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ABSTRACT

The metalorganic vapor phase epitaxy of wurtzite InP nanowires on GaN (0001) is demonstrated. The InP nanowires exhibit the same wurtzite structure as the underlying wurtzite GaN. The photoluminescence studies indicate that the InP nanowires are single-phase wurtzite with high crystalline quality which is supported by transmission and scanning electron microscopy images. The position of the second valence band or valence band splitting energy is also deduced from the photoluminescence data to be $\Delta_{AB} = 30$ meV at room temperature. The InP/GaN heterojunction can enable exotic optoelectronic and spintronic experiments and applications. In addition, these results can enable traditional III–V growth on III–N materials for heterojunction devices.

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In this work, we demonstrate the metalorganic vapor phase epitaxy (MOVPE) of wurtzite (WZ) InP nanowires (NWs) on GaN using the vapor–liquid–solid (VLS) method.¹ This is the first demonstration of epitaxial growth of InP on GaN and of any conventional III–V NW growth on GaN. The GaN/InP combination is interesting as the materials have extremely dissimilar band gaps: 1.43 eV for the WZ InP² in the infrared and 3.44 eV bandgap for WZ GaN³ in the ultraviolet region. Wurtzite InP NWs have been measured to have a lateral lattice parameter $a = 4.14$ Å,⁴ while the wurtzite GaN has an $a = 3.19$ Å.⁵ This presents a massive 23.07% lattice mismatch, which would be prohibitively large for thin films. Wurtzite InP NWs are also specifically interesting as it is commonly known that III–V compound semiconductors exhibit the zinc blende (ZB) crystal structure in the bulk form under normal conditions, with the exception of III-nitrides which crystallize to the WZ structure. The type I heterojunction⁶ of these 2 wurtzite materials presented here may also be interesting for conducting spintronic studies as both GaN and InP have the WZ structure exhibiting the Rashba effect.⁷ Finally, the work presented here paves way for epitaxial integration of III–V growth on III–N materials, enabling new interesting possibilities in regard to device fabrication, for example, for heterojunction bipolar transistors.

GaN was grown on c-plane sapphire substrates using a vertical reactor MOVPE system (Thomas Swan $3 \times 2''$). Trimethylgallium

(TMGa) was the used Ga source, and ammonia was the N source. The c-plane sapphire substrates were preheated and cleaned in a H₂ ambient at 1100 °C for 300 s, followed by nitridation under ammonia flow at 535 °C. A GaN nucleation layer was grown at the same 535 °C for 160 s at a V/III-ratio of 1500, followed by annealing at 1025 °C for 120 s, after which a 3.41 μm-thick (*in situ* reflectometry) GaN layer was grown at 1025 °C for 6400 s at a V/III-ratio of 750. This two-step growth is similar to Nakamura's GaN nucleation layer⁸ developed from AlN nucleation layer by Amano,⁹ and the initial surface nitridation is known to improve the quality of the final GaN.¹⁰

The InP NWs were grown on the GaN substrates in a horizontal-flow MOVPE system (Thomas Swan) at atmospheric pressure. The precursors for indium and phosphorus were trimethylindium (TMIn) and tertiarybutylphosphine (TBP), respectively. The NW growth mechanism was gold-assisted vapor–liquid–solid (VLS)¹ using poly-L-lysine and nominally 40 nm, 100 nm, and 150 nm Au particles deposited from colloidal solution (BBI international). The effect of 100 nm and 150 nm Au seeds can be found in the [supplementary material](#). In MOVPE, the NW growth was initiated at 385 °C – 450 °C by switching on TMIn and TBP simultaneously, with flow rates of 1.25–3.1 $\frac{\mu\text{mol}}{\text{min}}$ and 1276–1500 $\frac{\mu\text{mol}}{\text{min}}$, respectively. TBP flow was kept on during cooling down to 300 °C. H₂ was used as carrier gas and the total flow to the

reactor was 5 slm. Substrate annealing prior to growth resulted in micrometer-sized islands instead of NWs and was therefore not applied. Native oxide removal from GaN with concentrated HCl (37%) prior to growth did not result in observable effect on growth and was, therefore, not applied to the series presented in this paper.

The grown NWs were examined with scanning electron microscopy (SEM) using a Zeiss Supra 40 field emission SEM to study the NW morphology and overall growth, and transmission electron microscopy (TEM) was used to study the crystal quality and crystal structure (cubic or hexagonal). Photoluminescence (PL) spectra at room temperature were measured from ensembles of NWs for determining the bandgap of the grown material using a WITec alpha300 S microscope equipped with a 20× microscope objective with 0.4 numerical aperture (NA) for both excitation and collection, and a 532 nm frequency-doubled Nd:YAG laser, resulting in a minimum spot diameter of $1.22 \frac{\lambda}{NA} \approx 1.6 \mu\text{m}$ from Rayleigh's criterion. The microscope had 2 gratings, one for broad spectrum measurements ($150 \frac{\text{grooves}}{\text{mm}}$) and the other for finer detail high spectral resolution measurements ($1200 \frac{\text{grooves}}{\text{mm}}$). The PL also gives information of the crystal structure of the InP NWs as the WZ InP and ZB InP are known to have different band gaps.²

Several combinations of temperature and ratios of group 15 (group V) molar flow to group 13 (group III) molar flow (V/III-ratio or V/III) produced NW growth of varied quality, assessed by scanning electron microscopy (SEM), and trial-and-error optimization was used to find suitable parameters. Figure 1(a) shows a series of SEM images of the NWs grown at different temperatures at V/III = 600. Undramatically, the lowest temperature of 385 °C produces NWs with almost random growth directions and morphologies. Very low growth temperatures were also well reported by other works to cause irregular InP NW growth.^{2,11} The high temperature of 450 °C produces some well-defined but tapered NWs with larger Au diameters as seen in the [supplementary material](#) Fig. S1, but with the 40 nm Au diameter in Fig. 1(a), the horizontal NW growth seems to be enhanced as well at the highest temperature. InP NW lateral growth and tapering are known to be enhanced by higher growth temperatures,^{2,11} which has been attributed to the greater availability of group P adatoms on the

substrate due to the higher temperatures driving the pyrolysis.¹¹ Growth temperatures of 425 °C and 410 °C seem to produce morphologically the best NWs. Temperature of 425 °C was chosen to study the effect of the changing V/III-ratio. Figure 1(b) shows a series of SEM images of NWs grown with different V/III-ratios at 425 °C. At V/III = 415 a small amount of irregular shaped NWs are observed though most of the NWs appear straight and orderly. Interestingly increasing the V/III-ratio at 425 °C does not seem to cause tapering or island growth, as seen from Fig. 1(b). Paiman *et al.* observed at similar temperatures (420 °C) that increasing V/III-ratio caused small NW tapering,¹¹ but this happened when increasing the V/III-ratio from 110 to 700, over a sixfold increase, but the cases are not directly comparable as they used native substrates for InP growth and different P precursors. In Fig. 1(b), the increase in group V availability with higher V/III-ratio is, therefore, clearly not large enough to cause observable tapering. Even the NWs grown at the highest V/III = 1200 are not tapered.

What can be further noted from the higher V/III-ratio images in Fig. 1(b) is that the non-horizontal NWs seem to grow either at 120° or 60° angles from each other when looked from the top. This is an indicator that the NWs are copying the hexagonal orientation of the underlying WZ GaN substrate. While the NW crystal structure is primarily determined by the growth conditions, the initial growth and the resulting growth directions are clearly influenced by the substrate since without influence from the substrate the growth directions would be random. This is, therefore, a strong indication of the epitaxial nature of the InP NW growth on GaN.

Interesting horizontal NW growth is observed with all temperatures and V/III-ratios in Figs. 1(a) and 1(b). In the future, these could be studied further as the horizontal NWs might be under massive stress if not relaxed due to strained growth as the lattice parameters of GaN ($a = 3.19 \text{ \AA}$, $c = 5.19 \text{ \AA}$)⁵ are small compared to WZ InP ($a = 4.14 \text{ \AA}$, $c = 6.80 \text{ \AA}$).⁴

Throughout the V/III and temperature series (even with the optimized growth parameters), two types of NWs were observed: horizontal and out-of-plane. Practically, all of the NWs seem to initiate the growth as horizontal NWs, and a fraction of these NWs transition to out-of-plane direction after a brief growth of a “tail”-section.

FIG. 1. (a) SEM images of InP NWs grown on GaN at different temperatures with V/III = 600. The lowest temperature clearly results in decreased crystal quality while the highest leads to mainly horizontal NWs. (b) NWs grown at different V/III-ratios. V/III-ratios over 400 seem to produce high quality NWs. Interestingly horizontal NWs are observed even with optimized parameters. The growth temperature and the V/III-ratio are presented in every image. 40 nm diameter Au seeds were used in both series.

FIG. 2. SEM images of WZ InP NWs on GaN. The vertical NWs seem to have a short horizontal tail. (a) Shows an inclined image for better viewing. (b) Shows horizontal NWs where the Au seed particle is just touching an intersecting NW, and (c) shows two horizontal NWs after NW growth resulted in contact. (a) and (c) were grown with 100 nm Au seeds and (b) with 40 nm particles.

Figure 2(a) shows the typical out-of-plane NWs and their tail sections. Interestingly, different growth parameters were not observed to have a significant effect on the length of the tail section, instead it was roughly a hundred to a few hundred nm in all samples. In addition, the Au particle size was not observed to have a significant effect on the NW morphology (see Fig. S1 in the [supplementary material](#)). Qualitatively, the larger Au particles seem to produce somewhat larger fraction of horizontal NWs.

An important observation is that unless the NWs transitioned to out-of-plane growth in the initial stages of the growth, they would retain the horizontal growth for several micrometers and even when intersecting another horizontal InP NW trail. Figure 2(b) shows horizontal NWs where the Au particle is just touching an intersecting NW and Fig. 2(c) shows two horizontal NWs after they have intersected. In Fig. 2(b), it appears that the Au particle is in contact with the existing InP trail, and in Fig. 2(c) a “bridge” seems to have formed at the contact interface. Thus, the Au particle has precipitated InP to the sidewall of the existing NW and then moved on to a new direction along the GaN surface. In previous studies on InAs NW growth on GaAs(111)B,

FIG. 4. Photoluminescence spectra from the V/III-ratio series from Fig. 1(b). The vertical line ZB shows the ZB InP bandgap position and the WZ line shows the WZ InP bandgap position. All samples are clearly WZ with no observable ZB.

the InAs NWs grew horizontally until intersecting with another InAs trail, followed by pedestal growth and vertical InAs NW growth.¹² The initial horizontal growth was attributed to Au/GaAs interfacial energy being lower than that of Au/InAs.¹² Similarly here it is thought that the Au/GaN interface energy is lower than Au/InP. In fact the Au/GaN interface energy seems to be significantly lower since the intersecting horizontal NWs do not initiate out-of-plane growth even after forming a bridge with the existing InP trail.

The apparent preference of the Au particle to remain on GaN surface makes the initial tendency of some NWs to grow out-of-plane curious. The transition occurring exclusively in initial phases of the growth suggests that the conditions evolve initially, either in the Au particle or at the GaN surface. Of these, changes in the GaN surface are more likely since the growth parameters were not found to have a significant impact on the tail length. Although concluding the underlying phenomena is within the scope of another study, here it may be noted that the Au/GaN surface energy could be modified by the introduction of either indium or phosphorus on the GaN surface, or by indium incorporation to the Au particle.

TEM was used to study the crystallinity of the grown InP NWs. Figure 3(a) shows a high resolution TEM (HRTEM) image of an InP NW. The NW exhibits a high crystal quality as seen from Fig. 3(b). Figure 3(c) shows the Fourier transform of the image, which corresponds to the reciprocal lattice¹³ (k-space) of the crystal imaged. The Fourier transform shows spots corresponding to crystal planes, which correspond to reciprocal lattice vectors; thus, the NW can be indexed

FIG. 3. TEM analysis of WZ InP NWs. (a) A high-resolution TEM image of one NW. (b) Detail of the boxed area in Fig. 3(a). This magnification allows the high-quality single crystal nature of the NWs to be seen. (c) Two-dimensional Fourier transform of Fig. 3(b) that corresponds to the k-space of the crystal imaged in Fig. 3(b). The indexed Fourier transform confirms that the crystal is wurtzite and the NW growth direction is [001], that is [0001] in Miller–Bravais notation.

FIG. 5. High resolution photoluminescence recorded using a 1200 $\frac{\text{grooves}}{\text{mm}}$ grating. Two peaks are seen belonging to the A and B transitions, which the vertical lines mark out. The text inset tells the growth conditions of the NWs.

to have a wurtzite structure with [001] as the NW growth direction ([0001] in Miller–Bravais notation).

Photoluminescence spectra from the V/III-ratio series at room temperature are presented in Fig. 4. The vertical line ZB shows the position of the bandgap of the possible zinc blende InP. None of the graphs show remarkable emission in this area indicating no or very low amounts of ZB InP. The grown InP NWs are, therefore, single phase wurtzite as the bandgap position (≈ 1.43 eV) inferred from the PL matches that from literature (1.43 eV) for WZ InP.² Finer details of the spectra especially in the region close to the bandgap cannot be discerned from Fig. 4, so a higher resolution measurement is needed.

Figure 5 shows a high spectral resolution photoluminescence measurement. The high spectral resolution was obtained using a 1200 $\frac{\text{grooves}}{\text{mm}}$ grating. There are two clear peaks roughly at 1.43 eV and 1.46 eV; these are the bandgap or in other words the lowest conduction band minimum to highest valence band transition ($\Gamma_7^C \rightarrow \Gamma_9^V$ transition¹⁴) labeled here A and the lowest conduction band minimum to second highest valence band transition ($\Gamma_7^C \rightarrow \Gamma_7^V$ transition¹⁴) labeled here as B. We assign from Fig. 5 the energies to be A = 1.428 eV and B = 1.458 eV. These room temperature PL energies are extremely close to values measured by other groups, differing only by few meV.¹⁵ The room temperature valence band splitting energy measured here is $\Delta_{AB} = 30$ meV which is close to 37 meV measured by Tuin *et al.*¹⁵ also at room temperature. The computational value for the valence band

splitting energy of 63 meV by De and Pryor¹⁴ is on the same order of magnitude as the experimental values.

It should be mentioned here that as the GaN has a bandgap of 3.44 eV, the 532 nm (2.33 eV) continuous wave laser cannot excite GaN. Therefore, measuring emission from only the NWs is straightforward and no transfer of the NWs is needed, like when InP NWs are grown on native substrates.^{2,15} No special preparation is needed and unobscured PL can be obtained from as grown NWs. GaN might provide a facile platform for studying WZ NWs.

In conclusion high quality epitaxial WZ InP NWs were grown on GaN (0001) by VLS MOVPE. The NWs showed high crystalline quality from PL, SEM, and TEM. The position of the second highest valence band at room temperature was obtained from the PL data and was found to be $\Delta_{AB} = 30$ meV, slightly smaller than previous reports. This work is the first demonstration of traditional III–V compound semiconductor epitaxy on III–N. This type I heterojunction of highly dissimilar materials both in bandgap and lattice parameter can enable new optoelectronic and spintronic experiments and applications.

See the [supplementary material](#) for the effect of larger Au seed diameters on NW morphology.

AUTHOR'S CONTRIBUTION

C.K. and T.H. contributed equally to this work.

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