



**HAL**  
open science

## High-Aspect-Ratio GaN p – i – n Nanowires for Linear UV Photodetectors

Bruno César da Silva, Adam Biegański, Christophe Durand, Zahra Sadre Momtaz, Anjali Harikumar, David Cooper, Eva Monroy, Martien Ilse den Hertog

► **To cite this version:**

Bruno César da Silva, Adam Biegański, Christophe Durand, Zahra Sadre Momtaz, Anjali Harikumar, et al.. High-Aspect-Ratio GaN p – i – n Nanowires for Linear UV Photodetectors. *ACS Applied Nano Materials*, 2023, 6 (14), pp.12784-12791. 10.1021/acsanm.3c01495 . hal-04165154

**HAL Id: hal-04165154**

**<https://hal.science/hal-04165154v1>**

Submitted on 11 Sep 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

1 This document is the unedited Author's version post review of a Submitted Work that was subsequently  
2 accepted for publication in ACS Applied Nano Materials, copyright © American Chemical Society after peer  
3 review. To access the final edited and published work see [<https://doi.org/10.1021/acsnm.3c01495>].

# 5 High Aspect Ratio GaN p-i-n Nanowires for Linear UV 6 Photodetectors

7 Bruno César da Silva<sup>1\*</sup>, Adam Biegański<sup>2</sup>, Christophe Durand<sup>2</sup>, Zahra Sadre Momtaz<sup>1</sup>, Anjali  
8 Harikumar<sup>2</sup>, David Cooper<sup>3</sup>, Eva Monroy<sup>2</sup> and Martien Ilse den Hertog<sup>1\*</sup>

9 <sup>1</sup>University Grenoble Alpes, CNRS-Institut Néel, Grenoble F-38000, France

10 <sup>2</sup>University Grenoble Alpes, CEA, Grenoble INP, IRIG, PHELIQS, Grenoble F-38000, France

11 <sup>3</sup>University Grenoble Alpes, CEA-LETI, Grenoble F-38000, France

12  
13 **ABSTRACT:** Ultraviolet GaN photodetectors based on nanowires (NWs) fabricated by top-down  
14 strategies promise improved uniformity, morphology and doping control with respect to bottom-up ones.  
15 However, exploiting the advantages of the NW geometry requires sub-wavelength NW diameters. We  
16 present fabrication of large area sub-200-nm diameter top-down GaN *p-i-n* NW ultraviolet  
17 photodetectors with length over 2  $\mu\text{m}$  produced from a planar specimen using nanosphere lithography  
18 followed by a combination of dry and crystallographic-selective wet etching. Photocurrent  
19 measurements in single NW devices under bias show a linear response as a function of the optical power,  
20 with increased current levels under reverse bias. The linearity proves that the drift of photogenerated  
21 carriers at the junction is the dominating photodetection mechanism, with negligible contributions from  
22 surface effects. These results demonstrate that the unique properties of NW-based photodetectors can be  
23 assessed through a scalable and low-cost fabrication process.

24  
25 **KEYWORDS:** Gallium Nitride nanowires, top-down fabrication, nanosphere lithography, ultraviolet  
26 photodetectors, linear photoresponse

## 27 28 1 Introduction

29 The detection of ultraviolet (UV) radiation, covering the wavelength range from 10 to 400 nm,  
30 finds many uses, from military to space applications<sup>1-4</sup>. Restrictive specifications like low noise and  
31 high robustness to cosmic radiation exclude many conventional materials. Gallium Nitride (GaN) is a  
32 strong candidate to cover all the requirements, since it has a direct energy bandgap of 3.4 eV at room  
33 temperature, allowing the fabrication of devices with efficient absorption of UV radiation and making  
34 it solar blind at the same time, with *p-n* junction devices having excellent performance in terms of dark  
35 noise and speed<sup>5-8</sup>. The ongoing miniaturization of optoelectronic devices allows advantages like cost  
36 reduction, improved integration and reduced capacitance, which has motivated research in nanowire  
37 (NW) devices<sup>9-12</sup>. GaN NW UV photodetectors are interesting since they can present low dark current  
38 and excellent spectral selectivity, but their photoresponse usually scales sub-linearly with the optical  
39 power due to surface effects<sup>13,14</sup>. Linearity can be obtained in the case of reverse-biased very thin,  
40 entirely depleted NWs<sup>15</sup>, or in reverse-biased *p-n* junctions<sup>14</sup>.

41 Vertically aligned GaN NWs on a conductive substrate can be obtained by bottom-up methods  
42 (metal-seeded/catalyst-free growth or selective area growth) or by top-down fabrication from planar  
43 layers. The bottom-up synthesis of NWs offers lower density of extended defects<sup>16</sup> and the possibility  
44 to combine materials with different lattice parameter thanks to the elastic surface relaxation of the  
45 wires<sup>17,18</sup>. However, it suffers from issues like non-uniform doping<sup>19</sup>, defects due to the NW  
46 coalescence<sup>20,21</sup>, and morphological inhomogeneities<sup>22,23</sup>. On the other hand, top-down nanowires  
47 produced through etching processes<sup>24,25</sup> present improved doping control and higher uniformity, but the  
48 reduction in diameter may present limitations related to the crystalline defects induced during the etching

49 process<sup>26</sup>.

50 The fabrication of nanometer-scale patterns in top-down approaches can be achieved using  
51 various techniques such as electron beam lithography (EBL), nano-imprint and deep UV lithography.  
52 However, it is worth noting that the former is known for being expensive, due to the need to use  
53 dedicated patterning equipment, and EBL can be time-consuming (i.e., not scalable). In contrast,  
54 alongside nano-imprint, nanosphere lithography offers an approach that allows large-area fabrication  
55 (scalable) and at a relatively low cost. Nanosphere lithography is a route that has been used to produce  
56 large area top-down GaN NWs<sup>27-33</sup>. Long NWs require large nanospheres, in order to have a mask that  
57 withstands the long dry etching process. However, this imposes a limitation to reduce the nanowire  
58 diameter. Long nanowires with high aspect ratio are required for flexible electronics<sup>34</sup> or energy  
59 conversion devices<sup>35</sup>, for instance. Diameter and aspect ratio are also important in nanowire photonic  
60 devices: To exploit the advantages of the nanowire geometry, the diameter of the objects must be shorter  
61 than the wavelength of the interacting photons<sup>36,37</sup>, and the nanowire diameter is critical to obtain linear  
62 devices<sup>15,38</sup>.

63 In the last years, different authors<sup>30,32</sup> have shown the fabrication of GaN LEDs decoupling the  
64 NW pattern formation (defined by polystyrene nanospheres) and the nanowire length, by using a metal  
65 layer as hard mask for the dry/wet etching steps. However, the resulting nanowires were either relatively  
66 thick (diameter > 400 nm) or had limited aspect ratio (length/diameter < 17).

67 In this work, we have used a similar approach to demonstrate the fabrication of top-down UV  
68 photodetectors based on single GaN *p-i-n* junction nanowires, using Cl<sub>2</sub>-BCl<sub>3</sub> dry etching and KOH-  
69 based wet etching. We show that the combination of polystyrene nanospheres and a SiO<sub>2</sub> layer as hard  
70 mask allows the independent control over the nanowire length and pitch of the nanowire array and can  
71 produce large area thin nanowires with aspect ratio higher than 30. Current-voltage (I-V), differential  
72 phase contrast (DPC) with a segmented detector in scanning transmission electron microscopy (STEM)  
73 and electron beam induced current (EBIC) measurements confirm the presence of the built-in electric  
74 field due to the *p-i-n* junction, in a lamella sample and as-fabricated NW, respectively. The performance  
75 of a single GaN *p-i-n* junction NW is studied by photocurrent measurements: an enhancement in the  
76 photocurrent under reverse bias and a linear response with the excitation power is observed at all applied  
77 bias values between -2 and 2V. These results show that linear UV photodetectors based on GaN *p-i-n*  
78 nanowires can be achieved using a low-cost scalable process.

79

## 80 2 Experimental

81 The GaN *p-i-n* planar sample was grown on c-sapphire substrates by Metal Organic Vapor Phase  
82 Epitaxy (MOVPE), as schematically shown in Fig. 1(a), using trimethylgallium (TMGa) and ammonia  
83 (NH<sub>3</sub>) as precursors. The sample consists of a 700-nm-thick non-intentionally-doped GaN buffer layer  
84 grown at 1050°C, followed by 1.8-μm-thick *n*-doped GaN<sup>39</sup>, a 45-nm-thick intermediate (undoped)  
85 region, and a 1.9-μm-thick *p*-doped region<sup>40</sup>, as indicated in Fig. 1(a). Doping was achieved by using  
86 diluted silane (SiH<sub>4</sub>) at a growth temperature of 1050 °C for the *n*-type layer. Then, the silane flux is  
87 stopped and the temperature is reduced to 950°C in 90 s, corresponding to the growth of about 45 nm  
88 of unintentionally-doped GaN. Next, the *p*-type segment is grown using biscyclopentadienyl-  
89 magnesium (MgCp<sub>2</sub>) for the Mg doping. An annealing step at 700°C for 20 min under N<sub>2</sub> is performed  
90 at the end of the growth process, followed by a post-growth rapid thermal annealing at 800°C for 1 min  
91 under 500 sccm of N<sub>2</sub> to activate the Mg-dopants. As expected for a standard planar GaN growth by  
92 MOCVD on sapphire, the sample is a Ga-polar specimen.

93 A 350-nm-thick lamella specimen was prepared using a FEI Strata dual-beam focused ion beam  
94 (FIB). STEM-DPC was used to confirm the presence of the built-in electric field due to the *p-i-n*  
95 junction. The DPC was performed using a four-quadrant detector in a FEI Titan Ultimate aberration-  
96 corrected (S)TEM microscope operated at 200 kV with a condenser aperture of 50 μm, semi-  
97 convergence angle of 0.18 mrad, beam current of 93 pA, camera length of 13.5 m, pixel (step) size of 4  
98 nm and dwell time of 20 μs.

99 The electron beam induced current (EBIC) experiment was performed in an FEI Inspect F50  
100 SEM. Data were acquired at 4 kV with a beam current of 20 pA. The EBIC current was collected using  
101 a Keithley 6485 picoamp meter. Current-voltage (I-V) measurements were recorded using an Agilent  
102 4155C semiconductor parameter analyzer. Photocurrent measurements as function of optical power

103 were carried out using an unfocused continuous-wave HeCd laser at 325 nm. The nanowire was biased  
104 and connected to the  $\times 10^6$  V/A transimpedance amplifier integrated in a Stanford Research Systems  
105 SRS830 lock-in amplifier. All measurements were carried out at room temperature.

### 106 3 Results and discussion

108 Fig. 1(b) shows secondary ion mass spectrometry (SIMS) profiles of the planar GaN *p-i-n*  
109 sample under study. The dopant concentration in the bulk areas is about  $[\text{Si}] = 4.9 \times 10^{18} \text{ cm}^{-3}$  and  $[\text{Mg}] =$   
110  $3.9 \times 10^{19} \text{ cm}^{-3}$ . The presence of the built-in electric field due to the *p-i-n* junction was confirmed by  
111 DPC-STEM (Fig. 2(a)) using a low magnification STEM mode<sup>41,42</sup>, measured in a 350 nm thick lamella  
112 prepared by FIB, Fig. 2(b). In DPC, the deflection of the electron beam is measured on a four-quadrant  
113 detector. Taking the difference of incident electron intensity on opposing quadrants, the deflection of the  
114 electron beam due to the internal fields can be visualized at nm length scales. Due to the electric field,  
115 the beam is deflected towards the *n* layer (turquoise color coding in Fig. 2(a)). The sample was tilted  
116 off-axis in order to minimize the diffraction contrast. The field was clearly visible as a horizontal  
117 turquoise line parallel to the sample surface, at the expected location, i.e. 1.9  $\mu\text{m}$  below the sample  
118 surface. A depletion width of  $(50 \pm 11)$  nm was measured, as illustrated in Fig. 2(c), which is in good  
119 agreement with the expected width of the intermediate region. Both the SIMS and DPC experimental  
120 results allowed to validate the quality of the planar *p-i-n* junction according to the growth conditions in  
121 terms of doping concentration, presence of a built-in electric field and depletion region prior to the  
122 nanowire fabrication.

123 The fabrication process of top-down nanowires is adapted from the two-step crystallographic-  
124 selective etching described in ref.<sup>43</sup>. Taking that information as a reference, we performed tests using  
125 both silica and polystyrene spheres, and we considered several diameters (details can be found in  
126 supporting information S11). In a first experiment, we observed that it was not possible to use silica  
127 spheres directly as masks for producing a pattern of long GaN NWs since the etching cannot penetrate  
128 deep between the NWs (see Supporting Information Fig. S1a and b). Therefore, in order to create a  
129 pattern of well-separated dots to serve as a mask for the dry etching of GaN NWs, it is important to be  
130 able to shrink the diameter of the nanospheres, to separate them. Unfortunately, attempts to reduce the  
131 sphere diameter using  $\text{SF}_6$  and  $\text{O}_2$  led to a degradation of the spherical morphology (see Supporting  
132 Information Fig. S1c). As a result, they were unsuitable for generating a pattern of NWs. In view of  
133 these problems, we decided to use polystyrene spheres as a mask (details in Supporting Information  
134 SI2). In a first attempt, we used polystyrene spheres with a diameter of 3.2  $\mu\text{m}$ , as shown in Supporting  
135 Information SI2. This choice was motivated by the ability to uniformly reduce their diameter using a  
136 RIE  $\text{O}_2$  plasma. Well defined and separated array of GaN structures were produced (see Supporting  
137 Information Fig. S2), however, with limited aspect ratio and diameter, due to concurrent etching of the  
138 Ga-polar *c*-plane during the KOH-based etching process and the limited selectivity of the polystyrene  
139 as a mask for GaN dry etching, details can be found in Supporting Information SI2. Therefore, in order  
140 to achieve a well separated and defined array of high aspect (length/diameter) ratio nanowires with  
141 diameters below 200 nm, we decided to follow a process where we combine 1  $\mu\text{m}$  polystyrene spheres  
142 and a 600 nm thick  $\text{SiO}_2$  layer as mask. The shrunk polystyrene spheres are used to create the nm-scale  
143 pattern, then the pattern is transferred to the  $\text{SiO}_2$ , which is used as a hard mask for GaN dry and wet  
144 etchings.

145 The final process is described schematically in Figure 3, and experimental SEM images are  
146 shown of respective fabrication steps in Figure 4. The top down fabrication was carried out on  $7 \times 7 \text{ mm}^2$   
147 specimens that were diced from the as-grown wafer. First, a 600 nm  $\text{SiO}_2$  layer was deposited on top of  
148 the GaN *p-i-n* planar sample using plasma-enhanced chemical vapor deposition (PECVD). Then,  
149 polystyrene spheres with a diameter of 1  $\mu\text{m}$  were drop cast on top of the  $\text{SiO}_2$  layer. To obtain a  
150 monolayer coverage of the sample, we prepared a dilution of 1% weight in water so that the good amount  
151 of spheres is contained in a 50  $\mu\text{l}$  droplet. The droplet was applied on the sample with a micropipette,  
152 and dried at an angle of  $10^\circ$  (with respect to the horizontal plane)<sup>44</sup>. The result was the single-layer  
153 compact-hexagonal distribution, as depicted in Fig. 3(a) and shown in Fig. 4(a). The space between the  
154 nanospheres is a key parameter for the next etching steps: if there is not enough space between  
155 consecutive structures, the fabrication will produce connected nanowires (see Supporting Information  
156 S1). To obtain a good separation of the nanowires, the diameter of polystyrene nanospheres was reduced

157 to approximately 550 nm (leaving about 450 nm space between them) using oxygen plasma in a reactive  
158 ion etching (RIE) system, see Fig. 3(b) and Fig. 4(b). This was performed in two steps to prevent a  
159 degradation of the sphere morphology the shrinking was made in two steps, using first a 5 min O<sub>2</sub> plasma  
160 at RF power = 20 W (and O<sub>2</sub> flow = 50 sccm, DC bias 250V, 0.070 mbar), followed by a second softer  
161 etching performed at 10 W RF power (and O<sub>2</sub> flow = 50 sccm, DC bias 160V, 0.070 mbar) for 8 min. It  
162 is important to note that the nanospheres cannot shrink more than half of their diameter, otherwise they  
163 lose their spherical morphology (see Supporting Information Fig. S3), which will affect the uniformity  
164 of the nanowire array.

165 Using the shrunk spheres as a mask, SiO<sub>2</sub> etching was performed using a RIE system with CHF<sub>3</sub>  
166 chemistry (RF power of 50 W, DC bias 390V, 15 sccm CHF<sub>3</sub> flow, 0.02 mbar pressure) for 25 min, see  
167 Fig. 3(c) and Supporting Information Fig. S4. After nanosphere removal in an ultrasonic methanol bath,  
168 the GaN sample was dry etched in an inductively coupled plasma (ICP) RIE system using CL<sub>2</sub>-BCl<sub>3</sub>  
169 chemistry (30 W radio-frequency power, 100 W ICP power, 10 mTorr pressure, 10 sccm Cl<sub>2</sub> flow, 30  
170 sccm BCl<sub>3</sub> flow, at 20°C for 150 min), as depicted in Fig. 3(d) and shown in Fig. 4(c). The etching rate  
171 for the sample under study was around 17 nm/min, resulting in 2.6 μm-long GaN nanowires, see Fig.  
172 3(d) and Fig. 4(c). The sidewall angle formed after the dry etching was  $\theta = (6 \pm 1)^\circ$ , as illustrated in  
173 Fig. 3(d). Due to the sidewall angle obtained after dry etching, the maximum NW length ( $L_{dry,max}$ ) is  
174 a function of the separation between consecutive spheres ( $t_{gap}$ ) and given by  $L_{max} = \frac{t_{gap}}{2\tan(\theta)}$ . Thus,  
175 using the parameter described here,  $t_{gap} = 450\text{ nm}$ , the maximum achievable length an array of well  
176 separated nanowire is around  $(2.1 \pm 0.3)\ \mu\text{m}$ .

177 Finally, wet etching in AZ400K (KOH containing developer) was used to smooth the NW  
178 sidewalls, removing the damaged material and exposing the  $m$ -{10-10} planes,<sup>43</sup> as illustrated in Fig.  
179 3(e) and shown in Fig. 4(c). Wet etching was performed at 65°C for 6-8 h, depending on the desired  
180 nanowire diameter, resulting in an ~ 60 nm/h etching rate of the nanowire sidewalls. The final nanowire  
181 length was 2.3 μm (see Supporting Information Fig. S5), with a dispersion in NW diameter between 60-  
182 200 nm, see Fig. 3(e). A total yield as good as 70% was observed. Etching of the top c-plane in Ga-polar  
183 GaN using KOH is expected, as previously reported<sup>45,46</sup>. Thus, a shortening of the nanowire length is  
184 expected after the wet etching, as depicted in Fig. 3(e). We have measured a roughly SiO<sub>2</sub> etching rate  
185 during the dry etching (~ 2 nm/min), which means that an approximately 300 nm SiO<sub>2</sub> remained after  
186 the step IV. This remained SiO<sub>2</sub> layer acted as a protective layer for the wet etching, at least in the  
187 beginning of the process, since it will be also etched at same point, as illustrated in Fig. 3(e). We have  
188 measured also the etching rate of the SiO<sub>2</sub> on the AZ400K at 65 °C, ~ 100 nm/h. Then, some etching of  
189 the top facet in the fabricated nanowires is expected.

190 The nanowires were mechanically detached from the sample and dispersed on a 40-nm-thick  
191 Si<sub>3</sub>N<sub>4</sub> membrane chip by drop casting<sup>23</sup>. Single thin NWs (diameter below 100 nm) were electrically  
192 contacted by electron beam lithography and electron-beam evaporation of Ni/Au (150 nm/150 nm). In  
193 order to study the electric field created by the  $p$ - $i$ - $n$  junction, as well as the quality of the contacts on the  
194 fabricated NW devices, we performed EBIC measurements. In an EBIC experiment performed in a  $p$ - $n$   
195 junction, the electron-hole pairs created by the primary beam will be separated by the built-in electric  
196 field present in the depletion region, and the carriers will be collected in one of the two sides, generating  
197 an increase in the EBIC current only when its probing a region containing an internal field, mapping the  
198 presence of electric fields in the sample. In the absence of schottky induced fields, for a perfect  $p$ - $n$   
199 junction, a clear peak should be observed.<sup>47,48</sup> The collection side defines which carrier will be measured,  
200 electrons from the  $n$ -side (holes from the  $p$ -side); thus, inverting the collecting side, the same peak, with  
201 an inversion on the signal of EBIC current should be observed.

202 In Fig. 5(a) we can see the results of the EBIC performed in a single GaN NW. Collecting the  
203 current from the  $p$ -side, orange profile in Fig. 5(a), the presence of an internal field is clearly observed  
204 as a positive current peak close to the left contact in Fig. 5(a). We can also see that the contact at the  $p$ -  
205 side is ohmic: no current peak related with a Schottky barrier is observed near the right contact on the  
206  $p$ -type GaN. Inverting the current collection side, an inversion in the EBIC current is observed (see  
207 green EBIC signal in Fig. 5(a)), as expected in a  $p$ - $n$  junction. Using Ni/Au to contact the  $n$ -side, and  
208 due to its high doping level, we expect the formation of a low resistance contact due to tunneling  
209 transport, however, because of the proximity with the field created by the  $p$ - $i$ - $n$  junction, the observation  
210 of a possible Schottky contact in the  $n$ -side is hindered. The unique and very localized EBIC peak at the

211 expected position (more than 1  $\mu\text{m}$  from the p-side, i.e. the top facet of the planar sample), and the  
 212 inversion of the EBIC current when the collection side is changed, observed in Fig. 5(a), strongly suggest  
 213 the presence of a built-in electric field created by the *p-i-n* junction. In addition, it demonstrates that the  
 214 nanowire is not entirely depleted. In the case of a fully depleted NW it is expected that the EBIC signal  
 215 extends over the entire NW length, as previously observed<sup>14</sup>.

216 The relation between the depletion region width ( $W_d$ ) and the surface band bending ( $\phi_{sbb}$ ) is  
 217 given by  $\sqrt{4\epsilon_0\epsilon_s\phi_{sbb}/q^2N_{A,D}}$  where  $\epsilon_s = 9.5$  is the dielectric constant of GaN,  $\epsilon_0 = 8.85 \times 10^{-14} \text{ C}^2/\text{Vcm}$   
 218 is the vacuum permeability,  $q = 1.6 \times 10^{-19} \text{ C}$  is the elementary charge and  $N_{A,D}$  is the dopant  
 219 density of the *p* or *n* regions. Assuming a band bending of 1.4 eV for the p-side<sup>49</sup> and 0.6 eV for the n-  
 220 side<sup>50,51</sup> at the doping level measured by SIMS measurements ( $[Mg] = 3.9 \times$   
 221  $10^{19} \text{ cm}^{-3}$ ;  $[\text{Si}] = 4.9 \times 10^{18} \text{ cm}^{-3}$ ), the depletion region length at the surface of the *p*-type and *n*-  
 222 type sides of the nanowire would be around  $W_{d,p \text{ region}} \cong 9 \text{ nm}$  and  $W_{d,n \text{ region}} \cong 16 \text{ nm}$ , respectively,  
 223 much smaller than the diameter, around 75 nm (aspect ratio 31). However, the short intermediate  
 224 undoped region is expected to be fully depleted, as schematically shown in Fig. 5(b).

225 Fig. 5(c) shows the I–V characteristics of the same NW depicted in Fig. 5(a), recorded in the  
 226 dark and under illumination at 325 nm, applying bias to the *p*-side of the nanowire with the *n*-side  
 227 connected to ground. The device displays the expected rectifying behavior, with an increase of the  
 228 current under UV illumination. The variation of the photocurrent ( $I_{ph}$ ) as a function of the incident optical  
 229 power ( $P$ ) was studied under bias in the range of +2V to -2V, with the result presented in Fig. 6. The  
 230 photocurrent scales linearly with the optical power for all the values of bias under study, both forward  
 231 and reverse bias. This trend is consistent with the trend observed in planar GaN *p-i-n* photodiodes<sup>52</sup>, but  
 232 it is unusual in single-NW photodetectors. Linear single-NW photodetectors have been demonstrated  
 233 only under reverse bias, these detectors become non-linear under forward bias<sup>14,15</sup>. Under increasing  
 234 reverse bias (forward bias), a broadening (narrowing) of the *p-i-n* junction depletion region is expected  
 235 and, consequently, more (less) photogenerated electron-hole pairs are collected, increasing (decreasing)  
 236 the photocurrent. The linearity observed here at +2 V bias (Fig. 6) implies that there is still a depletion  
 237 region in the intrinsic segment, allowing the drift collection of photogenerated electron-hole pairs.

238 Previous UV photodetectors based on GaN nanowires containing a p-n junction<sup>14</sup> or not<sup>13,15</sup>  
 239 presented sublinear photoresponse for nanowires with a large diameter. In general, non-core-shell GaN  
 240 single-NW photodetectors present a sublinear photoresponse with excitation power due to the  
 241 modulation of the surface band bending under illumination.<sup>15</sup> As a result of Fermi level pinning at the  
 242 nanowire sidewalls, surface band bending occurs, and the region near to the nanowire surface is  
 243 depleted, however, mobile charges are still present in the nanowire core, for larger diameter nanowires.  
 244 Ultraviolet illumination is known to unpin the Fermi level at the nanowire sidewalls.<sup>53</sup> The photocurrent  
 245 will be mainly generated in the conductive nanowire core. Thus, the variation of the surface band  
 246 bending upon UV illumination will modify the region where photons are collected in a nonlinear way,  
 247 for the larger diameter NWs, leading to the sublinear photoresponse. It is interesting that the sublinear  
 248 photoresponse can be avoided by making NWs with a small diameter. In this case, they are totally  
 249 depleted, and the light-induced change in the Fermi level at the sidewalls will not be the dominant  
 250 phenomenon, making the photoresponse linear.<sup>15</sup>

251 Here, the linearity of the photocurrent is attributed to the presence of a *p-i-n* structure. The  
 252 photodetection occurs mainly in the intrinsic region due to the presence of the electric field generated  
 253 by the *p* and *n* regions. The intrinsic region is totally depleted, due to the small diameter of the nanowire  
 254 under study. Thus, the presence of the intrinsic region guarantees the linear photoresponse. Also, in the  
 255 NW under study, the *p* and *n* regions are not fully depleted, which means that the diode has a series  
 256 resistance that is sensitive to surface states. However, the linear photoresponse observed here implies  
 257 that the photocurrent is dominated by carrier drift in the depletion region, whose effect is dominant with  
 258 respect to the NW surface. The fact that, even under forward bias (in our work +2V), the detector  
 259 behaves linearly, indicates that we still have a depletion region in the intrinsic section, different from a  
 260 simple *p-n* junction nanowire.<sup>14</sup> Therefore, in contrast to previous works, our results show that it is  
 261 possible to fabricate linear UV photodetectors over a wider applied bias range based on GaN nanowires  
 262 by exploiting an axial *p-i-n* structure and a small diameter at the same time, leading to an axial built-in  
 263 electric field induced by the *p-i-n* junction being dominant over surface effects. In addition, a *p-i-n*  
 264 structure is interesting because the partially depleted *n* and *p*-segments, in principle, would allow the

265 detection of higher electrical currents (if better ohmic contacts are made), which is not the case in a  
266 linear single-NW photodetector that is entirely depleted.

267

## 268 **4 Conclusions**

269 In summary, we have developed a process to fabricate top-down GaN nanowires combining  
270 nanosphere lithography, CHF<sub>3</sub>-based ICP-RIE and KOH-based crystallographic-selective wet etching.  
271 Long (> 2 μm) NWs with diameters below 200 nm with smooth sidewalls and aspect ratios above 30  
272 were obtained from a planar sample containing a *p-i-n* structure. The formation of the *p-i-n* junction was  
273 investigated by SIMS and STEM-DPC on the as grown sample and a FIB lamella tailored from the as-  
274 grown sample. Moreover, the *p-i-n* junction was studied by EBIC, IV and power dependent photocurrent  
275 measurements. A dopant concentration of  $N_D = 4.9 \times 10^{18} \text{ cm}^{-3}$  and  $N_A = 3.9 \times 10^{19} \text{ cm}^{-3}$  was  
276 revealed by SIMS, with a 50 nm depletion width at zero-bias measured by DPC, as expected from the  
277 growth conditions. The top-down fabrication process did not affect the electrical behavior of the *p-i-n*  
278 junction, as confirmed by EBIC and current-voltage measurements. The investigation of the  
279 performance of the top-down NWs as single-NW photodetectors showed a linear response as a function  
280 of the UV excitation power, which implies that the photoresponse is dominated by carrier drift in the  
281 depletion region, whose effect is dominant with respect to the NW surface effects. As an outlook, it  
282 would be interesting to study the electro-optical variability between as fabricated single nanowire  
283 photodetectors, to assess the influence of small diameter variations as well as the potential influence of  
284 crystal defects. Moreover, it would be interesting to measure the internal electric field more  
285 quantitatively both inside the nanowire as well as in the FIB lamella, similar to the studies shown for  
286 more traditional semiconductors<sup>54</sup>. Finally, these studies will also show optimal NW fabrication  
287 conditions allowing reliable fabrication of planarized nanowire array photodetectors.

## 288 **Corresponding authors**

289 bruno-cesar.da-silva@neel.cnrs.fr, martien.den-hertog@neel.cnrs.fr

## 290 **Supporting Information**

291 The Supporting Information is available free of charge at  
292 <https://pubs.acs.org/doi/10.1021/acsanm.3c01495>.

293

- 294 • Additional SEM images of the NW fabrication process using nanosphere lithography (PDF)

295

## 296 **Acknowledgement**

297 This project received funding from the European Research Council under the European Union's  
298 H2020 Research and Innovation programme via the e-See project (Grant No. 758385). This work was  
299 also partially funded by the Program Initiatives de Recherche Stratégiques (IRS) of IDEX Université  
300 Grenoble Alpes (ANR-15-IDEX-0002) and by the French National Research Agency in the framework  
301 of the HARAIN program ANR-22-CE51-0032. A CC-BY public copyright license has been applied by  
302 the authors to the present document and will be applied to all subsequent versions up to the Author  
303 Accepted Manuscript arising from this submission, in accordance with the grant's open access  
304 conditions. These experiments have been performed at the Nanocharacterisation platform PFNC in  
305 Minatec, Grenoble.

## 306 **Data Availability Statement**

307 The data that support the findings of this study are available from the corresponding authors  
308 upon reasonable request.

## 309 **Notes**

310 The authors declare no competing financial interest.

## 311 **References**

- 312 (1) Cai, Q.; You, H.; Guo, H.; Wang, J.; Liu, B.; Xie, Z.; Chen, D.; Lu, H.; Zheng, Y.; Zhang, R.  
313 Progress on AlGa<sub>N</sub>-Based Solar-Blind Ultraviolet Photodetectors and Focal Plane Arrays. *Light*  
314 *Sci Appl* **2021**, *10* (1), 94. <https://doi.org/10.1038/s41377-021-00527-4>.
- 315 (2) Peng, L.; Hu, L.; Fang, X. Low-Dimensional Nanostructure Ultraviolet Photodetectors. *Adv.*  
316 *Mater.* **2013**, *25* (37), 5321–5328. <https://doi.org/10.1002/adma.201301802>.
- 317 (3) Chen, H.; Liu, K.; Hu, L.; Al-Ghamdi, A. A.; Fang, X. New Concept Ultraviolet Photodetectors.  
318 *Materials Today* **2015**, *18* (9), 493–502. <https://doi.org/10.1016/j.mattod.2015.06.001>.
- 319 (4) Sang, L.; Liao, M.; Sumiya, M. A Comprehensive Review of Semiconductor Ultraviolet  
320 Photodetectors: From Thin Film to One-Dimensional Nanostructures. *Sensors* **2013**, *13* (8),  
321 10482–10518. <https://doi.org/10.3390/s130810482>.
- 322 (5) Monroy, E.; Muñoz, E.; Sánchez, F. J.; Calle, F.; Calleja, E.; Beaumont, B.; Gibart, P.; Muñoz, J.  
323 A.; Cussó, F. High-Performance GaN p-n Junction Photodetectors for Solar Ultraviolet  
324 Applications. *Semicond. Sci. Technol.* **1998**, *13* (9), 1042–1046. <https://doi.org/10.1088/0268-1242/13/9/013>.
- 326 (6) Zhang, Y.; Shen, S.-C.; Kim, H. J.; Choi, S.; Ryou, J.-H.; Dupuis, R. D.; Narayan, B. Low-Noise  
327 GaN Ultraviolet p-i-n Photodiodes on GaN Substrates. *Appl. Phys. Lett.* **2009**, *94* (22), 221109.  
328 <https://doi.org/10.1063/1.3148812>.
- 329 (7) Ji, M.-H.; Kim, J.; Detchprohm, T.; Dupuis, R. D.; Sood, A. K.; Dhar, N. K.; Lewis, J. Uniform  
330 and Reliable GaN P-i-n Ultraviolet Avalanche Photodiode Arrays. *IEEE Photon. Technol. Lett.*  
331 **2016**, *28* (19), 2015–2018. <https://doi.org/10.1109/LPT.2016.2580038>.
- 332 (8) Ji, D.; Ercan, B.; Benson, G.; Newaz, A. K. M.; Chowdhury, S. 60 A/W High Voltage GaN  
333 Avalanche Photodiode Demonstrating Robust Avalanche and High Gain up to 525 K. *Appl. Phys.*  
334 *Lett.* **2020**, *116* (21), 211102. <https://doi.org/10.1063/1.5140005>.
- 335 (9) Kind, H.; Yan, H.; Messer, B.; Law, M.; Yang, P. Nanowire Ultraviolet Photodetectors and Optical  
336 Switches. *Advanced Materials* **2002**, *14* (2), 158–160. [https://doi.org/10.1002/1521-4095\(20020116\)14:2<158::AID-ADMA158>3.0.CO;2-W](https://doi.org/10.1002/1521-4095(20020116)14:2<158::AID-ADMA158>3.0.CO;2-W).
- 338 (10) Soci, C.; Zhang, A.; Bao, X.-Y.; Kim, H.; Lo, Y.; Wang, D. Nanowire Photodetectors. *J nanosci*  
339 *nanotechnol* **2010**, *10* (3), 1430–1449. <https://doi.org/10.1166/jnn.2010.2157>.
- 340 (11) LaPierre, R. R.; Robson, M.; Azizur-Rahman, K. M.; Kuyanov, P. A Review of III–V Nanowire  
341 Infrared Photodetectors and Sensors. *Journal of Physics D: Applied Physics* **2017**, *50* (12),  
342 123001. <https://doi.org/10.1088/1361-6463/aa5ab3>.
- 343 (12) Spies, M.; Monroy, E. Nanowire Photodetectors Based on Wurtzite Semiconductor  
344 Heterostructures. *Semicond. Sci. Technol.* **2019**, *34* (5), 053002. <https://doi.org/10.1088/1361-6641/ab0cb8>.
- 346 (13) González-Posada, F.; Songmuang, R.; Den Hertog, M.; Monroy, E. Room-Temperature  
347 Photodetection Dynamics of Single GaN Nanowires. *Nano Lett.* **2012**, *12* (1), 172–176.  
348 <https://doi.org/10.1021/nl2032684>.
- 349 (14) Cuesta, S.; Spies, M.; Boureau, V.; Donatini, F.; Hocevar, M.; den Hertog, M. I.; Monroy, E.  
350 Effect of Bias on the Response of GaN Axial p–n Junction Single-Nanowire Photodetectors. *Nano*  
351 *Lett.* **2019**, *19* (8), 5506–5514. <https://doi.org/10.1021/acs.nanolett.9b02040>.
- 352 (15) Spies, M.; Polaczyński, J.; Ajay, A.; Kalita, D.; Luong, M. A.; Lähnemann, J.; Gayral, B.; den  
353 Hertog, M. I.; Monroy, E. Effect of the Nanowire Diameter on the Linearity of the Response of  
354 GaN-Based Heterostructured Nanowire Photodetectors. *Nanotechnology* **2018**, *29* (25), 255204.  
355 <https://doi.org/10.1088/1361-6528/aab838>.
- 356 (16) Bertness, K. A.; Sanford, N. A.; Davydov, A. V. GaN Nanowires Grown by Molecular Beam  
357 Epitaxy. *IEEE J. Select. Topics Quantum Electron.* **2011**, *17* (4), 847–858.  
358 <https://doi.org/10.1109/JSTQE.2010.2082504>.
- 359 (17) Knelangen, M.; Consonni, V.; Trampert, A.; Riechert, H. *In Situ* Analysis of Strain Relaxation  
360 during Catalyst-Free Nucleation and Growth of GaN Nanowires. *Nanotechnology* **2010**, *21* (24),  
361 245705. <https://doi.org/10.1088/0957-4484/21/24/245705>.
- 362 (18) Landré, O.; Bougerol, C.; Renevier, H.; Daudin, B. Nucleation Mechanism of GaN Nanowires  
363 Grown on (111) Si by Molecular Beam Epitaxy. *Nanotechnology* **2009**, *20* (41), 415602.  
364 <https://doi.org/10.1088/0957-4484/20/41/415602>.



- 365 (19) Kim, W.; Güniat, L.; Fontcuberta i Morral, A.; Piazza, V. Doping Challenges and Pathways to  
366 Industrial Scalability of III–V Nanowire Arrays. *Applied Physics Reviews* **2021**, *8* (1), 011304.  
367 <https://doi.org/10.1063/5.0031549>.
- 368 (20) Grossklaus, K. A.; Banerjee, A.; Jahangir, S.; Bhattacharya, P.; Millunchick, J. M. Misorientation  
369 Defects in Coalesced Self-Catalyzed GaN Nanowires. *Journal of Crystal Growth* **2013**, *371*, 142–  
370 147. <https://doi.org/10.1016/j.jcrysgro.2013.02.019>.
- 371 (21) Brandt, O.; Fernández-Garrido, S.; Zettler, J. K.; Luna, E.; Jahn, U.; Chèze, C.; Kaganer, V. M.  
372 Statistical Analysis of the Shape of One-Dimensional Nanostructures: Determining the  
373 Coalescence Degree of Spontaneously Formed GaN Nanowires. *Crystal Growth & Design* **2014**,  
374 *14* (5), 2246–2253. <https://doi.org/10.1021/cg401838q>.
- 375 (22) Gomes, U. P.; Ercolani, D.; Zannier, V.; Beltram, F.; Sorba, L. Controlling the Diameter  
376 Distribution and Density of InAs Nanowires Grown by Au-Assisted Methods. *Semicond. Sci.*  
377 *Technol.* **2015**, *30* (11), 115012. <https://doi.org/10.1088/0268-1242/30/11/115012>.
- 378 (23) Spies, M.; Sadre Momtaz, Z.; Lähnemann, J.; Anh Luong, M.; Fernandez, B.; Fournier, T.;  
379 Monroy, E.; I den Hertog, M. Correlated and In-Situ Electrical Transmission Electron Microscopy  
380 Studies and Related Membrane-Chip Fabrication. *Nanotechnology* **2020**, *31* (47), 472001.  
381 <https://doi.org/10.1088/1361-6528/ab99f0>.
- 382 (24) Melanson, B.; Hartensveld, M.; Liu, C.; Zhang, J. Realization of Electrically Driven AlGaIn  
383 Micropillar Array Deep-Ultraviolet Light Emitting Diodes at 286 Nm. *AIP Advances* **2021**, *11* (9),  
384 095005. <https://doi.org/10.1063/5.0061381>.
- 385 (25) Hartensveld, M.; Melanson, B.; Liu, C.; Zhang, J. AlGaIn Nanowires with Inverse Taper for  
386 Flexible DUV Emitters. *J. Phys. Photonics* **2021**, *3* (2), 024016. <https://doi.org/10.1088/2515-7647/abf6be>.
- 388 (26) Olivier, F.; Tirano, S.; Dupré, L.; Aventurier, B.; Llargeron, C.; Templier, F. Influence of Size-  
389 Reduction on the Performances of GaN-Based Micro-LEDs for Display Application. *Journal of*  
390 *Luminescence* **2017**, *191*, 112–116. <https://doi.org/10.1016/j.jlumin.2016.09.052>.
- 391 (27) Cheung, C. L.; Nikolić, R. J.; Reinhardt, C. E.; Wang, T. F. Fabrication of Nanopillars by  
392 Nanosphere Lithography. *Nanotechnology* **2006**, *17* (5), 1339–1343.  
393 <https://doi.org/10.1088/0957-4484/17/5/028>.
- 394 (28) Kim, B.-J.; Jung, H.; Kim, H.-Y.; Bang, J.; Kim, J. Fabrication of GaN Nanorods by Inductively  
395 Coupled Plasma Etching via SiO<sub>2</sub> Nanosphere Lithography. *Thin Solid Films* **2009**, *517* (14),  
396 3859–3861. <https://doi.org/10.1016/j.tsf.2009.01.144>.
- 397 (29) Li, Q.; Westlake, K. R.; Crawford, M. H.; Lee, S. R.; Koleske, D. D.; Figiel, J. J.; Cross, K. C.;  
398 Fatholouloumi, S.; Mi, Z.; Wang, G. T. Optical Performance of Top-down Fabricated InGaIn/GaN  
399 Nanorod Light Emitting Diode Arrays. *Opt. Express* **2011**, *19* (25), 25528.  
400 <https://doi.org/10.1364/OE.19.025528>.
- 401 (30) Won Woo Chung; Gang Yeol Yoo; Park, H. K.; Kim, W.; Young Rag Do. Fabrication of an  
402 InGaIn/GaN-Based LED Nanorod Array by Nanosphere Lithography and Its Optical Properties.  
403 In *2015 IEEE 15th International Conference on Nanotechnology (IEEE-NANO)*; IEEE: Rome,  
404 2015; pp 216–219. <https://doi.org/10.1109/NANO.2015.7388961>.
- 405 (31) Granz, T.; Mariana, S.; Hamdana, G.; Yu, F.; Fatahilah, M. F.; Clavero, I. M.; Puranto, P.; Li, Z.;  
406 Brand, U.; Prades, J. D.; Peiner, E.; Waag, A.; Wasisto, H. S. Nanofabrication of Vertically  
407 Aligned 3D GaN Nanowire Arrays with Sub-50 Nm Feature Sizes Using Nanosphere Lift-off  
408 Lithography. In *Proceedings of Eurosensors 2017, Paris, France, 3–6 September 2017*; MDPI,  
409 2017; p 309. <https://doi.org/10.3390/proceedings1040309>.
- 410 (32) Mariana, S.; Gülink, J.; Hamdana, G.; Yu, F.; Stempel, K.; Spende, H.; Yulianto, N.; Granz, T.;  
411 Prades, J. D.; Peiner, E.; Wasisto, H. S.; Waag, A. Vertical GaN Nanowires and Nanoscale Light-  
412 Emitting-Diode Arrays for Lighting and Sensing Applications. *ACS Appl. Nano Mater.* **2019**, *2*  
413 (7), 4133–4142. <https://doi.org/10.1021/acsanm.9b00587>.
- 414 (33) Zou, X.; Zhang, X.; Zhang, Y.; Lyu, Q.; Tang, C. W.; Lau, K. M. GaN Single Nanowire p–i–n  
415 Diode for High-Temperature Operations. *ACS Appl. Electron. Mater.* **2020**, *2* (3), 719–724.  
416 <https://doi.org/10.1021/acsaelm.9b00801>.
- 417 (34) Zhang, H.; Dai, X.; Guan, N.; Messanvi, A.; Neplokh, V.; Piazza, V.; Vallo, M.; Bougerol, C.;  
418 Julien, F. H.; Babichev, A.; Cavassilas, N.; Bescond, M.; Michelini, F.; Foldyna, M.; Gautier, E.;  
419 Durand, C.; Eymery, J.; Tchernycheva, M. Flexible Photodiodes Based on Nitride Core/Shell p–n

- 420 Junction Nanowires. *ACS Appl. Mater. Interfaces* **2016**, *8* (39), 26198–26206.  
 421 <https://doi.org/10.1021/acsami.6b06414>.
- 422 (35) Gogneau, N.; Chrétien, P.; Sodhi, T.; Couraud, L.; Leroy, L.; Travers, L.; Harmand, J.-C.; Julien,  
 423 F. H.; Tchernycheva, M.; Houzé, F. Electromechanical Conversion Efficiency of GaN NWs:  
 424 Critical Influence of the NW Stiffness, the Schottky Nano-Contact and the Surface Charge Effects.  
 425 *Nanoscale* **2022**, *14* (13), 4965–4976. <https://doi.org/10.1039/D1NR07863A>.
- 426 (36) Krogstrup, P.; Jørgensen, H. I.; Heiss, M.; Demichel, O.; Holm, J. V.; Aagesen, M.; Nygard, J.;  
 427 Fontcuberta i Morral, A. Single-Nanowire Solar Cells beyond the Shockley–Queisser Limit.  
 428 *Nature Photonics* **2013**, *7* (4), 306–310. <https://doi.org/10.1038/nphoton.2013.32>.
- 429 (37) Xu, Y.; Gong, T.; Munday, J. N. The Generalized Shockley-Queisser Limit for Nanostructured  
 430 Solar Cells. *Scientific Reports* **2015**, *5*, 13536.
- 431 (38) Calarco, R.; Marso, M.; Richter, T.; Aykanat, A. I.; Meijers, R.; v.d. Hart, A.; Stoica, T.; Lüth, H.  
 432 Size-Dependent Photoconductivity in MBE-Grown GaN–Nanowires. *Nano Lett.* **2005**, *5* (5), 981–  
 433 984. <https://doi.org/10.1021/nl0500306>.
- 434 (39) Mukhtarova, A.; Valdueza-Felip, S.; Redaelli, L.; Durand, C.; Bougerol, C.; Monroy, E.; Eymery,  
 435 J. Dependence of the Photovoltaic Performance of Pseudomorphic InGaN/GaN Multiple-  
 436 Quantum-Well Solar Cells on the Active Region Thickness. *Appl. Phys. Lett.* **2016**, *108* (16),  
 437 161907. <https://doi.org/10.1063/1.4947445>.
- 438 (40) Mukhtarova, A.; Valdueza-Felip, S.; Durand, C.; Pan, Q.; Grenet, L.; Peyrade, D.; Bougerol, C.;  
 439 Chikhaoui, W.; Monroy, E.; Eymery, J. InGaN/GaN Multiple-quantum Well Heterostructures for  
 440 Solar Cells Grown by MOVPE: Case Studies. *Phys. Status Solidi C* **2013**, *10* (3), 350–354.  
 441 <https://doi.org/10.1002/pssc.201200682>.
- 442 (41) Haas, B.; Rouvière, J.-L.; Boureau, V.; Berthier, R.; Cooper, D. Direct Comparison of Off-Axis  
 443 Holography and Differential Phase Contrast for the Mapping of Electric Fields in Semiconductors  
 444 by Transmission Electron Microscopy. *Ultramicroscopy* **2019**, *198*, 58–72.  
 445 <https://doi.org/10.1016/j.ultramic.2018.12.003>.
- 446 (42) da Silva, B. C.; Momtaz, Z. S.; Bruas, L.; Rouviere, J.-L.; Okuno, H.; Cooper, D.; den-Hertog, M.  
 447 I. The Influence of Illumination Conditions in the Measurement of Built-in Electric Field at p–n  
 448 Junctions by 4D-STEM. *Applied Physics Letters* **2022**, *121* (12), 123503. [https://doi.org/DOI:  
 449 10.1063/5.0104861](https://doi.org/DOI:10.1063/5.0104861).
- 450 (43) Cuesta, S.; Denaix, L.; Castioni, F.; Dang, L. S.; Monroy, E. Reduction of the Lasing Threshold  
 451 in Optically Pumped AlGaIn/GaN Lasers with Two-Step Etched Facets. *Semicond. Sci. Technol.*  
 452 **2022**, *37* (7), 075013. <https://doi.org/10.1088/1361-6641/ac7164>.
- 453 (44) Liu, J.; Chen, C.; Yang, G.; Chen, Y.; Yang, C.-F. Effect of the Fabrication Parameters of the  
 454 Nanosphere Lithography Method on the Properties of the Deposited Au-Ag Nanoparticle Arrays.  
 455 *Materials* **2017**, *10* (4), 381. <https://doi.org/10.3390/ma10040381>.
- 456 (45) Oliva, M.; Kaganer, V.; Pudelski, M.; Meister, S.; Tahraoui, A.; Geelhaar, L.; Brandt, O.; Auzelle,  
 457 T. A Route for the Top-down Fabrication of Ordered Ultrathin GaN Nanowires. *Nanotechnology*  
 458 **2023**, *34* (20), 205301. <https://doi.org/10.1088/1361-6528/acb949>.
- 459 (46) Li, D.; Sumiya, M.; Yoshimura, K.; Suzuki, Y.; Fukuda, Y.; Fuke, S. Characteristics of the GaN  
 460 Polar Surface during an Etching Process in KOH Solution. *phys. stat. sol. (a)* **2000**, *180* (1), 357–  
 461 362. [https://doi.org/10.1002/1521-396X\(200007\)180:1<357::AID-PSSA357>3.0.CO;2-F](https://doi.org/10.1002/1521-396X(200007)180:1<357::AID-PSSA357>3.0.CO;2-F).
- 462 (47) Conlan, A. P.; Moldovan, G.; Bruas, L.; Monroy, E.; Cooper, D. Electron Beam Induced Current  
 463 Microscopy of Silicon p–n Junctions in a Scanning Transmission Electron Microscope. *Journal of*  
 464 *Applied Physics* **2021**, *129* (13), 135701. <https://doi.org/10.1063/5.0040243>.
- 465 (48) Tchoulfian, P.; Donatini, F.; Levy, F.; Dussaigne, A.; Ferret, P.; Pernot, J. Direct Imaging of p–n  
 466 Junction in Core–Shell GaN Wires. *Nano Lett.* **2014**, *14* (6), 3491–3498.  
 467 <https://doi.org/10.1021/nl5010493>.
- 468 (49) Hashizume, T. Effects of Mg Accumulation on Chemical and Electronic Properties of Mg-Doped  
 469 p -Type GaN Surface. *Journal of Applied Physics* **2003**, *94* (1), 431–436.  
 470 <https://doi.org/10.1063/1.1580195>.
- 471 (50) Van de Walle, C. G.; Segev, D. Microscopic Origins of Surface States on Nitride Surfaces. *Journal*  
 472 *of Applied Physics* **2007**, *101* (8), 081704. <https://doi.org/10.1063/1.2722731>.
- 473 (51) Lymperakis, L.; Weidlich, P. H.; Eisele, H.; Schnedler, M.; Nys, J.-P.; Grandidier, B.; Stiévenard,  
 474 D.; Dunin-Borkowski, R. E.; Neugebauer, J.; Ebert, Ph. Hidden Surface States at Non-Polar GaN

- 475 (101<sup>-0</sup>) Facets: Intrinsic Pinning of Nanowires. *Appl. Phys. Lett.* **2013**, *103* (15), 152101.  
476 <https://doi.org/10.1063/1.4823723>.
- 477 (52) Monroy, E.; Omnès, F.; Calle, F. Wide-Bandgap Semiconductor Ultraviolet Photodetectors.  
478 *Semicond. Sci. Technol.* **2003**, *18* (4), R33–R51. <https://doi.org/10.1088/0268-1242/18/4/201>.
- 479 (53) Pfüller, C.; Brandt, O.; Grosse, F.; Flissikowski, T.; Chèze, C.; Consonni, V.; Geelhaar, L.; Grahn,  
480 H. T.; Riechert, H. Unpinning the Fermi Level of GaN Nanowires by Ultraviolet Radiation. *Phys.*  
481 *Rev. B* **2010**, *82* (4), 045320. <https://doi.org/10.1103/PhysRevB.82.045320>.
- 482 (54) da Silva, B. C.; Sadre Momtaz, Z.; Monroy, E.; Okuno, H.; Rouviere, J.-L.; Cooper, D.; Den  
483 Hertog, M. I. Assessment of Active Dopants and p–n Junction Abruptness Using In Situ Biased  
484 4D-STEM. *Nano Lett.* **2022**, *22* (23), 9544–9550. <https://doi.org/10.1021/acs.nanolett.2c03684>.
- 485

486

487

488

489

490

491

492

493

494

495

496

497

498

499

500

501

502

503

504

505

506

507  
508  
509  
510  
511  
512  
513  
514  
515  
516  
517  
518  
519  
520  
521  
522  
523  
524  
525  
526  
527  
528  
529  
530  
531  
532  
533  
534  
535  
536  
537  
538  
539  
540  
541  
542  
543  
544  
545  
546  
547

## FIGURE CAPTIONS

**Figure 1** - (a) Schematic of the sample under study, a planar GaN *p-i-n* junction specimen grown by MOCVD. (b) SIMS of the sample shown in (a), indicating the dopant concentration in the bulk regions as  $n = 4.9 \times 10^{18} \text{ cm}^{-3}$  and  $p = 3.9 \times 10^{19} \text{ cm}^{-3}$ .

**Figure 2** - (a) Modulus of DPC-STEM image reflecting the strength of the electric field present in the 350 nm thick GaN lamella prepared from the sample shown in Figure 1. The DPC signal is proportional to the deflection of the electron beam, caused by the internal fields present in the sample. It is measured by taking the difference of incident electron intensity on two opposing quadrants of the DPC detector. A clear signal due to the presence of a built-in electric field created by the *p-i-n* is observed at the expected position (1.9  $\mu\text{m}$  below the top surface). Some artifacts are still present due to the strong dynamical diffraction in the GaN, in spite of the off-axis orientation. (b) High Angle Annular Dark Field (HAADF) STEM image of the lamella prepared by FIB of the sample shown in (a). (c) Beam deflection profile averaged over the entire DPC map shown in (a) taken across the *p-i-n* junction: a depletion region width of 50 nm is measured, in agreement with the expected intermediate intrinsic region.

**Figure 3** - Schematic of the optimized fabrication protocol to obtain the top-down GaN *p-i-n* junction nanowires: (a) Step I: Dispersion of 1  $\mu\text{m}$  polystyrene nanospheres. (b) Step II: Shrinking of the spheres using a RIE oxygen plasma. (c) Step III: Etching of  $\text{SiO}_2$  using RIE with  $\text{CHF}_3$  chemistry. (d) Step IV: Dry etching of GaN performed in an ICP-RIE using  $\text{BCL}_3\text{-Cl}_2$  chemistry. (e) Step V: Wet etching using AZ400K developer. As indicated in (c), due to the sidewall angle obtained after dry etching, the maximum NW length ( $L_{dry,max}$ ) is a function of the separation between consecutive spheres ( $t_{gap}$ ). The final NW length ( $L_{final}$ ) will be slightly shorter than  $L_{dry,max}$ , due to the etch of the top GaN facet, once the remaining  $\text{SiO}_2$  layer is removed.

**Figure 4** - SEM images of some of the GaN nanowire fabrication steps described in Figure 3. (a) step I. (b) step II. (c) step IV. (d) step V.

**Figure 5** - (a) EBIC scan along a single nanowire overlaid on an SEM image of the nanowire under study to illustrate where the scan was performed. The orange and green EBIC line scans correspond to current collection from the *n*-side and the *p*-side of the NW, respectively. (b) Schematic showing that the nanowire under study is partially depleted in the *n* and *p*-channels, while the intrinsic region is fully depleted. (c) I-V characteristics of the same NW shown in (a), in the dark (blue) and under ultraviolet illumination at 325 nm (red).

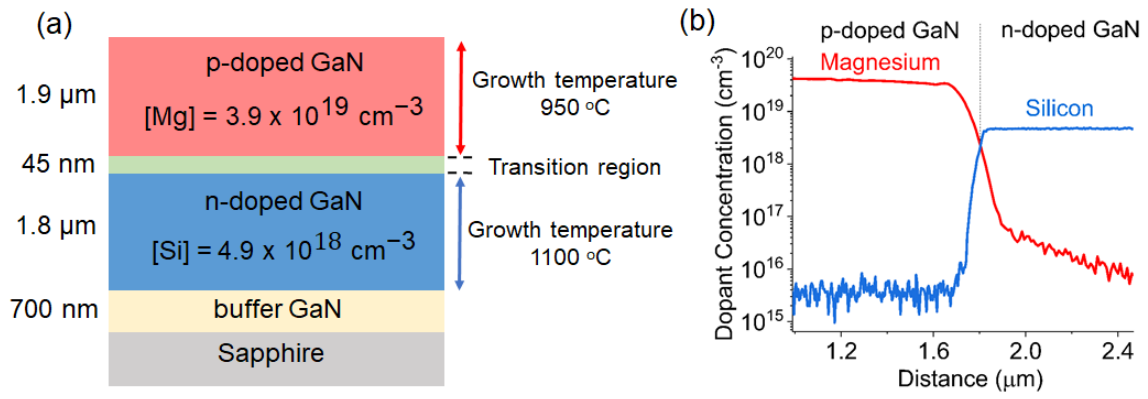
**Figure 6** - Photocurrent measurements of the GaN *p-i-n* NW shown in Figure 5 as a function of the impinging optical power at 325 nm, measured under forward and reverse bias. The red dashed line illustrates the photocurrent scaling linearly with the optical power.

548

549

550

Figure 1

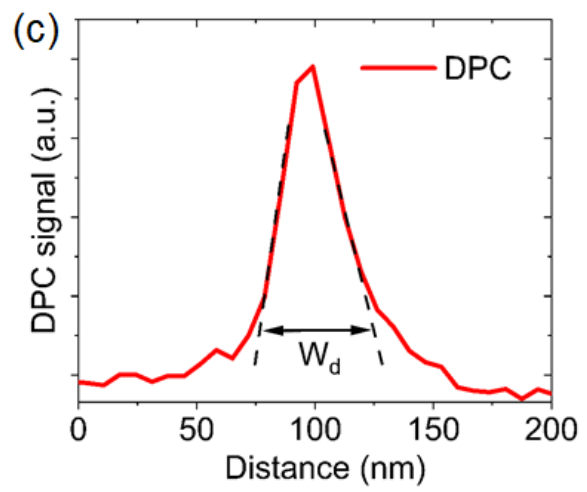
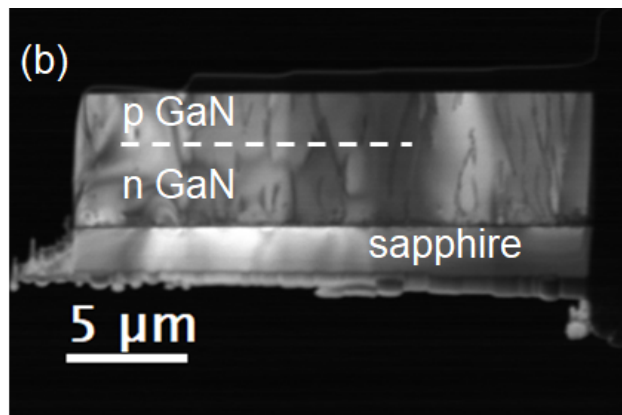
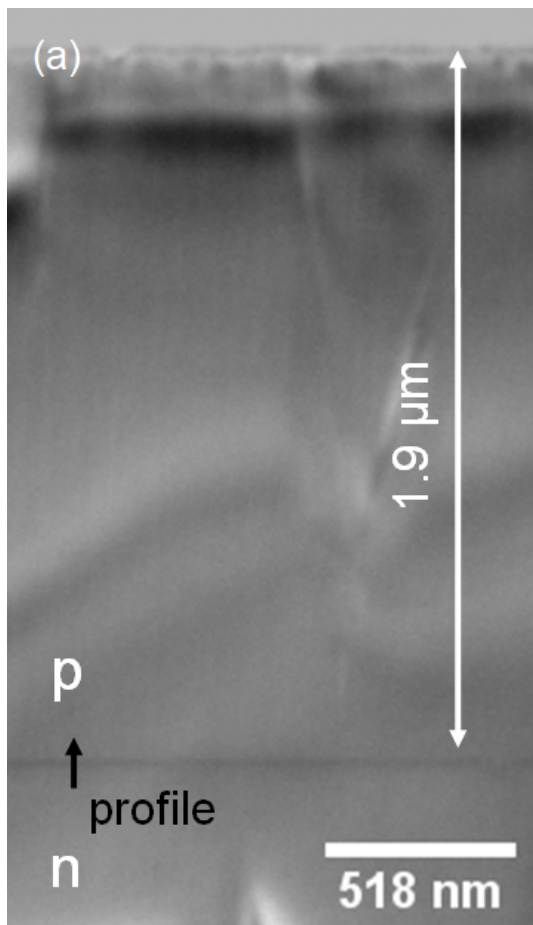


551

552

553

Figure 2



554

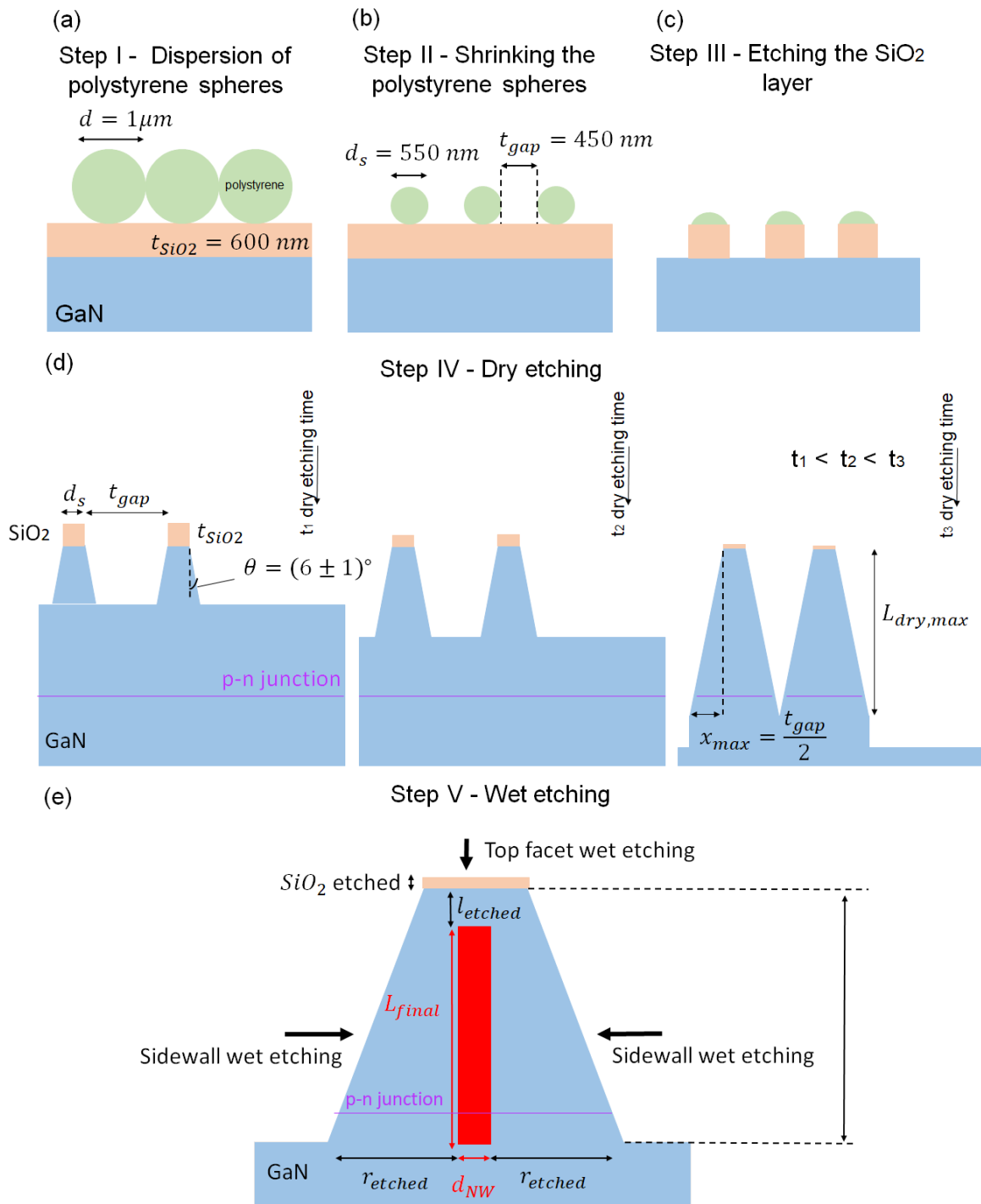
555

556

557

Figure 3

558



559

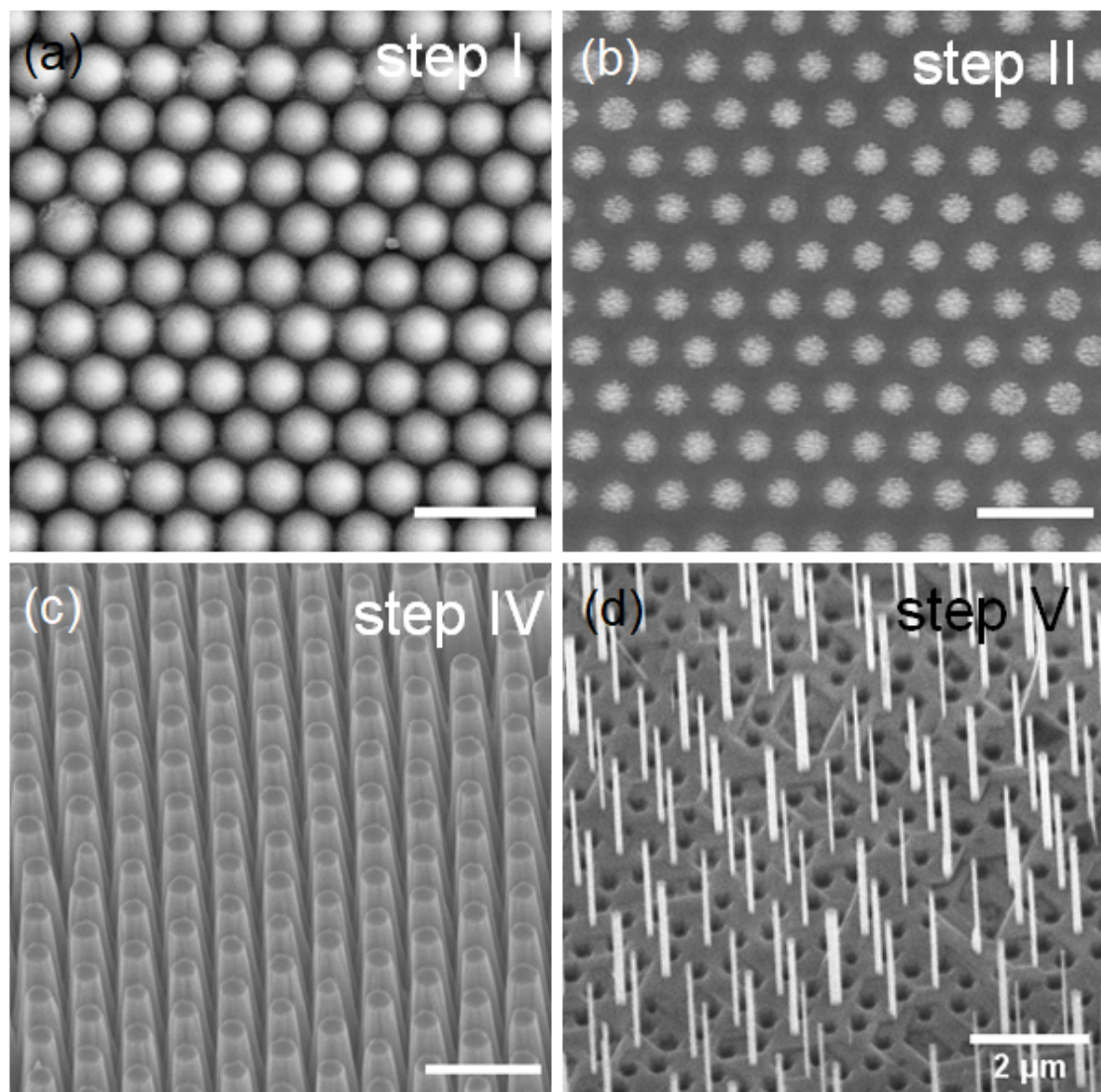
560

561

562

563

Figure 4



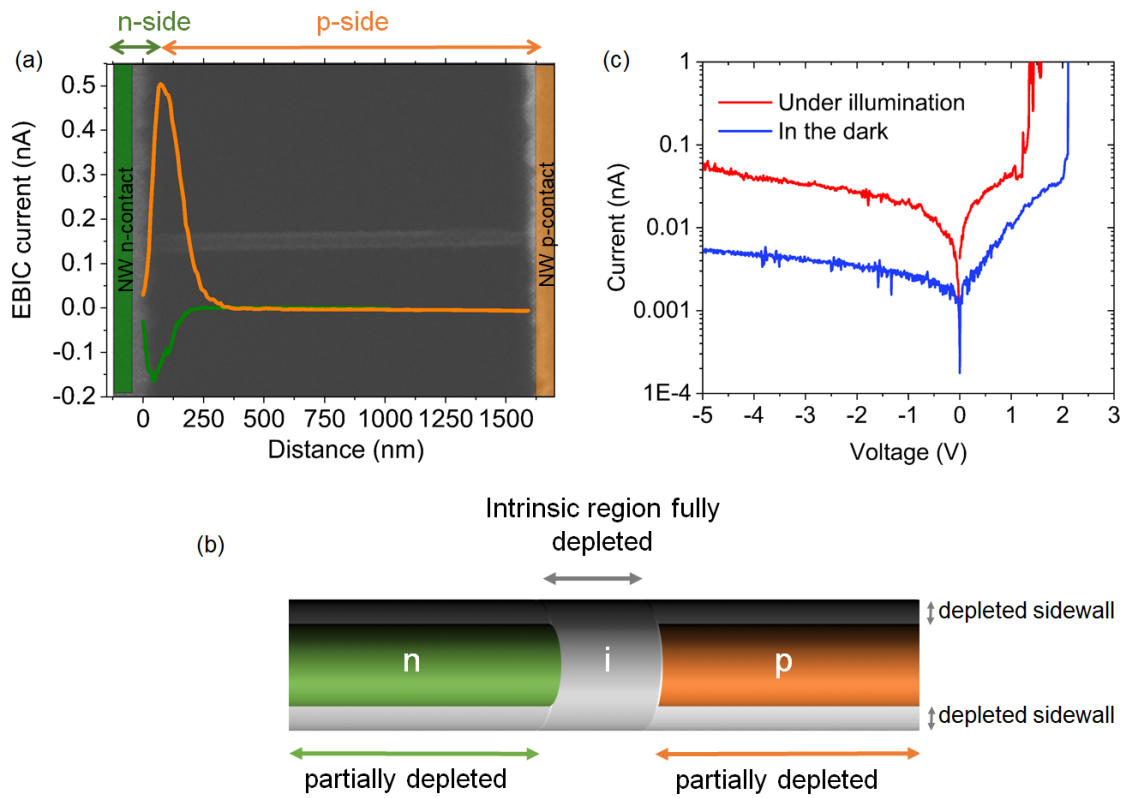
565

566



567

Figure 5



568

569

570

571

572

573

574

575

576

577

578

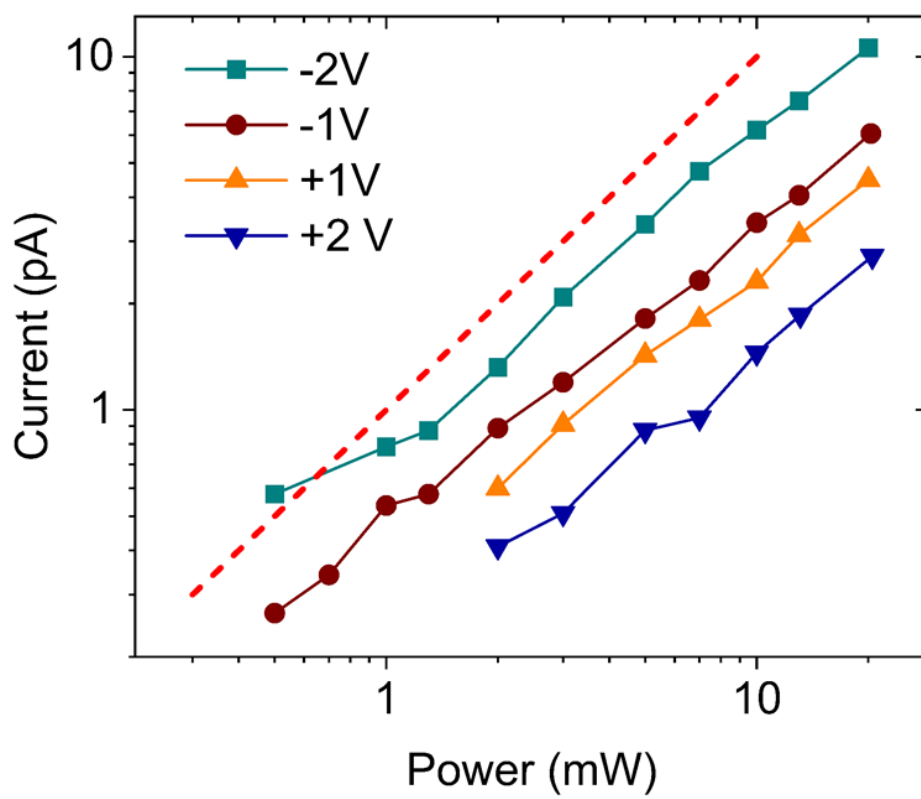
579

580

581

582

Figure 6



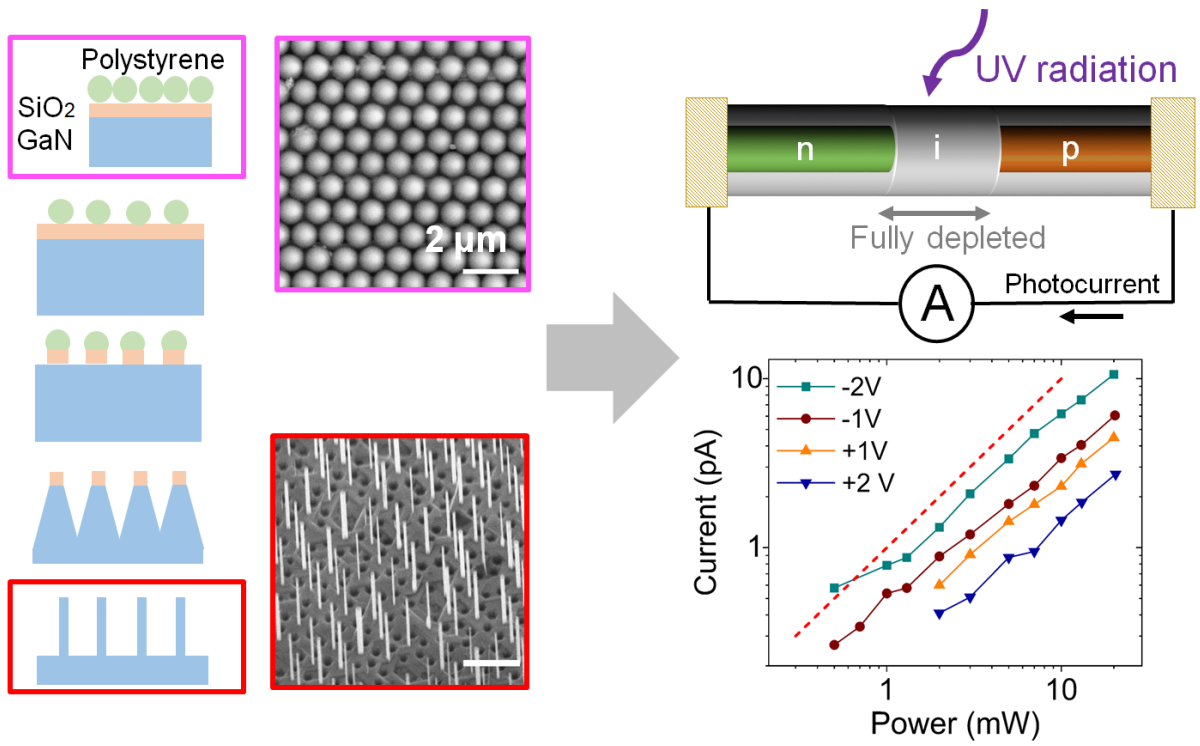
584

585

586

TOC Figure

587



588

589

590

591