to (001) GaP substrates migth be explained by an increased P-desorption rate on (111)A steps

→ increased gas-phase composition p_P/p_N compared to the growth of GaAsN (p_{As}/p_N) due to the higher P-partial pressure

Photoluminescence



→ impurity limit ($y = 0.06\%$): luminescence due to excitons bound to NN_1 pairs with corresponding phonon replicas

→ redshift of PL peak with inccreasing y

→ $y > 1.35\%$: finestructure of PL peaks disappears

→ possible explanation:
- $0.6\% \le y \le 2.85\%$: luminescence due to N-cluster states with more than two nitrogen atoms
- $y \le 1.35\%$: finestructure of PL peaks due to phonon replicas ($\omega_{TO}^{GaP} \sim 45$ meV)
- $y > 1.35\%$: absence of phonon replicas for $y = 2.2\%$, and 2.75% as possible hint for indirect to direct crossover* between $y = 1.35\%$ and 2.2%

* theoretically predicted for $y \sim 3\%$ by L. Bellaiche *et al.* Phys. Rev. B **56**, 10233 (1997)

Room-temperature PL

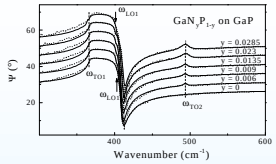
Structure	Substrat	y_N (%)	PL/300K (eV)
3D	(001)	0.61	1.98
3D	(001)	0.89	1.95
3D	5°[110]	1.0	1.94
3D	(001)	1.1	1.93
3D	(001)	1.35	1.92
3D	(001)	2.2	--
3D	5°[110]	2.75	--
MQW	(001)	1.0	1.92
MQW	5°[110]	1.1	--

→ increased room-temperature (rt) PL intensity for layers grown on (001) oriented substrates

→ redshift of rt-PL peak with y

→ no rt-PL for $y > 1.35\%$

Phonon Properties



→ method: mid-infrared spectroscopic ellipsometry

→ we detect a GaP-like ($\omega_{TO1} \approx 366$ cm^{-1}, $\omega_{LO1} \approx 403...401$ cm^{-1}) and a GaN-like ($\omega_{TO2} \approx 495$ cm^{-1}, $\omega_{LO2} \approx 495...498$ cm^{-1}) phonon band

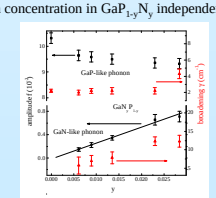
→ ω_{LO1} is redshifted with increasing y as a result of tensile strain and alloying

→ the TO-frequencies ω_{TO1} and ω_{TO2} are nearly unchanched with increasing y → for ω_{TO2}, the effects of alloying and biaxial tensile strain compensate

→ $\omega_{TO2} = (494.4 \pm 0.6)$ cm^{-1} agrees well with the calculated local-mode frequency of N in GaP ($\omega_{GaP:N} = 495$ cm^{-1}, extended linear diatomic chain model), and with several experimental results for N-doped GaP ($\omega_{GaP:N} = 492...496$ cm^{-1})

→ ω_{LO2} is blueshifted with increasing y and accounts for the increasing amplitude f ($f = [\omega_{LO2} - \omega_{TO2}] / \omega_{TO2}$) of the GaN-like phonon

→ linear increase of f with y ($\Delta f/\Delta y = 0.27 \pm 0.02$) gives possibility to measure the nitrogen concentration in $GaP_{1-y}N_y$ independently



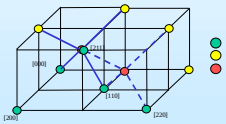
N-N pairs in GaP:N

e.g.: D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966)

→ N is isovalent impurity in GaP and causes binding states within the band gap of the host material

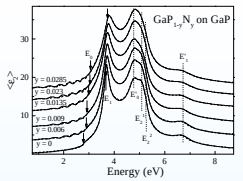
→ electron is bound in the shortranging potential of two nitrogen atoms (distance: d_{NNi},see below), binding energy decreases with increasing distance d_{NNi} (i < 8)

→ Ne^-N-complex acts as an ionized acceptor (i < 8)

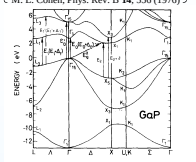


Pairing Direction	Distance d_{NNi} (nm)	Label	PL (4K) (eV)
[110]	0.385	NN_1	2.1854
[200]	0.545	NN_2	2.1901
[211]	0.667	NN_3	2.2644
[220]	0.771	NN_4	2.2894
[310]	0.862	NN_5	2.2971
[222]	0.945	NN_6	2.3033
[321]	1.020	NN_7	2.3059
[400]	1.090	NN_8	2.3076
[411]	1.156	NN_9	2.3101
[330]	1.156	NN_9	2.3101
[420]	1.219	NN_{10}	2.3110
∞	∞	A-line	2.3171

Critical points



bandstructure from J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B **14**, 556 (1976)



→ method: near-infrared to vacuum-ultra violet spectroscopic ellipsometry*

→ all critical point (CP)-energies are affected by the combined effects of tensile strain, which should result in a redshift of CP's, and of alloying (linear interpolation to the CP energies of β-GaN); quantitative calculation of both effects is difficult because there is a lack of CP-energies of β-GaN, and a lack of deformation potentials of both, GaP and β-GaN

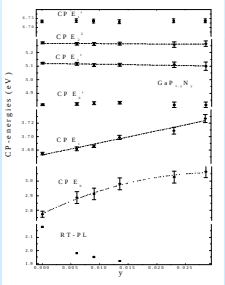
→ blueshift of critical points E_0^{direct} and E_1 with y, due to dominating influence of alloying ($E_g^{\beta\text{-}GaN} \approx 3.25$ eV, $E_1^{\beta\text{-}GaN} \approx 7.0$ eV) in contrast to redshift of the absorption tail and the PL peak

→ small redshift of CP's E_2 with y,due to dominating influence of tensile strain

→ no shift of CP's E_0' and E_1' with y due to compensation of both effects

→ direct Γ-, L- and X-transitions do not follow the nitrogen-induced unusual behaviour of the absorption tail in agreement with recent pseudopotential supercell calculations by P. R. C. Kent *et al.* [Phys. Rev. Lett. **86**, 2613 (2001)]

* Special thanks to T. Theuß (J. A. Woollam Co., Inc.) and T. Hofmann (University of Leipzig) for the measurements



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