Supporting Information

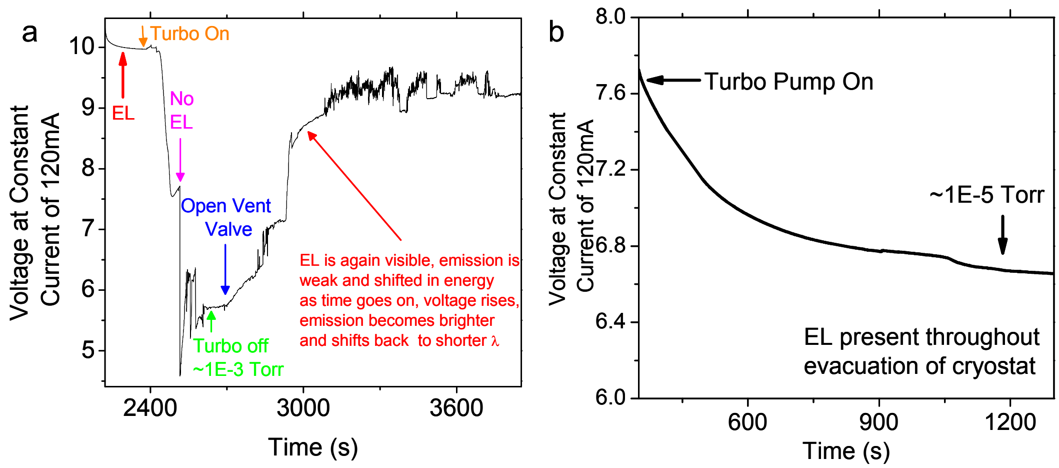
Materials and Methods

Before entering the PAMBE system all wafers are cleaned with solvents in an ultrasonic. All samples are grown using a Veeco 930 system. Standard effusion cells are used to supply ultra high purity Ga and Al. A radio frequency plasma source operated at 350 W supplies the active ultra high purity nitrogen. Before growth beam fluxes are measured using a nude ion gauge at the sample position. Once in the growth chamber the native oxide layer on the Si substrate is removed using thermal desorption at temperatures >1000^{o}C. Substrate temperature is determined using an infrared pyrometer. The first 35 nm of each nanowire is Si doped grown during the initial nucleation steps of the two-step growth process. The remainder of the nanowires are graded AlGaN with or without impurity doping as specified in the figures. Standard photolithography and e-beam evaporation is used to deposit circular, 0.75 mm^2 contacts on top of the nanowires. This contact is semi-transparent and consists of 10 nm Ni / 20 nm Au. A second contact is formed to the n-Si substrate by first removing nanowires from the surface with a diamond scribe then pressing on and annealing a small In contact directly to the n-Si. All scanning electron microscope (SEM) images are obtained on an FEI Sirion scanning electron microscope operating at an accelerating voltage of 15 kV using the "in lens" secondary electron detector. EL spectra were collected using a 0.5m spectrometer and CCD detector. Samples were mounted in an optical cryostat connected to a closed cycle He cryocooler. Spectra were collected for a wide range of sample temperatures and constant currents. Variable temperature I-V curves were collected with the device mounted in the optical cryostat and a multimeter and DC power supply. High-resolution STEM was performed with an FEI Titan^3 80-300 probe-corrected monochromated S/TEM operated at 300 kV. Images were acquired in high-angular annular darkfield (HAADF) mode with the specimen aligned parallel to a principal zone axis. The minimum scattering angle of the detector was set to approximately 2.3 - 3 times the probe convergence angle, thus yielding directly interpretable images with contrast that approaches the square of the atomic number (Z-contrast). EDXS results were obtained on an FEI TF20 S/TEM operated at 200 kV with the sample tilted to maximize detector counts, although in all cases the specimen normal was near a principal zone axis.

Surface Passivation Effects

Initial nanowire samples were grown using "one-step" conditions. This means that nanowires are nucleated and grown at the same temperature. This temperature was chosen to be low so nucleation time is short and a high density can quickly be reached. Under these conditions both GaN and AlN will grow coaxially to some degree. By the end of the growth this will lead to a coaxial layer of AlGaN on the sidewalls on the nanowires. If the sample is kept under forward bias and the atmosphere surrounding the sample is pumped down, the voltage required to achieve a given constant current is drastically reduced and EL emission disappears (SI Fig. 1a). When the sample is exposed again to the atmosphere both the voltage and EL slowly come back to normal levels. This clearly shows that the surface state of the nanowires has some effect on the device performance. We believe that this is due to molecular charging effects on the surface of the nanowires.

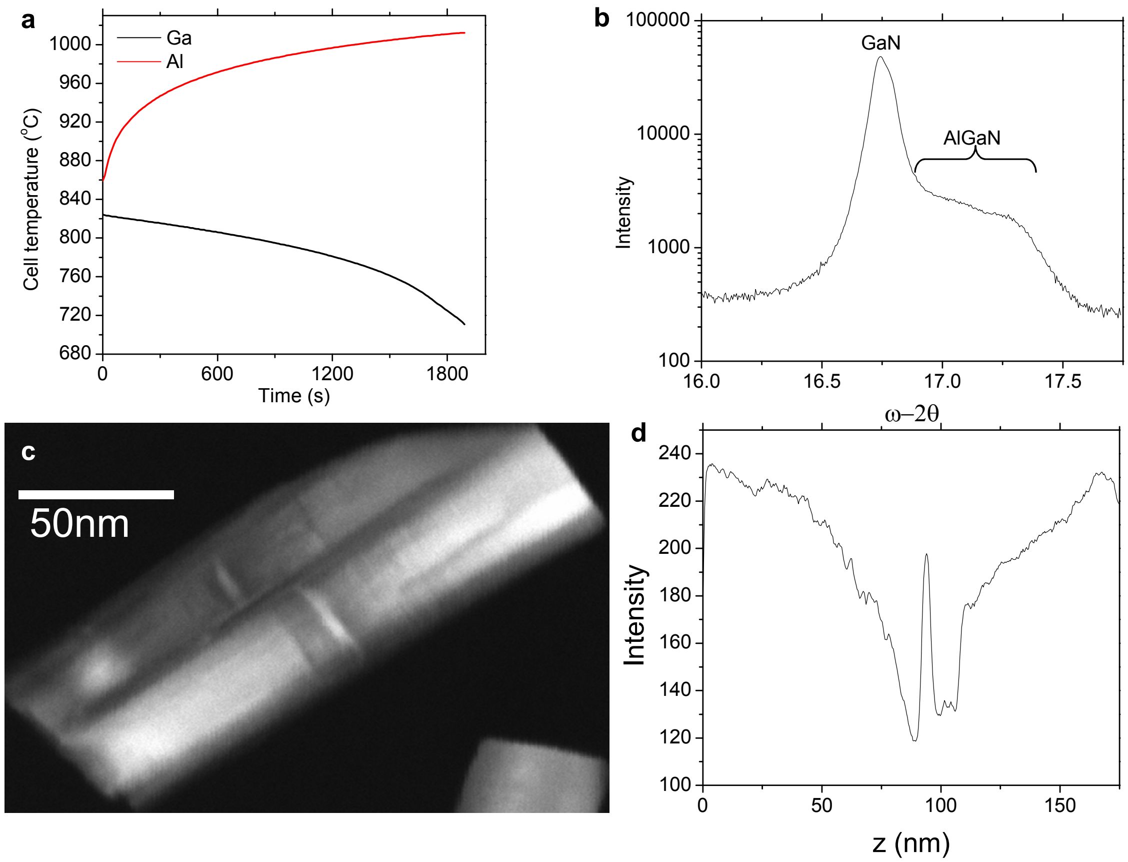
To solve this problem, samples were grown using a "two-step" method. In this method, nanowires are nucleated at low temperature for a small amount of time. After this nucleation period, the substrate temperature is increased, causing no further nucleation of nanowires to occur and the already existing nanowires to grow vertically. Under these conditions only AlN grows coaxially. This leads to a thick layer of AlN on the sidewalls of the nanowires. When samples grown in this manner were pumped down only a slight change in voltage and EL emission are observed (SI Fig. 1b). We believe this is because the AlN coaxial shell acts as a passivation layer for the nanowire, leading to less sensitivity to changes in its environment.



Supporting Information Figure 1 - Electrical measurements over time during pump down for **a** “one-step” and **b** “two-step” grown sample.

<u>Compositional Grading of Nanowires</u>

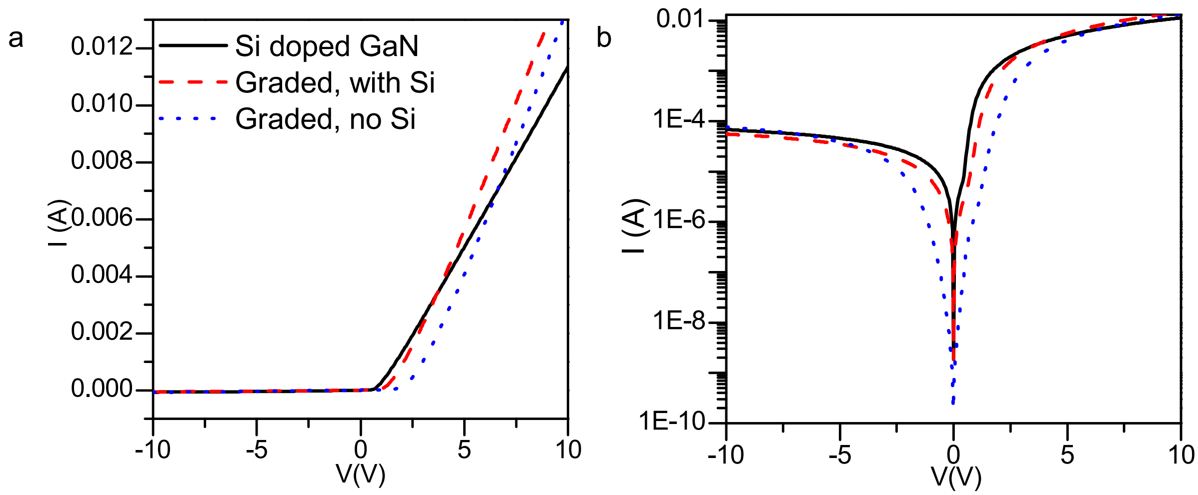
Given that III-nitride nanowires grow in the III-limited regime (i.e. with an excess of active nitrogen on the surface), the growth rate of a nanowire is determined by the amount of impinging III-material impinging on the surface. Therefore, it is possible to linearly grade an AlGaN nanowire’s composition by grading the Ga and Al fluxes during deposition. Since the flux is exponentially related to effusion cell temperature, a script must be used to (anti)logarithmically change the effusion cell temperature to achieve a linearly (decreasing)increasing flux(SI Fig 2a). For initial samples, X-ray diffraction (XRD) was used to verify that the nanowires include both GaN and AlGaN (SI Fig. 2b). To access how the nanowire changed compositionally, STEM images are taken (SI Fig. 2c). The intensity of the image is related to the atomic number of the material. Therefore by simply taking a line scan of the image's intensity and plotting intensity across the length of the nanowire one can determine how the composition qualitatively changes (SI Fig. 2d). Since Ga is heavier than Al, the change in intensity shown in 2d closely tracks with changes in %Ga.



Supporting Information Figure 2 - a Measured effusion cell temperatures as a function of time. **b** XRD measurements of a graded nanowire device. The more prominent GaN peak is due to a coalesced top p-GaN layer grown for this particular sample. **c** STEM image of nanowire devices grown using one-step conditions (i.e. constant substrate temperature during deposition). **d** A line scan of intensity down the center of the nanowire.

Polarization-induced N-type Nanowires

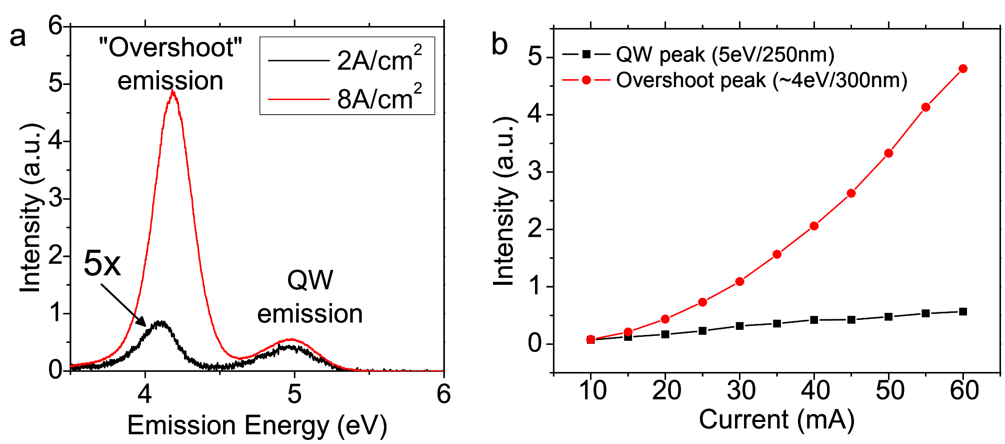
By grading from GaN to AlN, polarization-induced n-type nanowires are grown both with and without impurity doping. As a means of comparison, n-GaN (Si doped) nanowires are also grown. I-V measurements of these nanowires in forward bias show that the most conductive sample is the polarization-induced wire with Si doping, followed by the polarization induced sample without doping, then the nGaN control (SI Fig. 3a and b).



Supporting Information Figure 3 – a Linear and **b** log plot of current (I) versus voltage (V) measurements of samples with different methods of achieving n-type doping.

Carrier Overshoot at High Currents in Samples with Wide Bandgap Active Regions

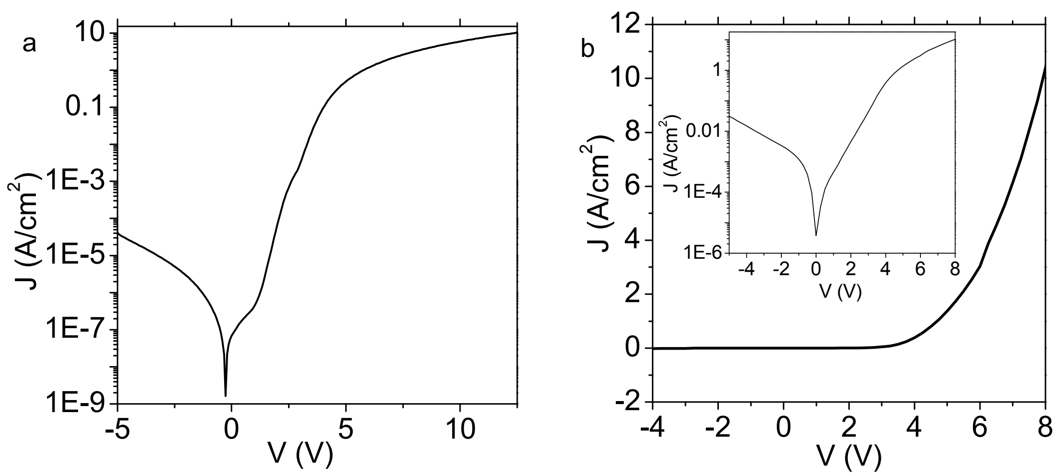
As mentioned in the main text, in our device design it is possible to insert a quantum well between the cladding layers of AlN that can have a bandgap anywhere between GaN and AlN (3.4 and 6.1eV). However, our measurements show that for active regions with wide band gaps electrons overshoot the quantum well. In a sample with an active region nominally of $Al_{0.8}Ga_{0.2}N$, at room temperature and for small currents there is a weak peak at 5eV (250nm) (close to what one would expect for $Al_{0.8}Ga_{0.2}N$) and a second peak near 4eV (300nm) (SI Fig. 4a). In this case the 5eV peak is emission from the quantum well, whereas the 4eV peak is believed to be caused by carrier overshoot. This view is supported by how each of the two peaks changes with increasing current (SI Fig. 4b). As current is increased a greater proportion of carriers will overshoot the quantum well. Thus even though the peaks at 250nm and 300nm start off at roughly the same value for small currents, the peak at 300nm increases much more rapidly as current is increased. Moving forward, better confinement of carriers in the quantum well should aid in improving the emission at deep UV wavelengths for this device.



Supporting Information Figure 4 – a EL emission at two currents **b** EL peak emission intensity as a function of current for the two peaks seen in **a**.

Additional Electrical Measurements of Devices Presented in Main Text

In the interest of space, some plots of electrical data were moved from the main text to the supplementary information. Below is a log J-V for the device describes in Fig. 3 a-g at room temperature (SI Fig. 5a) ,namely a polarization-induced UV LED with a GaN active region, and next to it are J-V plots (both linear and log scale) for the device described in Fig. 3h, which is the same as the previous device structure only with an $Al_{0.8}Ga_{0.2}N$ active region.



Supporting Information Figure 5 – a Log scale J-V for the UV LED sample with a GaN active region **b** Linear scale (log scale inset) J-V characteristics for a UV LED sample with an $Al_{0.8}Ga_{0.2}N$ active region.

List of All Samples

Below is a list of all the samples grown for this study. In total, 16 samples were grown, all of which show UV EL emission. Several different parameters were changed from growth to growth, including the conditions of growth (i.e. whether the samples were grown with a one-step or two-step procedure), the composition and layer thicknesses of the active region, and whether or not impurity doping was included. Given the large number of samples grown and that all of them provide EL, our method for growing polarization-induced UV LEDs (and pn junctions in general) is very reproducible.

Sample #	One-Step or Two-step		SQW or MQW		Nominal QW Thickness			QW Composition	Impurity Doping?		Peak EL wavelength (nm)	Peak EL Energy (eV)
	One	Two	SQW	MQW	3nm	5nm	7nm	$Al_xGa_{1-x}N$	Si	Mg		
1	X		X		X			0.6	X	X	336.8	3.68
2	X		X		X			0.5	X	X	325.1	3.81
3	X		X		X			0.5	X	X	325.4	3.81
4	X		X		X			0.6	X	X	335.7	3.69
5	X		X		X			1	X	X	322.4	3.85
6	X		X		X			0.8	X	X	347.7	3.57
7		X	X				X	0	X	X	376.9	3.29
8		X	X		X			0.5	X	X	298.0	4.16
9		X		X	X			0.5	X	X	297.0	4.18
10		X	X		X			0.8	X	X	294.1	4.22
11		X	X			X		0.8	X	X	294.2	4.21
12		X	X				X	0.8	X	X	293.3	4.23
13		X	X				X	0.8	X	X	293.3	4.23
14		X		X	X			0.8	X	X	282.4	4.39
15		X		X	X			0.8			287.2	4.32
16		X		X	X			0.8		X	290.5	4.27

Supporting Information Table 1 – A list of all the samples grown for this study and details regarding their active regions, growth conditions, and peak EL emission wavelength/energy.