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

7 Bruno César da Silva^{1*}, Adam Biegański², Christophe Durand², Zahra Sadre Momtaz¹, Anjali
8 Harikumar², David Cooper³, Eva Monroy² and Martien Ilse den Hertog^{1*}

9 ¹University Grenoble Alpes, CNRS-Institut Néel, Grenoble F-38000, France

10 ²University Grenoble Alpes, CEA, Grenoble INP, IRIG, PHELIQS, Grenoble F-38000, France

11 ³University 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 μm 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 applications¹⁻⁴. 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 speed⁵⁻⁸. 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) devices⁹⁻¹². 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^{13,14}. Linearity can be obtained in the case of reverse-biased very thin,
40 entirely depleted NWs¹⁵, or in reverse-biased *p-n* junctions¹⁴.

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 defects¹⁶ and the possibility
44 to combine materials with different lattice parameter thanks to the elastic surface relaxation of the
45 wires^{17,18}. However, it suffers from issues like non-uniform doping¹⁹, defects due to the NW
46 coalescence^{20,21}, and morphological inhomogeneities^{22,23}. On the other hand, top-down nanowires
47 produced through etching processes^{24,25} 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 process²⁶.

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 NWs²⁷⁻³³. 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 electronics³⁴ or energy
59 conversion devices³⁵, 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^{36,37}, and the nanowire diameter is critical to obtain linear
62 devices^{15,38}.

63 In the last years, different authors^{30,32} 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 Cl₂-BCl₃ dry etching and KOH-
69 based wet etching. We show that the combination of polystyrene nanospheres and a SiO₂ 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 (NH₃) 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- μ m-thick *n*-doped GaN³⁹, a 45-nm-thick intermediate (undoped)
85 region, and a 1.9- μ m-thick *p*-doped region⁴⁰, as indicated in Fig. 1(a). Doping was achieved by using
86 diluted silane (SiH₄) 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 (MgCp₂) for the Mg doping. An annealing step at 700°C for 20 min under N₂ 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 N₂ 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 μ m, 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 μ s.

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^{41,42}, 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 μm below the sample
118 surface. A depletion width of (50 ± 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.⁴³. 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 SF_6 and 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 μm , as shown in Supporting
135 Information SI2. This choice was motivated by the ability to uniformly reduce their diameter using a
136 RIE 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 μm polystyrene spheres
142 and a 600 nm thick 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 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 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 μm were drop cast on top of the 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 μl droplet. The droplet was applied on the sample with a micropipette,
152 and dried at an angle of 10° (with respect to the horizontal plane)⁴⁴. 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 O₂ plasma
160 at RF power = 20 W (and O₂ flow = 50 sccm, DC bias 250V, 0.070 mbar), followed by a second softer
161 etching performed at 10 W RF power (and O₂ 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, SiO₂ etching was performed using a RIE system with CHF₃
166 chemistry (RF power of 50 W, DC bias 390V, 15 sccm CHF₃ 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 CL₂-BCl₃
169 chemistry (30 W radio-frequency power, 100 W ICP power, 10 mTorr pressure, 10 sccm Cl₂ flow, 30
170 sccm BCl₃ 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,⁴³ 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^{45,46}. 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 SiO₂ etching rate
185 during the dry etching (~ 2 nm/min), which means that an approximately 300 nm SiO₂ remained after
186 the step IV. This remained SiO₂ 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 SiO₂ 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 Si₃N₄ membrane chip by drop casting²³. 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.^{47,48} 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 μm 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 observed¹⁴.

216 The relation between the depletion region width (W_d) and the surface band bending (Φ_{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-side⁴⁹ and 0.6 eV for the n-
 220 side^{50,51} at the doping level measured by SIMS measurements ($[Mg] = 3.9 \times$
 221 10^{19} 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* photodiodes⁵², 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^{14,15}. 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 junction¹⁴ or not^{13,15}
 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.¹⁵ 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.⁵³ 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.¹⁵

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.¹⁴ 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, CHF₃-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 semiconductors⁵⁴. 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/acsnm.3c01495>.

293

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

295

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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
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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.

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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 μm 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 μm polystyrene nanospheres. (b) Step II: Shrinking of the spheres using a RIE oxygen plasma. (c) Step III: Etching of SiO_2 using RIE with 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 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).

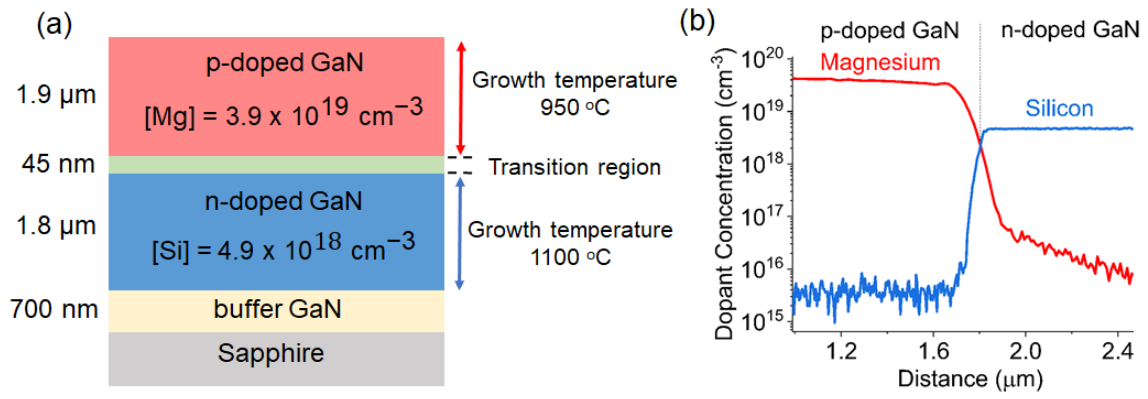
Figure 6 - Photocurrent measurements of the GaN *p-i-n* NW shown in Figure 5 as a function of the impinging optical power at 325 nm, measured under forward and reverse bias. The red dashed line illustrates the photocurrent scaling linearly with the optical power.

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Figure 1

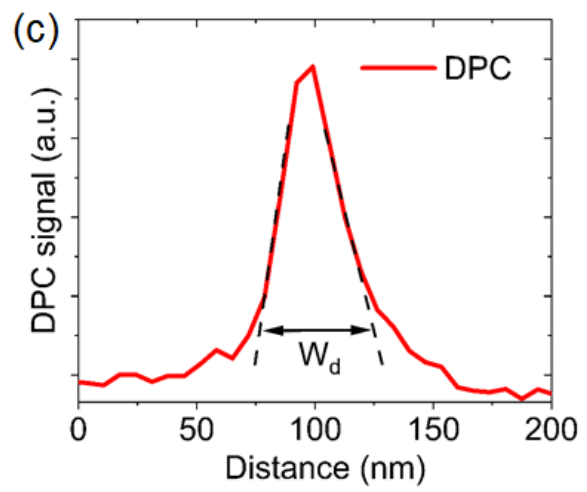
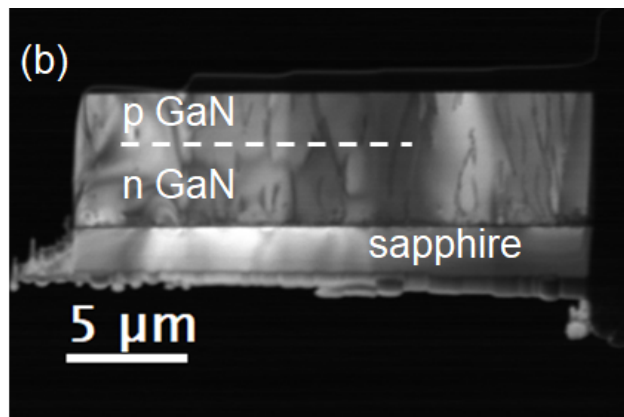
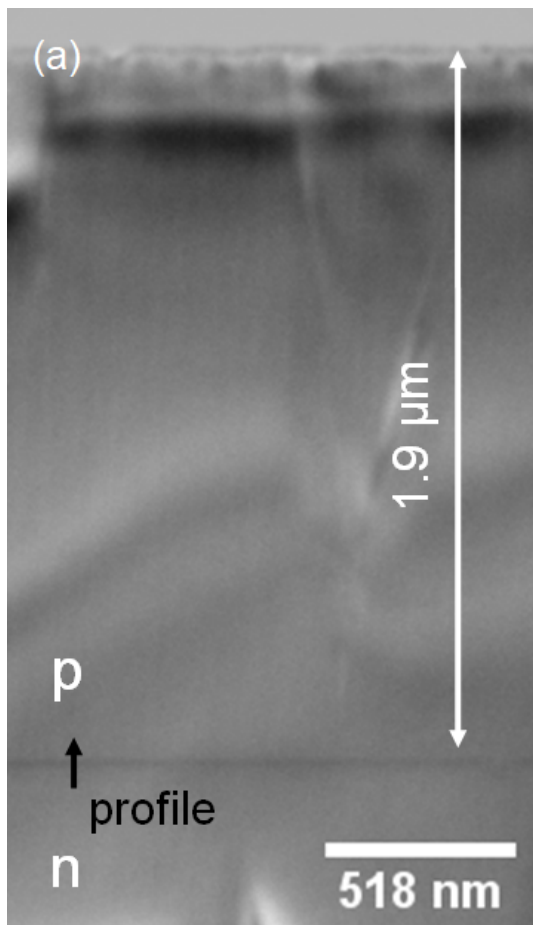


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Figure 2



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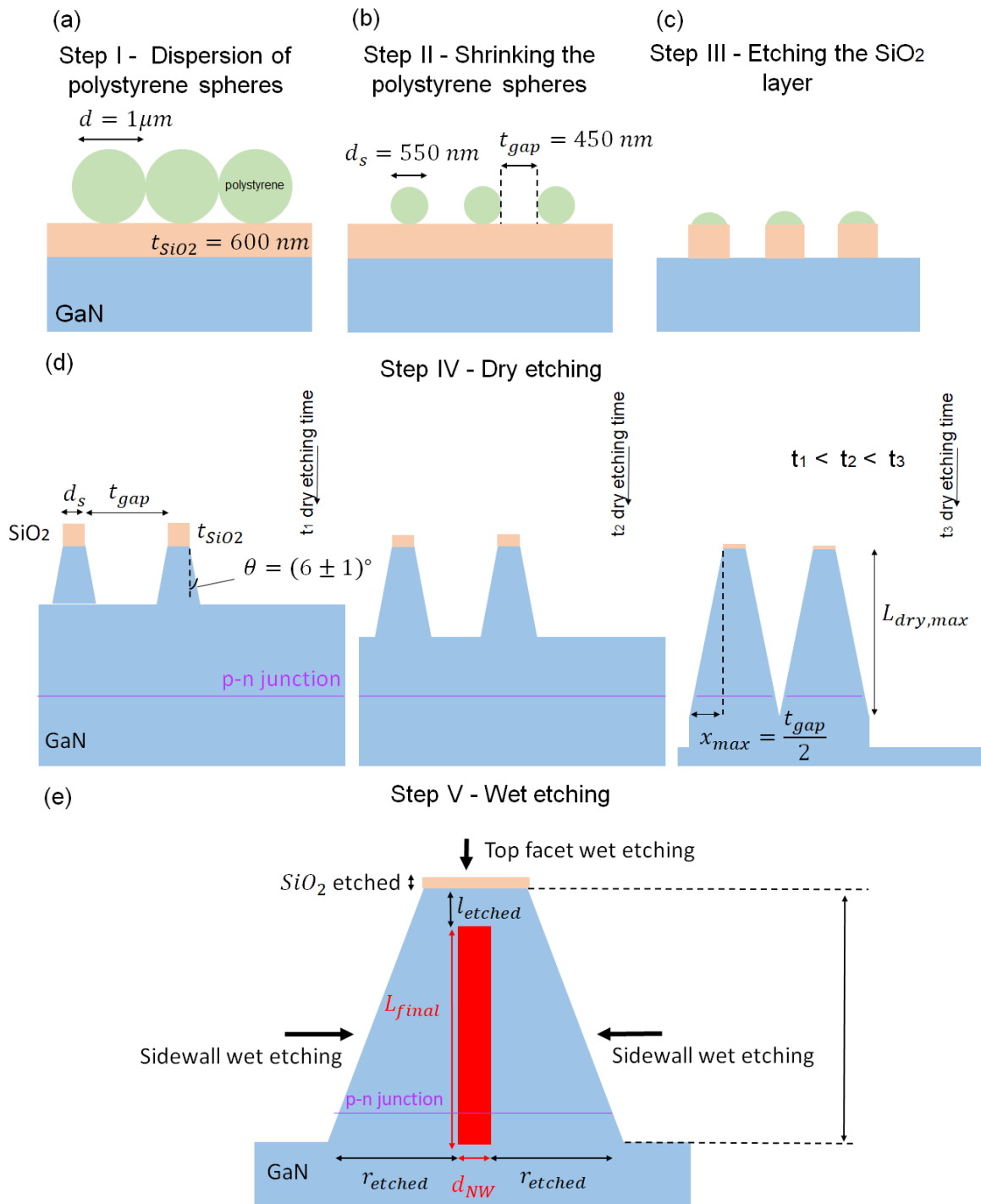
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Figure 3

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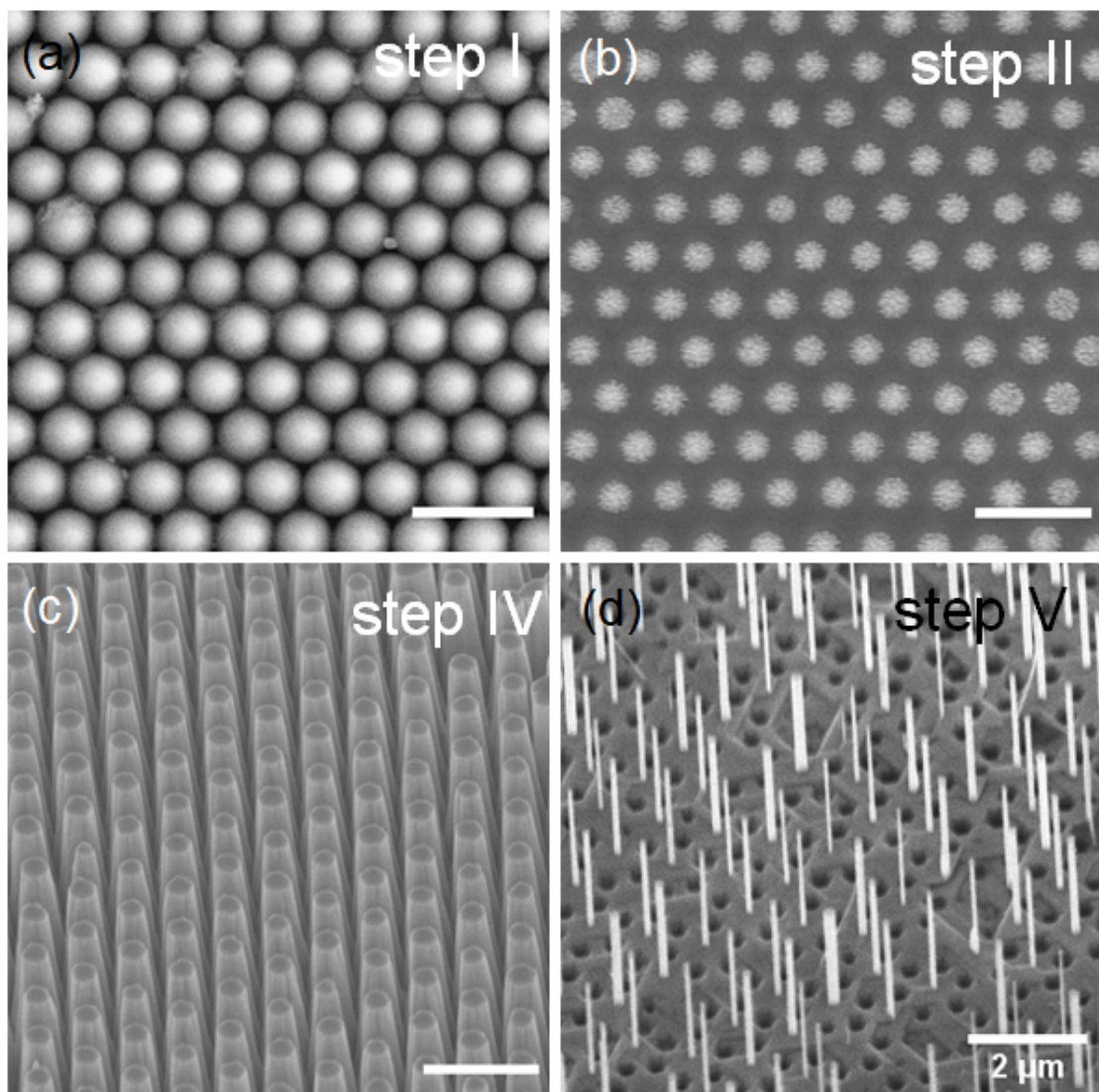
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Figure 4

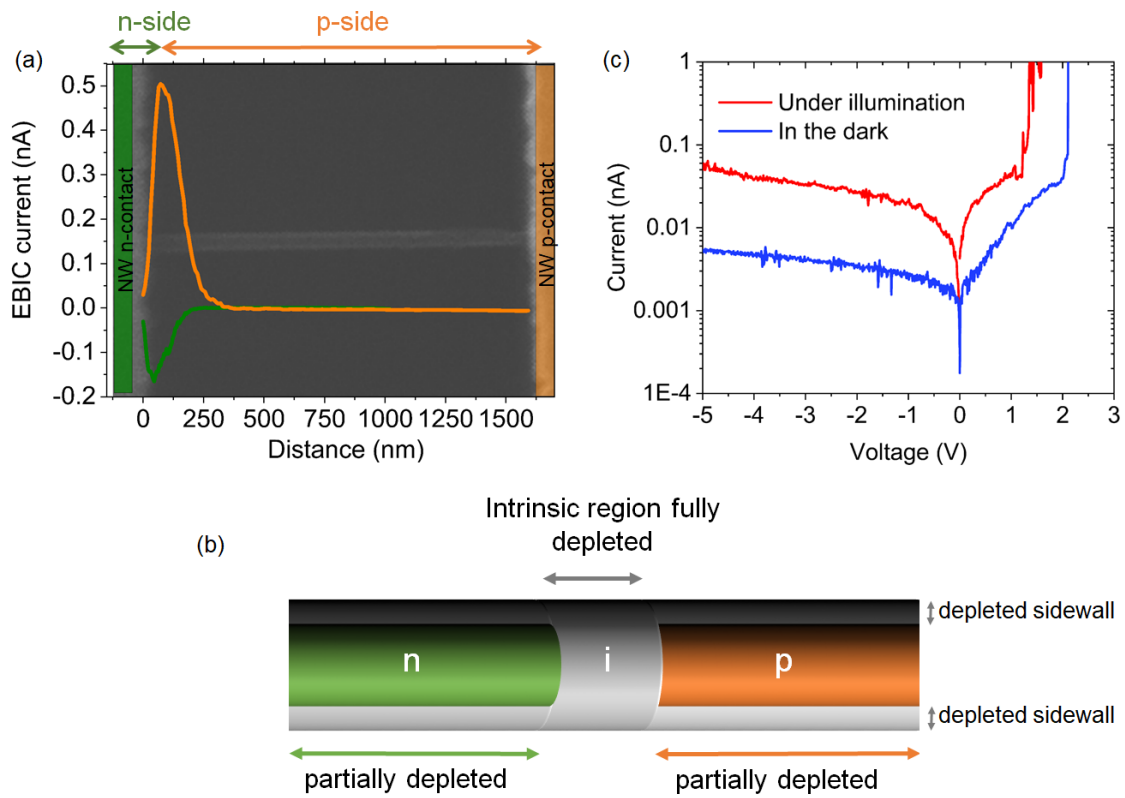


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Figure 5



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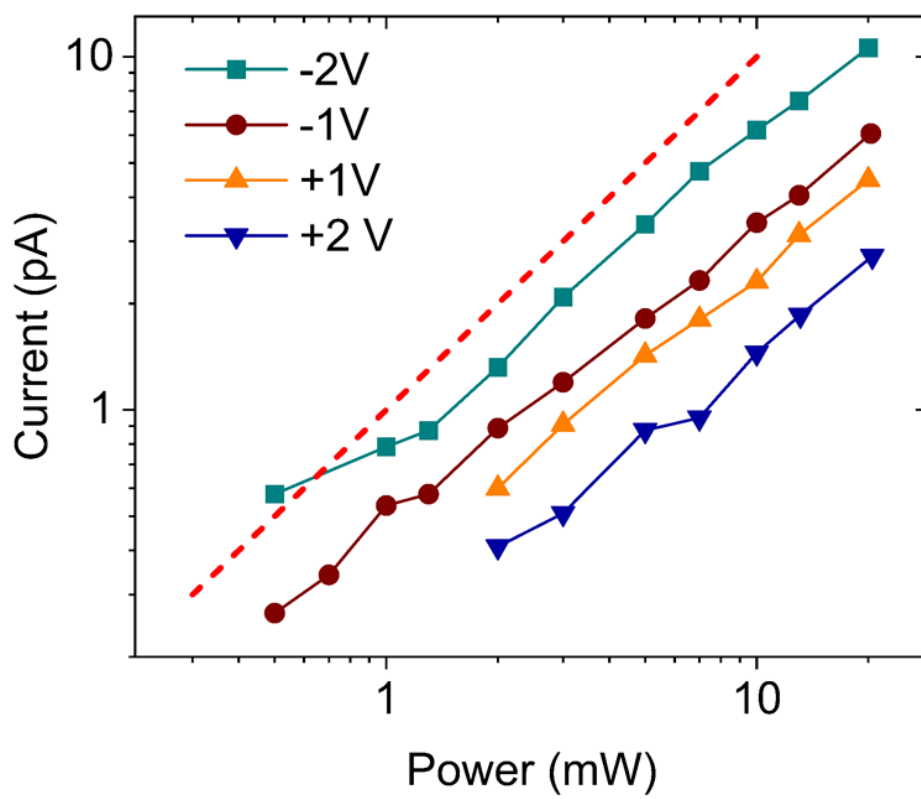
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Figure 6



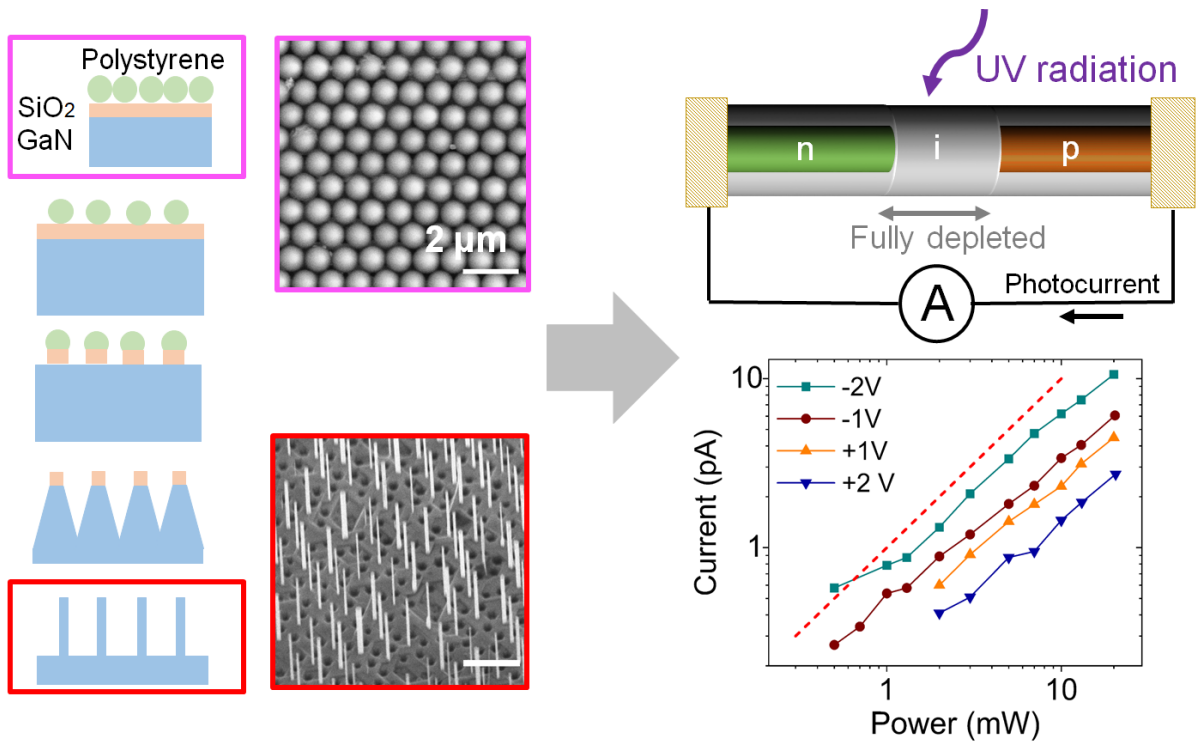
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TOC Figure

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