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Citation: [AIP Conference Proceedings](#) **1399**, 481 (2011); doi: 10.1063/1.3666463

View online: <https://doi.org/10.1063/1.3666463>

View Table of Contents: <http://aip.scitation.org/toc/apc/1399/1>

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# Probing the valence band structure of wurtzite InP nanowires by photoluminescence excitation spectroscopy

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**Abstract** We use time-resolved photoluminescence and photoluminescence excitation spectroscopy to obtain the valence band parameters of wurtzite InP nanowires. We observe the A, B, and C hole bands for these nanowires and obtain both the crystal field and the spin-orbit energies for wurtzite InP nanowires.

**Keywords:** InP, wurtzite, photoluminescence excitation spectroscopy, crystal field, spin orbit energy.

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## INTRODUCTION

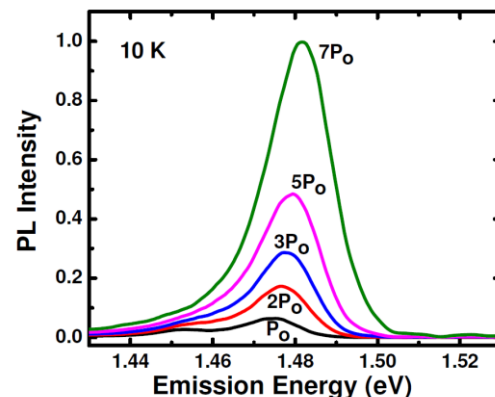
III-V nanowires often exhibit polytypism, where the nanowire can grow along the [111] axis and exhibit zincblende (ZB) symmetry or along the [0001] axis and exhibit wurtzite (WZ) symmetry. InP is one of these types of wires, where it is known that the WZ phase shows a band gap 80 meV larger than the ZB phase ( $E_{ZB} = 1.42$  eV,  $E_{WZ} = 1.50$  eV), and in a mixed phase the nanowire has a Type-II band offset of 45 meV with the holes confined to the WZ phase and the electrons confined to the ZB phase [1,2]. We present photoluminescence excitation measurements (PLE) and also photocurrent spectroscopy to illuminate the valence band structure of hexagonal WZ InP nanowires (NWs). We observe the A, B, and C hole bands for these nanowires and obtain both the crystal field and the spin-orbit energies for WZ InP nanowires.

## RESULTS AND DISCUSSION

The WZ InP nanowires were grown using monodisperse gold nanoparticles (5 to 150 nm diameter) which catalyzed growth of WZ InP nanowires at 420 C and a V/III ratio of 700. The NWs were removed from the [111]B oriented growth substrate by sonication into solution and dispersed onto a silicon substrate with a  $\text{Si}_3\text{N}_4/\text{SiO}_2$  insulating layer. Individual nanowires were then identified for study.

In order to be certain that the nanowires we are probing are indeed fully the WZ phase of InP, we have carried out both power dependent CW

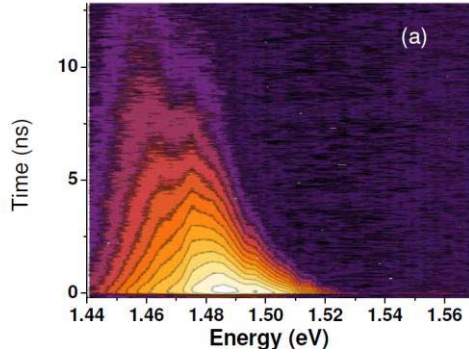
photoluminescence (PL) and time-resolved PL measurements. Wurtzite nanowires which have a significant amount of ZB phases show a distinctive power dependence of the CW-PL. At low powers the emission is observed near the ZB band edge and at higher power shift rapidly to higher energies close to the WZ band edge [1]. The power-dependent CW-PL shown in Fig. 1 for a 100 nm WZ InP NW shows PL at the lowest powers well above the ZB band edge but about 25 meV below the WZ band edge that moves to higher energy by about 10 meV over a factor of 7 in power suggesting the this nanowire does not contain significant mixed phases.



**FIGURE 1.** Power-dependent CW-PL spectra for a single 100 nm WZ InP NW (from ref. 4).

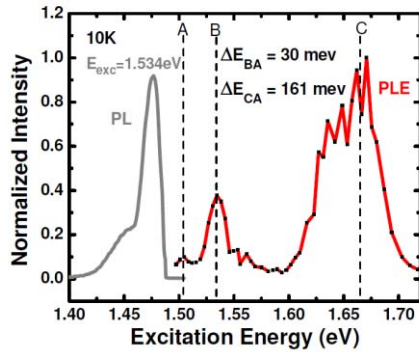
Detailed time-resolved photoluminescence measurements at 10K also show that these wires are predominantly WZ with a short-lived band edge emission at 1.5 eV and a significant long-lived defect

emission band 30 to 50 meV lower in energy (1.45 to 1.47 eV).



**FIGURE 2.** Time-resolved spectral map of a single 100 nm WZ InP NW (from ref. 4). Note the long-lived defect state at  $\sim 1.46$  eV.

The coupling of the band edge states to this defect line provided the opportunity to carry out photoluminescence excitation spectroscopy (PLE). We detect the intensity of the PL at the defect emission band as we tune a CW Ti-Sapphire laser from 1.48 eV to 1.70 eV. Figure 3 displays a photoluminescence spectrum for laser excitation at the energy marked B as well as the PLE over the full energy range. Resonances in the PLE are observed at



**FIGURE 3.** Photoluminescence spectrum (left) for laser excitation at energy marked B and photoluminescence excitation spectroscopy (right) for a 100 nm WZ InP nanowire (from ref. 4).

the energy positions marked A, B, C corresponding to the three excitons expected for the WZ structure. The lowest energy resonance corresponds to the A-exciton at 1.504 eV. The two stronger resonances are the B-exciton at 1.534 and the C-exciton resonance at 1.665 eV. From the energy difference between the A and B hole bands and the A and C hole bands, we can obtain

the both the crystal field splitting and the spin orbit splitting energies in the quasi-harmonic approximation by using the following equation where the plus sign is for  $E_C - E_A$  and the minus for  $E_B - E_A$ . [5].

$$\frac{\Delta_{SO} + \Delta_{CR}}{2} \pm \sqrt{\left(\frac{\Delta_{SO} + \Delta_{CR}}{2}\right)^2 - \frac{2}{3}\Delta_{SO}\Delta_{CR}}$$

We obtain a value of 52 meV for the crystal field splitting and a value of 139 meV for the spin-orbit energy, comparable to expected values [5,6].

In summary, we have shown that PLE measurements can illuminate the valence band structure of a 100 nmWZ InP nanowire and obtain both the crystal field splitting and spin orbit energies. PLE and photocurrent measurements for WZ InP nanowires ranging in diameter from 20 – 150 nm show similar behavior.

## ACKNOWLEDGMENTS

We acknowledge the financial support of the National Science Foundation through Grant Nos. DMR-0806700, 086572, and ECCS-0701703, and the Australian Research Council. The Australian National Fabrication Facility is acknowledge for access to the facilities used in this research.

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