Single GaInP nanowire p-i-n junctions near the direct to indirect bandgap crossover point

Wallentin, Jesper; Poncela, Laura Barrutia; Jansson, Anna M.; Mergenthaler, Kilian; Ek, Martin; Jacobsson, Daniel; Wallenberg, Reine; Deppert, Knut; Samuelson, Lars; Hessman, Dan; Borgström, Magnus

Published in:
Applied Physics Letters

DOI:
10.1063/1.4729929

2012

Link to publication

Citation for published version (APA):
Single GaInP nanowire p-i-n junctions near the direct to indirect bandgap crossover point
Jesper Wallentin, Laura Barrutia Poncela, Anna M. Jansson, Kilian Mergenthaler, Martin Ek et al.

Citation: Appl. Phys. Lett. 100, 251103 (2012); doi: 10.1063/1.4729929
View online: http://dx.doi.org/10.1063/1.4729929
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v100/i25
Published by the American Institute of Physics.

Related Articles
Valence band offset of n-ZnO/p-MgxNi1–xO heterojunction measured by x-ray photoelectron spectroscopy
Diamond/aluminium nitride composites for efficient thermal management applications
Illumination effects on electrical characteristics of GaN/AlGaN/GaN heterostructures and heterostructure field effect transistors and their elimination by proper surface passivation
Hole transport in pure and doped hematite
AISb nucleation induced anisotropic electron mobility in AISb/InAs heterostructures on GaAs

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT
Single GaInP nanowire p-i-n junctions near the direct to indirect bandgap crossover point

Jesper Wallentin,1,a) Laura Barrutia Poncela,1 Anna M. Jansson,1 Kilian Mergenthaler,1 Martin Ek,2 Daniel Jacobsson,1 L. Reine Wallenberg,2 Knut Deppert,1 Lars Samuelson,1 Dan Hessman,1 and Magnus T. Borgström1
1Solid State Physics, Lund University, Box 118, S-221 00, Lund, Sweden
2Polymer & Materials Chemistry/CHREM, Lund University, Box 124, S-221 00, Lund, Sweden

(Accepted 1 January 2012; accepted 3 June 2012; published online 19 June 2012)

We grew Au-seeded GaInP NWs on InP (111)B substrates in metal organic vapor phase epitaxy (MOVPE), starting from an InP NW and using a GaP barrier for improved photoluminescence (PL). The yield of vertical NWs was close to 100%. In this work, we focus on doped GaInP NWs, while a growth parameter study of undoped NWs was close to 100%. In this work, we focus on doped GaInP NWs, while a growth parameter study of undoped NWs was close to 100%.

We investigated the effect of doping on the composition of the ternary GaInP NWs using energy dispersive x-ray spectroscopy (EDS) line scans along the length of p-i-n doped NWs, shown in Fig. 1(a). The undoped segment showed an average composition of around x = 0.77 (standard deviation 0.05). The line scan indicated a slightly decreasing Ga concentration along the NW.

Transmission electron microscopy (TEM) of the p-i-n NWs revealed that the undoped segment had the zincblende crystal structure with rotational twins and some short wurtzite segments. The Zn-doped segment had longer segments of pure zinc blende and more regular twinning, which is expected since both InP (Refs. 18 and 19) and GaP (Ref. 20) NWs form zinc blende with regular twinning when doped with Zn. The S-doped segment was almost pure wurtzite, similar to S-doped InP NWs.21

We investigated the effect of doping on the composition of the ternary GaInP NWs using energy dispersive x-ray spectroscopy (EDS) line scans along the length of p-i-n doped NWs, shown in Fig. 1(a). The undoped segment showed an average composition of around x = 0.77 (standard deviation 0.05). The line scan indicated a slightly decreasing Ga concentration along the NW.

The S-doped segment was a bit more In-rich, with x = 0.70, and showed a slightly decreasing Ga concentration in the growth direction. Possibly, the change in crystal structure affected the group III diffusion lengths in favor of In.

The effect from DEZn was more complicated, creating first a segment with lower Ga content, x = 0.63, which then gradually increased up to about x = 0.85. Zn has a high solubility in liquid metals, and we speculate that Zn affects the equilibrium composition of the seed particle to low Ga levels when it is introduced. Note that the use of DEZn lowered the growth rate significantly. We speculate that DEZn decreases the diffusion length of In precursors, as previously observed for InP NWs,17 thereby gradually increasing the Ga concentration.

The optical properties were investigated using single NW PL at low temperature (4.2 K), shown in Fig. 1(b), and macro-PL at room temperature of the as-grown NWs. For these measurements, homogeneously doped GaInP NWs were investigated, grown under the same respective conditions as in the combined p-i-n structure. The non-intentionally doped NWs showed a low temperature PL signal in the range 1.95 to 2.3 eV, with many relatively sharp peaks, as well as room temperature macro-PL displaying one relatively broad peak centered at 2.14 eV. The average composition, x = 0.77, is
slightly above the predicted direct to indirect crossover, and the highest PL signal at about 2.25 eV fits well with the predicted crossover bandgap at low temperature. The lower-energy peaks at low temperature could be related to the observed stacking faults, or possibly surface-related states. Ordering is another possible explanation for the relatively low-energy PL, but synchrotron-based x-ray diffraction measurements do not show any signs of this. There may also be In-rich segments, which could be shorter than the resolution in EDS (about 5 nm), and could occur both axially, radially, as observed in GaInN NWs, or at the NW edges as observed in AlInP NW shells. Note, however, that we did not observe radial growth of a Ga-rich shell in TEM, as previously found in MBE-grown GaInP. At room temperature, the carriers recombine before diffusing to these low-bandgap regions, thereby explaining the observed single peak.

The S-doped NWs showed low-T PL with one broad peak around 1.95 eV, while the Zn-doped NWs showed one main peak at 1.65 eV and several weaker peaks. Similar to the low-energy peaks in the undoped NWs, both types of doping thus resulted in PL about 0.4 eV below the bandgap as expected from the composition measured with EDS. We speculate that similar effects as in the undoped NWs, i.e., short In-rich segments, are responsible for the discrepancy. In the Zn-doped NWs, there could also be significant redshift from Fermi level pinning at the surface and acceptor states.

Regarding the S-doped NWs, the spectrum shows qualitative similarity with highly S-doped InP NWs. Electrical measurements (see below) indicate quite high doping levels. We speculate that the high electron concentration leads to state-filling, causing the In-rich regions to be filled with electrons up to a common Fermi level. This would explain the lack of distinct peaks as in the undoped material.

For electrical characterization of homogeneously doped NWs, we created NW-FETs. S-doped devices showed linear source-drain behavior with resistances of around 10 MΩ, several orders of magnitude higher than InP NWs grown with similar HCl and H₂S molar fractions. See supplementary material for details. The current increased with a positive gate which demonstrated n-type conductance, but the mobility as calculated from the transconductance in gate-sweep measurements gave an unreasonably low value of around 10⁻² cm²/Vs. We believe that the contacts, despite showing ohmic behavior, dominated the device resistance rather than the NW themselves.

Zn-doped NW-FETs showed non-linear I-V characteristics, indicating Schottky-like barriers at the contacts. The currents were significantly higher than in Zn-doped InP NW-FETs, which demonstrates better contacts but not necessarily higher doping of the NWs. The gate-sweep measurements showed weak gate dependence but clear p-type behavior.

Having demonstrated p- and n-doping, we synthesized p-i-n doped devices. Dark I-V measurements, shown in Fig. 2(a), displayed clear rectification with typical diode behavior. The ideality factor, n, was around 2.1 at low bias, which is slightly higher than similar InP (Ref. 4) and GaAs (Ref. 30) devices. The rectifying behavior demonstrates that HCl prevents the overgrowth of a conductive n-type shell.

The photocurrents were on the same order of magnitude as single NW InP p-n junctions. A proper solar cell efficiency could not be calculated since we used a laser for excitation, and since the absorption in nanowires is difficult to evaluate. However, using a simple analysis with a projected absorption area equal to the i-region, we achieve similar efficiencies as previously published single-NW devices. We plotted the short-circuit current vs. laser power (Fig. 2(b)) and found a linear dependence over five orders of magnitude. The open-circuit voltage \(V_{\text{oc}}\) should depend on the power as \(V_{\text{oc}} = (nkT/q)\ln(I_L/I_0)\). Here, \(I_L\) is the light-induced current, which was proportional to the laser intensity, and \(I_0\) the dark current. In good agreement with this model, we found a logarithmic dependence of \(V_{\text{oc}}\) on the excitation power, with a slope of 53 mV. Assuming \(kT/q = 26\) mV, this gives an ideality factor of 2.04 in close agreement with the dark I-V measurements. The fill factor at the highest excitation was 43%, and was almost independent of laser power.

Next, we investigated the spectral dependence of the photocurrent, shown in Fig. 2(c). The device showed a quite sharp onset around 2.15 eV, in good agreement with the room-T PL and sharper than the broad peak observed in low-T PL. This indicates that the many small peaks observed in low-T PL are indeed related to small narrow-bandgap regions. Also surprising is the plateau in photocurrent above 2.25 eV. This effect could be related to the indirect X and L
bands, which both have minima of around 2.2–2.3 eV at this composition.\textsuperscript{11} Absorption should be effective in these bands due to the high effective masses, where possibly carriers get trapped without contributing to the photocurrent. However, the saturation could also be an optical effect due to reduced coupling of short wavelength light into the NWs.\textsuperscript{32}

Finally, we investigated the electroluminescence spectrum under forward bias, i.e., in LED mode, shown in Fig. 2(d). The spectrum shows two peaks. The high-energy peak at 2.18 eV is in good agreement with the photocurrent spectroscopy and the room-T PL, and is presumably due to recombination in the undoped region. Note that this peak has a wavelength of about 569 nm, i.e., yellow-green. There is a second, broader peak around 1.5 to 1.8 eV, which we attribute to recombination in the lower-bandgap doped regions. The quantum efficiency was only around 4 \times 10^{-8}, which is very low even for a NW p-n junction and several orders of magnitude less than single NW InP LEDs.\textsuperscript{33} With the measured variations in composition, the band structure shows a high-bandgap i-region surrounded by lower-bandgap p- and n-segments. Thus, carriers will tend to escape the i-region which enhances carrier separation rather than recombination. It is therefore not surprising that the GaInP p-i-n junctions showed good photocurrent characteristics but poor LED efficiency. It should be possible to achieve a more beneficial band structure for LEDs, by tuning the TMG to TMI ratio during growth to create a low-bandgap i-region.

In conclusion, we have demonstrated p- and n-doping of GaInP NWs. Both types of doping affected the bandgap and crystal structure, but in different ways. The efficient PL and photovoltaic effect, despite the stacking faults and lack of a high-bandgap shell, indicates a low density of non-radiative traps. The p-i-n doped devices show good photocurrent behavior but poor LED efficiency, attributed to the high-bandgap middle segment. These results demonstrate that GaInP NW optoelectronic devices can be made with bandgaps significantly exceeding the composition range available in thin films.

This work was performed within the Nanomter Structure Consortium at Lund University (nmC@LU) and was supported by the Swedish Research Council, the Swedish Foundation for Strategic Research, and the EU program AMON-RA (214814). This report is based on a project which was funded by E.ON AG as part of the E.ON International Research Initiative.

15See supplementary material at http://dx.doi.org/10.1063/1.4729929 for methods details and electrical measurements of homogenously doped NWs.