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Article

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ACS Photonics, **Just Accepted Manuscript** • DOI: 10.1021/acsphotonics.7b01235 • Publication Date (Web): 19 Dec 2017

ACS Photonics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

ACS Photonics Revised Manuscript # ph-2017-01235t

Surface-Passivated AlGaN Nanowires for Enhanced Luminescence of Ultraviolet Light Emitting Diodes

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KEYWORDS

Aluminum gallium nitride nanowire, passivation, ultraviolet light emitting diode, potassium hydroxide, surface oxides and states, surface recombination

ABSTRACT

Spontaneously-grown, self-aligned AlGaN nanowire ultraviolet light emitting diodes still suffer from low efficiency partially because of the strong surface recombination caused by surface states, i.e., oxidized surface and high density surface states. Several surface passivation methods have been introduced to reduce surface non-radiative recombination by using complex and toxic chemicals. Here, we present an effective method to suppress such undesirable surface recombination of the AlGaN nanowires via diluted potassium hydroxide (KOH) solution; a commonly used chemical process in semiconductor fabrication which is barely used as surface passivation solution in self-assembled nitride-based nanowires. The transmission electron microscopy investigation on the samples reveals almost intact nanowire structures after the passivation process. We demonstrated an approximately 49.7% enhancement in the ultraviolet light output power after 30-s KOH treatment on AlGaN nanowires grown on titanium-coated silicon substrates. We attribute such a remarkable enhancement to the removal of the surface

dangling bonds and oxidized nitrides (Ga-O or Al-O bonds) at the surface as we observe the change of the carrier lifetime before and after the passivation. Thus, our results highlight the possibility of employing this process for the realization of high performance nanowire UV emitters.

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Ultraviolet light emitting diodes (UVLEDs) are crucial for a number of applications such as water/air/food sterilization, free-space non-line-of-sight communication and various medical applications.[1, 2] The bandgap of $Al_xGa_{1-x}N$ ($0 \leq x \leq 1$) alloys can be tuned from 3.4 to 6.1 eV by changing the alloy composition which covers the entire UV spectral region from 360 to 210 nm. This makes AlGaN alloys particularly suitable for the realization of UVLEDs.[3] Nevertheless, the development of UVLEDs performance has not yet reached the level achieved in the visible-spectrum LEDs. Despite intense efforts to improve the performance of AlGaN-based UVLEDs, the existing AlGaN-based planar UVLEDs suffer from high threading dislocation densities in the AlGaN epitaxial layer, limited light extraction channels, poor p-type doping efficiency, and difficulties in heat dissipation under high current injection.[4, 5, 6] As a result, the maximum external quantum efficiency (EQE) of fully packaged AlGaN-based UVLEDs, in the entire UV spectral region (360 to 210 nm), is extremely low (≤15%). However, recently, Takano et al. claimed achieving a maximum EQE of 20% of EQE for a 275 nm LED.[1] These EQE values are much lower than that obtained in highly commercialized InGaN-based blue LEDs, the EQE efficiency of which can be as high as 80%.[7] Thus, developing the conventional planar UVLED structure to obtain high EQE remains tremendously challenging. Recently, the AlGaN nanowires (NWs) emerged as an alternative approach for the realization of UVLEDs and UV laser diodes. AlGaN nanowire structure possesses many advantages relative to planar structures. In particular, because of the effective lateral stress relaxation during growth, nearly defect-free AlGaN nanowires can be formed directly on silicon or other foreign substrates (such as metal and graphene) with high internal quantum efficiency.[8,9] Moreover, the p-type doping efficiency in AlGaN has been significantly improved due to the reduced activation energy of Mg dopant in nanowire structures.[10] In addition, the emitted photons can easily escape and thus enhance the light extraction efficiency owing to the large surface-to-volume ratio and the multiple scattering effects in nanowire structures.[11] Consequently, by adopting AlGaN nanowires instead of planar structures, researchers were able to achieve an electrically-pumped deep UV laser emitting at a very short wavelength of 239 nm[12] and attain a droop-free UVLED on metal substrates.[13]

Even though significant progress has been made in the past few years, the development of AlGaN nanowire-based emitters is at its early stage. Due to the large surface-to-volume ratio of nanowire structures, for all nitride-based devices, the optical and electrical properties of these

structures are highly sensitive to their surroundings. For example, a significant presence of surface states, surface Fermi level pinning effects, and an enhanced surface recombination due to the Shockley-Read-Hall(SRH) non-radiative recombination at these surface state/defect centers will lead to the light emitting devices of low efficiency. Significant efforts have been dedicated to the development of methodologies aimed at removing such surface defects (such as dangling bonds) and suppressing surface recombination to improve the performance of the nitride-based nanowire devices.[14, 15, 16, 17] Zhao et al. achieved success in mitigating SRH recombination by octadecylthiol (ODT) and sulfide passivation process in InGaN/GaN nanowires, resulting in an improved device efficiency.[16] Hetzl et al. introduced a self-regulated AlGaN shell on GaN nanorod as a mean of passivating defect-related recombination centers.[17] Mi et al. investigated the use of inorganic sulfides, such as $(NH_4)_2S_X$, for nanowire surface passivation. They found that such sulfides can reduce the surface recombination velocity and hence improve the LED performance.[18] In addition, Si_4N_3 and SiO_2 were used to passivate GaN surface.[19] All of these passivation approaches, while using different chemicals, demonstrated the effectiveness of this process in improving the device performance. However, in these studies, toxic and hazardous chemicals were used or their techniques required an additional material deposition procedure to passivate the nanowires.

In this paper, we propose the use of diluted potassium hydroxide (KOH) solution to passivate our spontaneously grown AlGaN nanowires prior to device fabrication. The KOH solution is commonly used as a follow-up step after dry etching of GaN-based thin films to improve the sidewall roughness for light emitting devices[20,21] or in the fabrication of GaN-based metal–insulator–semiconductor power devices.[22] Here, we demonstrate that KOH can also be used as a surface passivation solution. We investigate the underlying passivation mechanism and its effects on the optical properties of AlGaN nanowires. We study the effect of the KOH passivation processes of different durations on the optical performance of these AlGaN nanowires, compared to that unpassivated nanowires.

METHODS

The AlGaN nanowire LED structures studied in this work were grown on n-type Si (001) coated with a 100-nm Ti film by e-beam evaporator using *Veeco Gen* 930 plasma-assisted

molecular beam epitaxy (PAMBE) under nitrogen-rich conditions. A 2-step growth process was implemented. The nanowires were first nucleated at relatively low temperature of ~500 °C, followed by the growth of the AlGaN layers at a higher temperature of ~630 °C. The nominal Al composition was estimated by taking the ratio of Al to the total metal beam equivalent pressure as measured by the beam flux monitor. To fill the gap between nanowires, we used parylene-C, consisting of a deposition step followed by the etch-back process to reveal the p-GaN contact layers. More details of the growth conditions and fabrication process can be found in our earlier work.[13] The p-i-n nanowire LED started with a 100-nm n-GaN layer, followed by ~50-nm Si-doped $Al_{0.3}Ga_{0.7}N$ layer and then the active region of 30-nm-thick $Al_{0.14}Ga_{0.86}N$ layers. Afterwards, a ~50 nm Mg-doped $Al_{0.3}Ga_{0.7}N$ layer was grown and the structures completed with a ~20 nm Mg-doped GaN layer as the p-type contact layer. After the growth, the nanowires were treated in a KOH solution with a concentration 10 wt. % KOH at 45°C for different durations from 10 to 40 s. After passivation, the nanowires were rinsed in deionized water for 10 mins. The nanowire LEDs were then fabricated immediately using the standard UV contact lithography process. Ni (5 nm) / Au (5 nm) were deposited directly on the top of the p-GaN layer, which forms an ohmic contact with p-GaN, upon annealing at 600 °C under O_2 gas ambient for 1 min. Ni (10 nm) / Gold (Au) (500 nm) was then deposited as the top p-contact for probing. For n-contact, a thickness of ~100 nm of silicon was etched from the back side of the sample to expose a clean surface. Ti (10 nm) / Au (150 nm) were then sputtered as an n-pad followed by annealing in N_2 gas ambient at 250 °C for 1 min to form an n-type ohmic contact. Room temperature photoluminescence (PL) measurements were performed using a 266 nm excitation pulse laser (SNU-20F-100). The PL signal was collected by using a UV objective and then measured by the OceanOptics QEPro spectrometer. Electroluminescent (EL) signal was also measured and the current was injected by a Keithley source 2450C operating in continuous mode under different injection currents. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) measurements were performed to analyze the nanowire structures before and after passivation. The TEM specimens were prepared by using an FEI Helios dual-beam focused ion beam scanning electron microscope (DBFIB-SEM) system with a Ga ion source. The TEM microscope (Titan 80-300 ST) was operated at the accelerating voltage of 300 kV. Atomic-number sensitive (Z-contrast) STEM was realized by acquiring the data with high-angle annular dark-field (HAADF) detector. The high-resolution X-ray photoelectron spectroscopy

(HRXPS) measurements were carried out using a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) operating at 150 W, a multichannel plate, and delay line detector under a vacuum of ~10^{-9} mbar. The high-resolution spectra were collected within the limits of spatial resolution at a fixed analyzer pass energy of 20 eV. The remnant binding energy shifts were referenced to the adventitious carbon (C 1s) signal. Time-resolved PL (TRPL) measurements were performed using a frequency-tripled Ti:Sapphire laser (293 nm) with a pulse width of 150 fs and a synchro-scan streak-camera system. The overall temporal resolution of our setup is 2 ps. The average excitation power on the sample surface was maintained to be 1 mW at a 76 MHz repetition rate.

RESULTS AND DISCUSSION

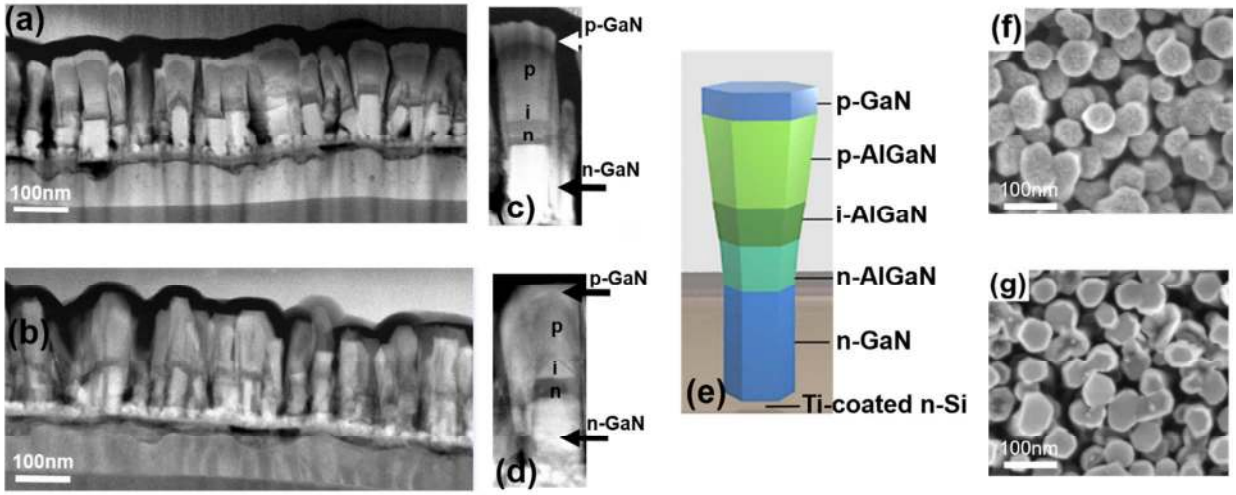

Figure 1. Structural characterization of the AlGaN nanowires before and after KOH passivation process. (a) and (b) Cross-sectional STEM-HAADF images show the vertically aligned nanowires before and after 30-s passivation, respectively. (c) and (d) Cross-sectional STEM-HAADF images show a single nanowire before and after passivation, respectively. Each nanowire includes a bottom n-GaN layer, n-type AlGaN layer, i-AlGaN active layer, p-type AlGaN layer, and top p-GaN layer. (e) 3D schematics of the studied nanowire LEDs grown on Ti/Si template substrate. (f) and (g) Top view SEM images of the AlGaN nanowires show tightly packed nanowires before and after passivation, respectively.

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Fig. 1 (a) and (b) show the cross-sectional STEM-HAADF images of the compact and nearly vertically aligned nanowires nucleated on Ti-coated Si (100) substrates before and after KOH Overall, after 30 s passivation, the nanowires remained almost intact. From the enlarged images shown in Fig. 1(c) and (d), we observe each layer in the nanowires along the growth direction, which is also schematically depicted in Fig. 1(e). We notice that the nanowire surface flattened after KOH passivation (see Fig. 1(d)). The surface flattening is further confirmed by comparing the top-view SEM images of the nanowires shown in Fig. 1(f) and 1(g). This phenomenon may potentially be attributed to the KOH etching of the top p-GaN contact layer during the passivation process. Even though a 5-10 nm p-GaN was etched away, most of the p-GaN layer still remained at the top part of the nanowires after immersion in the KOH solution for 30-s.

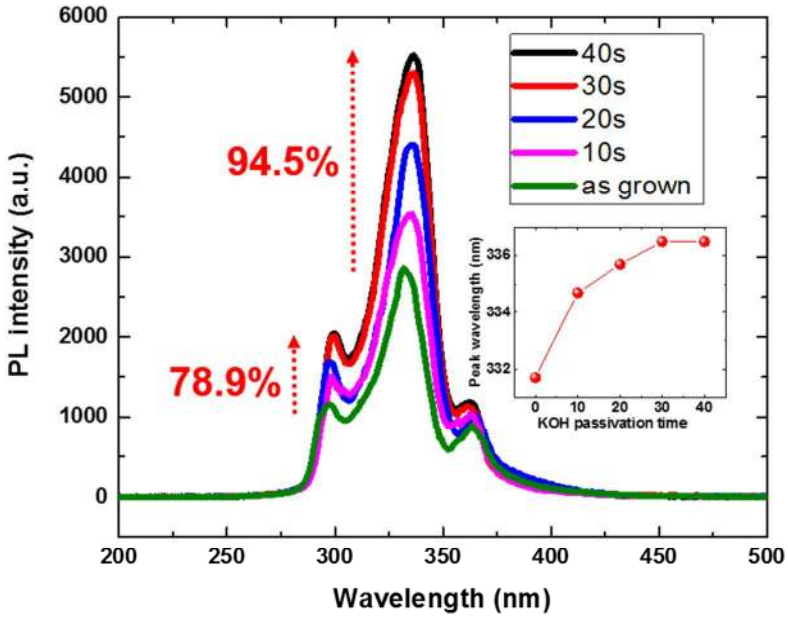

Figure 2. Room temperature PL spectra of the as-grown sample and the samples after 10, 20, 30, 40-s KOH passivation.

PL spectra of the nanowires pertaining to different KOH passivation durations are shown in Fig. 2. Three distinct peaks are observed in the PL spectrum of the as-grown sample (before passivation): the left shoulder of the major peak emitting at 296 nm arises from the higher Al-

content AlGaN layer (n and p-$Al_{0.3}Ga_{0.7}N$ layer), the most intense peak of 332 nm originates from the active layer, and the right shoulder of the major peak emitting around 360 nm is related to the PL emission from the top and bottom GaN layer. As the passivation time is increased from 10 to 40 s, it is evident the left shoulder peak and the major peak exhibit a slight redshift of 3.3 and 4.8 nm, respectively. Most importantly, after 40 s passivation, the intensity of the peaks located at 296 nm and 332 nm increases by 78.9% and 94.5%, respectively. We did not extend the passivation time further, as the PL enhancement after 40 s was not significant (as shown in the inset of Fig. 2). During the growth, the AlGaN shell can be formed naturally as a result of the diffusion-controlled growth mechanism of III-nitride nanowires under nitrogen-rich conditions.[8] Due to the limited diffusion of Al atoms with respect to Ga (Al atoms have a shorter diffusion mean free path), a large amount of Al atoms may accumulate near the nanowire sidewalls, resulting in the formation of an Al-rich $Al_xGa_{1-x}N$ shell on the nanowire lateral surfaces.[12, 23] Due to the formation of the core-shell structure, after the KOH passivation, the Al-rich AlGaN shell might be etched which could lead to the observation of the redshift. This observation is consistent with the result reported by Martin et al. in which they observed a blueshift by adding an AlGaN shell to the GaN rods. [17] In our case, since we partially removed Al-rich shell layer after passivation, the redshift would be expected. We believe the subject of the redshift mechanism after passivation is worthy of a separated detailed investigation, for example, by using nanoscale Cathodoluminescence and TEM, as reported by Aditya et al.[24]

There are various explanations for such PL emission enhancement after sample passivation. A flattened top surface of the nanowire indicated that we have possibly removed a portion (~5-10 nm) of the p-GaN layer. Since GaN is rather absorptive in the UV region, this removal of a few nm of GaN could affect the total amount of escaped photons. To exclude this possibility, we grew an AlGaN nanowire LED without p-GaN and capped the nanowire with only a high Al content p-type AlGaN layer on top of the active region. Then, we carried out the passivation process with identical KOH solution and collected a series of PL spectra from these samples. On average, we still observe a strong enhancement (of ~60.1%) of the PL intensity with a noticeable redshift in the PL peak. This observation further confirms that the partial removal of p-GaN is not the only factor contributing to the observed PL intensity enhancement. Additionally, the KOH treatment could also remove part of bottom n-GaN and thus contribute to the increase

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of the PL intensity. To further explore possible reasons for the PL intensity enhancement due to KOH passivation, we performed a surface analysis of the nanowires using an HRXPS. In this study, to verify the possible changes in surface status, the Ga *2p*, Ga *3d*, and Al *2p* core levels were investigated for the analysis before and after passivation process. Comparing the peak positions of Ga *2p*, Ga *3d*, and Al *2p* core levels, this allowed us to verify the bonding status of these elements in the as-grown sample and the samples after KOH passivation. Fig. 3 shows the acquired core-level spectra of the Ga *2p*, Ga *3d*, and Al *2p* before and after 40 s passivation. Before passivation, the Ga *2p*, Ga *3d*, and Al *2p* peaks located at 1117.7 ± 0.1, 19.9 ± 0.1 and 74.4 ± 0.1 eV, which is ascribed to the Ga-O, Ga-O, and Al-O bonding, respectively, as shown in Fig. 3a.[25] After passivation, the peak positions of Ga *2p*, Ga *3d* and Al *2p* shift to lower binding energy values of 1117.0 ± 0.1, 19.3 ± 0.1 and 73.1 ± 0.1 eV, which is ascribed to the Ga-N, Ga-N and Al-N bonding. The shift in the binding energy associated with Ga and Al in the Ga *2p*, Ga *3d* and Al *2p* core level spectra is a clear evidence of the removal of surface oxides due to KOH passivation. [25] This observation is also consistent with the findings of an earlier study, in which researchers observed a reduction in the surface chemical composition ratio of Ga to N (from 2.68 to 1.73) in a three-dimensional GaN nano-cone array after the KOH treatment, resulting in an enhancement in the PL intensity by 60%.[26] In addition, the texturing surface of GaN nano-pillars by subjecting them to the KOH treatment could also improve the light extraction efficiency reflected in an enhancement in the PL.[27, 28] Via the KOH post-treatment, The PL enhancement was ascribed to the alleviation of some of the surface damage in the formation of nano-cones or nano-pillars through the top-down fabrication. In our study, we reveal, for the first time, that KOH solution can also be used in the fabrication of self-assembled AlGaN nanowire-based devices.

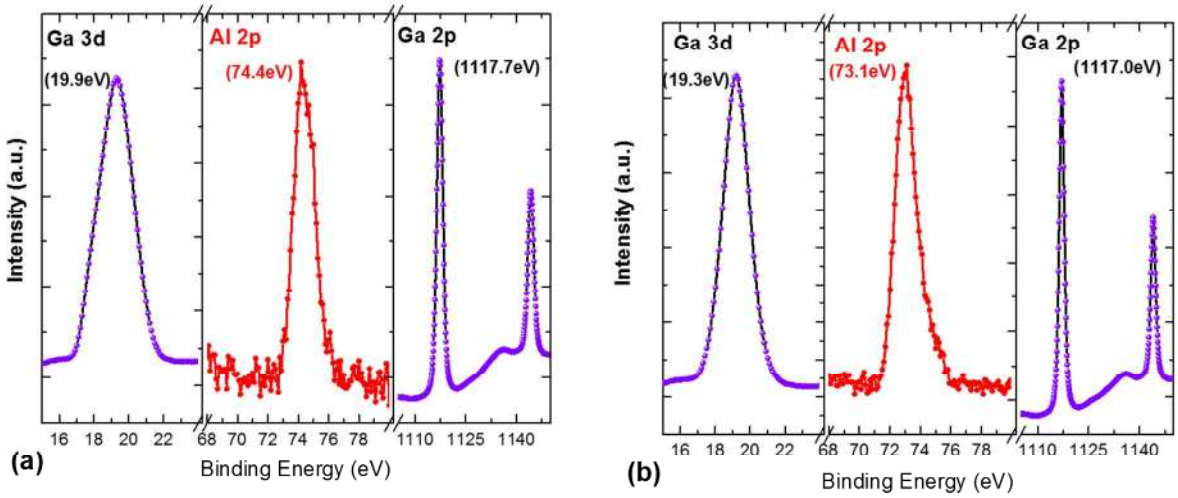

Figure 3. (a) and (b) Ga 2p, Ga 3d and Al 2p core-level spectra before and after 40-s KOH passivation, respectively. The peak positions of core levels are shown in parentheses.

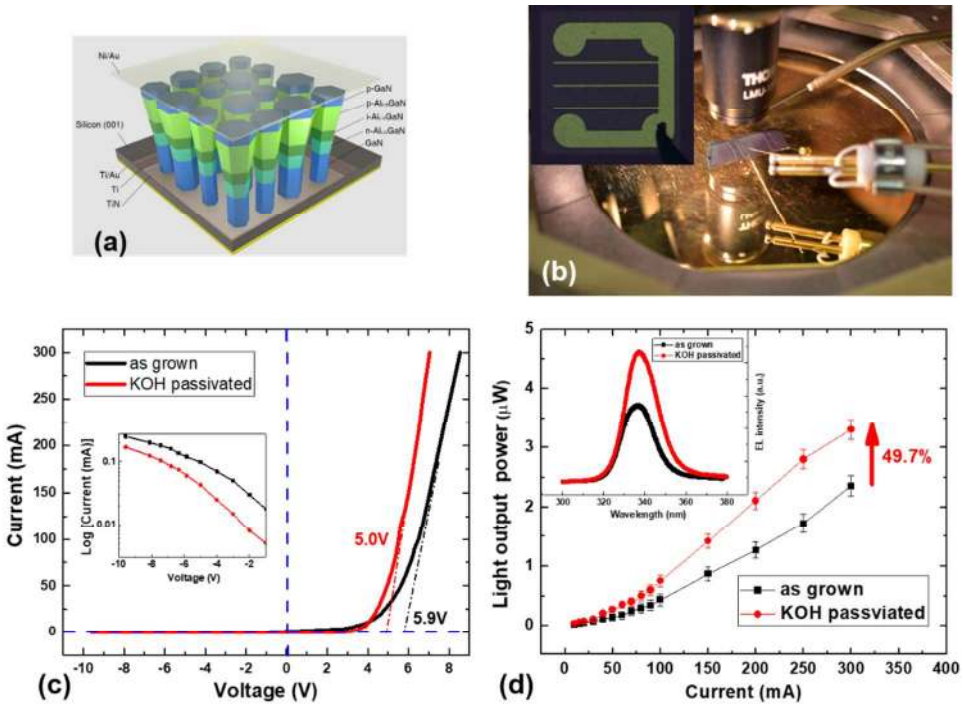

Figure 4. (a) 3D schematic depiction of the fabricated 300×300 μm^2 nanowire UVLED. (b) The EL measurement setup on a probe station. The inset shows the probed device in operation. (c) Current-voltage characteristics of the fabricated sample before and after passivation. The inset shows the reverse current in log scale. (d) The measured light output power as a function of the

injection current. The inset of (d) shows the EL spectra at an injection current of 300 mA before and after passivation at room temperature.

After the passivation, the nanowire UVLEDs were immediately fabricated with a chip size of 300×300 μm^2. Fig. 4(a) shows a 3D schematic depiction of the fabricated device. To avoid the potential performance variations across the 2-inch wafer during the MBE growth, similar parts of the wafer were used for comparison. Fig. 4(b) shows the probe station and EL measurement setup. Fig. 4 (c) shows the representative current−voltage (I−V) characteristics for UVLEDs. A slight decrease (~0.9 V) in the turn-on voltage and a small reduction in the sheet resistance were observed by comparing the fabricated devices before and after KOH passivation, revealing an improvement in the contact resistivity of p-GaN after the KOH solution treatment. It was found that the lowest contact resistivity can be achieved by the surface treatment of the p-type GaN thin film using a KOH solution prior to the metal deposition due to their success in removing the surface oxides formed on p-type GaN during epitaxial growth. [29,30] Such oxides play a vital role in inhibiting the hole transport from metal to p-type GaN. Reducing the turn-on voltage is very important for improving the overall LED performance because it is correlated with the device reliability and power consumption. High turn-on voltage is commonly believed to be linked with high contact resistivity and low-conductive films. Additionally, a smaller leakage current was observed in the device after the KOH treatment, as shown in the inset of Fig. 4(c), indicating that the KOH may have removed surface defects which could act as leakage current paths.

Fig. 4(d) shows the light output power as a function of the injection current of the studied UVLEDs at room temperature. Noticeably, the light output power of the UVLEDs shows a great enhancement (49.7%) after KOH passivation. The inset of Fig. 4(d) shows the EL signal with a maximum peak wavelength of 336 and 338 nm—without parasitic emission—for the studied LEDs before and after passivation, respectively. The full width at half maximum (FWHM) is 18.9 and 17.6 nm for these LEDs before and after passivation, respectively. Worth mentioning that it is important to note that the output power continuously increases as the current density increases up to 120 A/cm^2. This finding is similar to the results that we have reported in our earlier work,[13] where we demonstrated that the AlGaN nanowire UVLEDs exhibited no efficiency droop at a high injected current density as the nanowires were grown on metal

substrates, which have better heat dissipation. In contrast, we observed a significant efficiency degradation in the nanowires grown on Si substrate,[31] confirming the feasibility of using metal substrate for growing AlGaN nanowire-based emitters. However, the output power of our fabricated device was still low. To improve the device performance, there are many approaches such as (1) one can use AlGaN/AlGaN multiple quantum well structures in the active region instead of using a AlGaN double heterostructure, (2) one can optimize the growth condition (nanowire dimensions and density) to further improve the quantum efficiency of the device, (3)one can use different metal substrates to improve the light extraction efficiency, e.g., Aluminum which has much higher reflectivity (>95%) than Titanium (>80%) in UV spetrumal range, (4) one can minimize the thickness of the bottom n-GaN layer which is UV-absorptive, and (5) one can apply a tunneling junction to replace the p-GaN layer to avoid its absorption.[5]

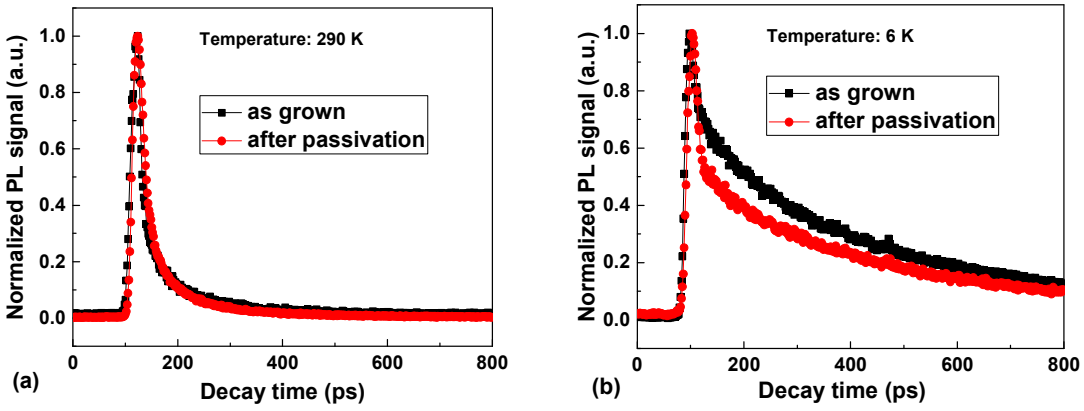

Figure 5. PL transients of as-grown and passivated AlGaN nanowires collected at (a) Room-temperature and (b) 6K.

To further investigate the effects of the surface passivation on the photo-excited carrier dynamics, we also performed TRPL measurements on both as-grown and KOH-passivated AlGaN nanowires. Fig. 5 shows the low-temperature (LT) and room-temperature (RT) TRPL spectra of the major peak (□337 nm) emitted from the active region. A pulse-width limited rise in the emission signal was followed by a PL decay that could be fitted fairly well with a double exponential function that is due to multiple recombination centers.[32] Our study shows that the carrier lifetimes are relatively short, indicating the efficient radiative recombination of photo-excited carriers in the AlGaN nanowires in the absence of competition from carrier localization

states, which is consistent with the decay profiles previously reported for MBE-grown nitrides nanowires.[14,15] While the slow decay time is □340 ps at LT for as-grown nanowires, it is □285 ps for KOH-passivated nanowires. At LT, the recombination process is dominated by the radiative recombination.[33] However, the role of non-radiative recombination centers is reduced but still presents. The reduced value of the slow decay time of KOH-passivated nanowires at LT indicates a better radiative recombination process and reflects the improved quality of the nanowires. In other words, the KOH passivated nanowires have relatively less defect states than the as-grown ones. On the other hand, the slow decay time is □108 and □125 ps for as-grown and KOH-passivated nanowires at RT, respectively. The non-radiative recombination centers dominate the recombination process at RT.[32] Again, the reduced density of defect states in the passivated nanowires causes the non-radiative recombination process to be slower than that of the as-grown ones. This may cause an increase in the overall carrier lifetime in the passivated nanowires. These observations provide strong evidence for the elimination of surface states via KOH passivation, resulting in a more efficient LED device performance.

CONCLUSIONS

In this article, we have presented an effective and environmentally-friendly method to significantly remove surface oxidation and reduce surface states in MBE-grown AlGaN nanowires by using KOH passivation. The STEM investigation has been used to demonstrate the almost intact nanowires after passivation. Both PL and EL results showed a significant enhancement in the optical performance of the studied UVLEDs. In particular, the optical output power is increased by about 49.7% with a better I-V characteristic in the fabricated UVLEDs emitting at 337 nm after KOH passivation. The observation of the changes of carrier lifetime before and after passivation both at room and low temperature is mainly due to the success in reducing of surface states. We anticipate that this passivation procedure will find broad practical applications in fabricating self-assembled nanowire-based high-efficient light emitting devices.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

We acknowledge the financial support from King Abdullah University of Science and Technology (KAUST) baseline funding, BAS/1/1614-01-01 and BAS/1/1664-01-01. Also, BSO, TKN, MKS and BJ gratefully acknowledge funding support from King Abdulaziz City for Science and Technology, grant no. KACST TIC R2-FP-008. The time-resolved PL measurements have been carried out and analyzed by M. M. Muhammed and I. S. Roqan.

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ACS Photonics Revised Manuscript # ph-2017-01235t

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Surface-Passivated AlGaN Nanowires for Enhanced Luminescence of Ultraviolet Light Emitting Diodes

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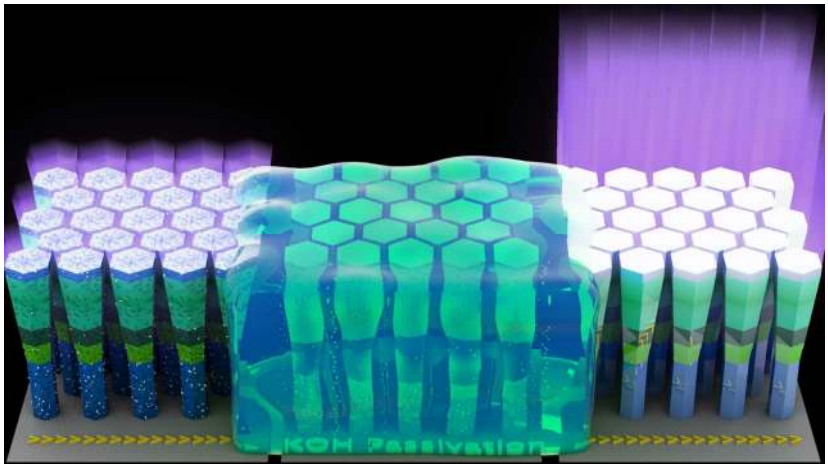
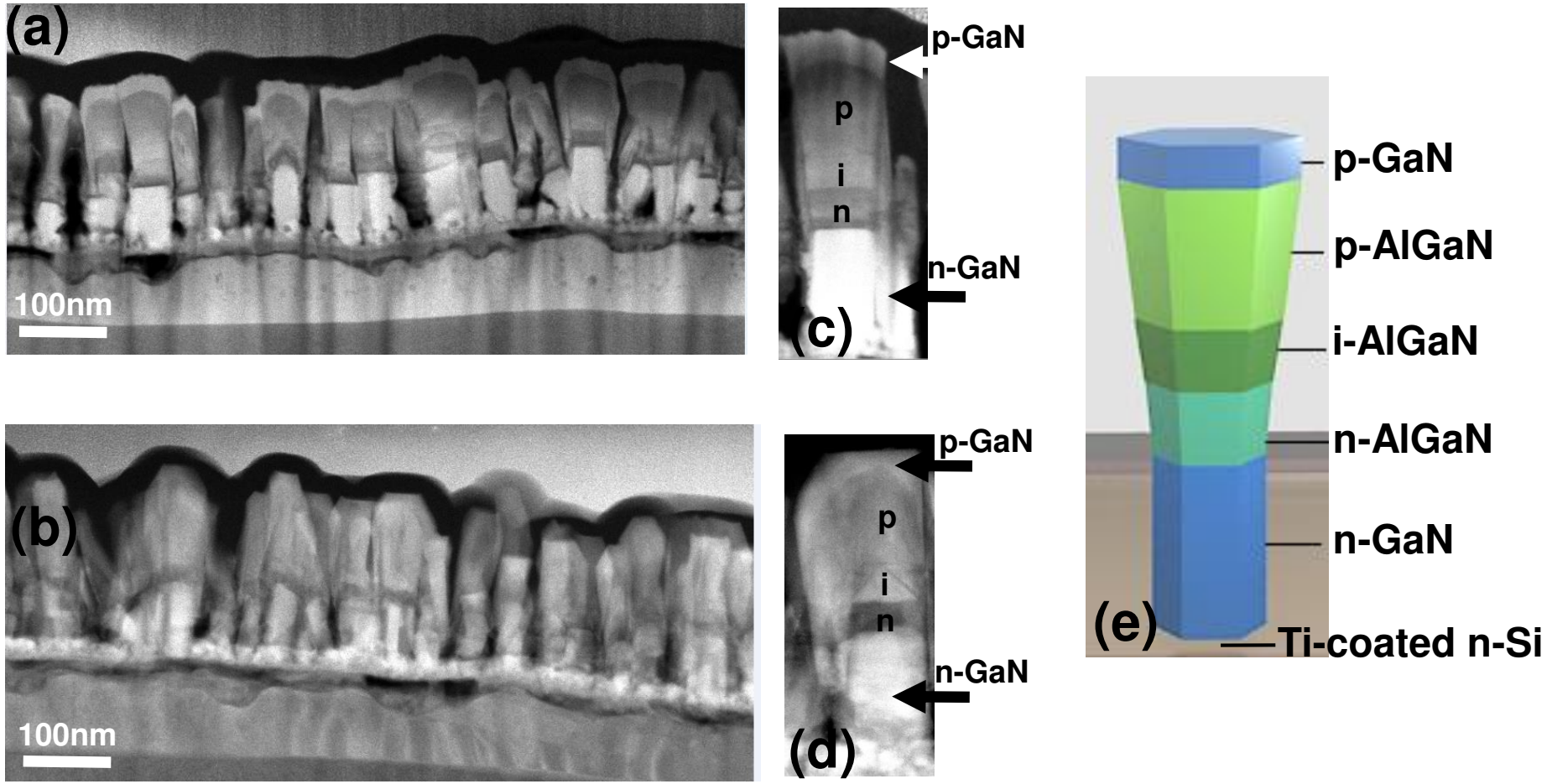
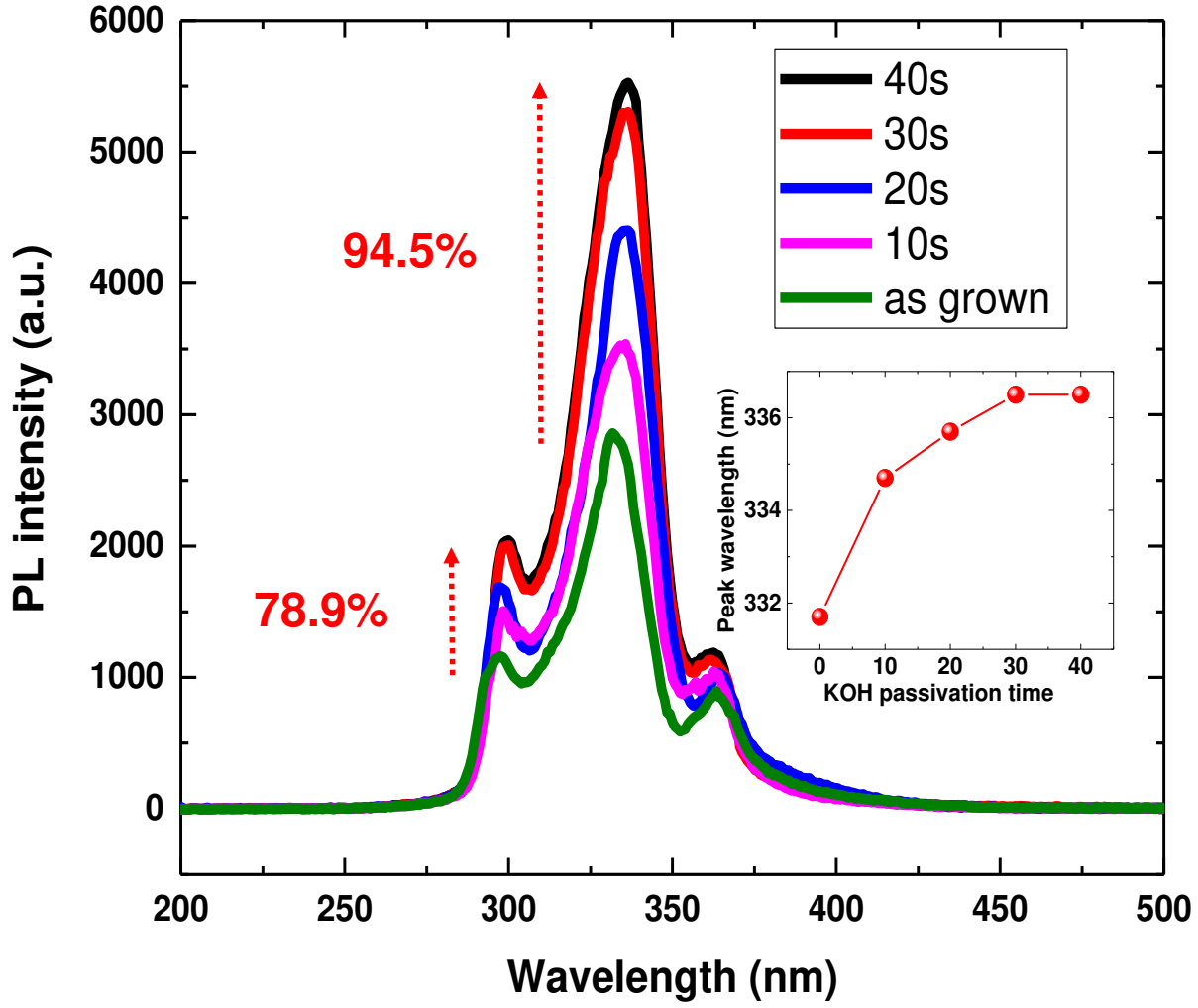
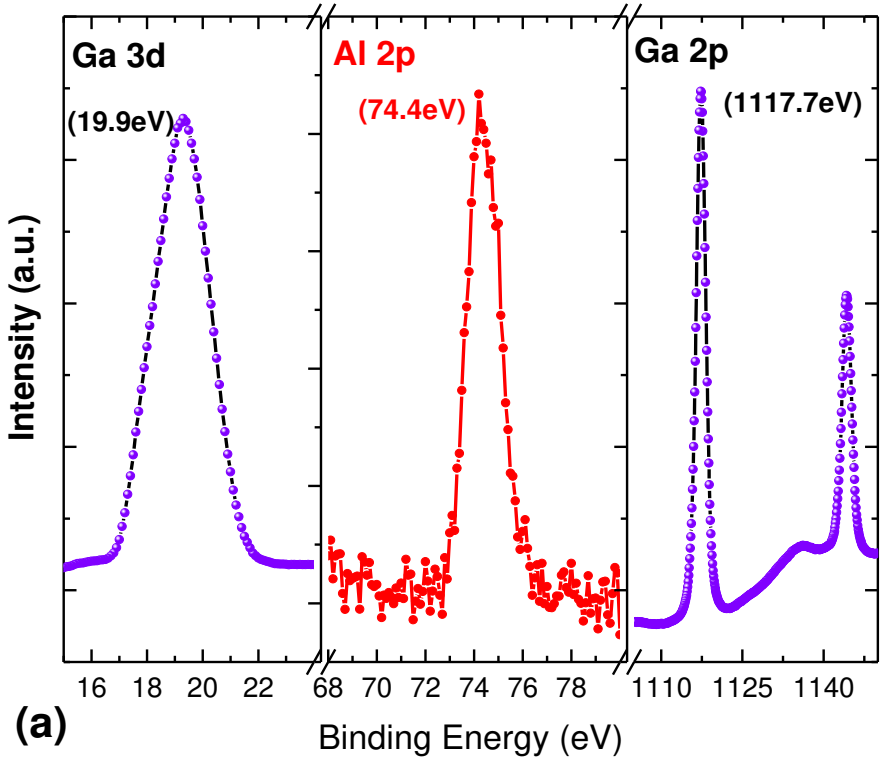
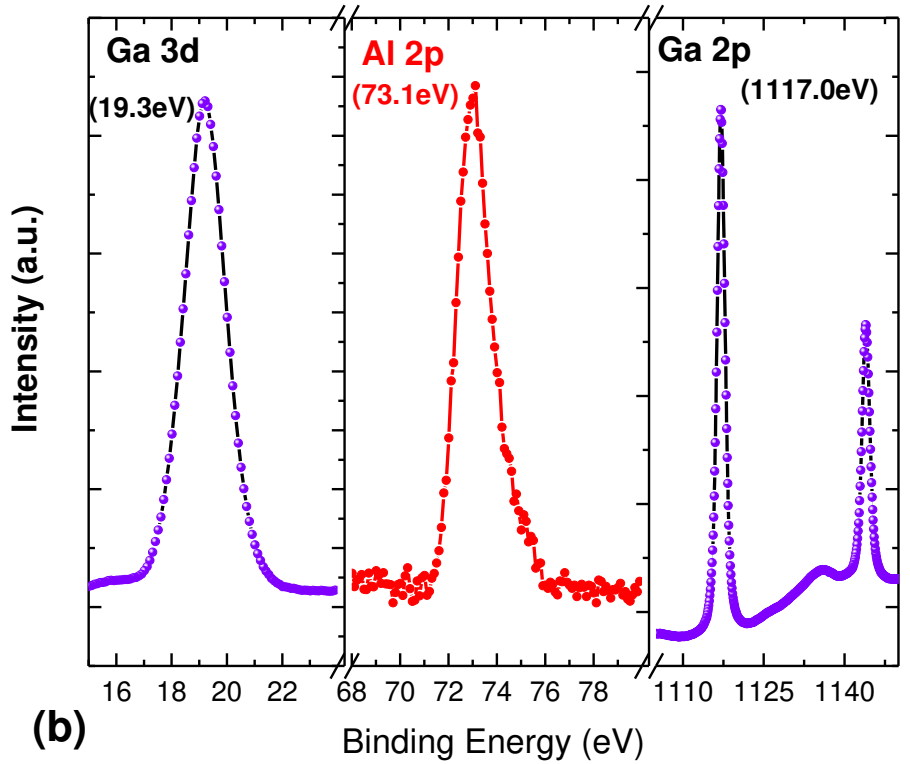


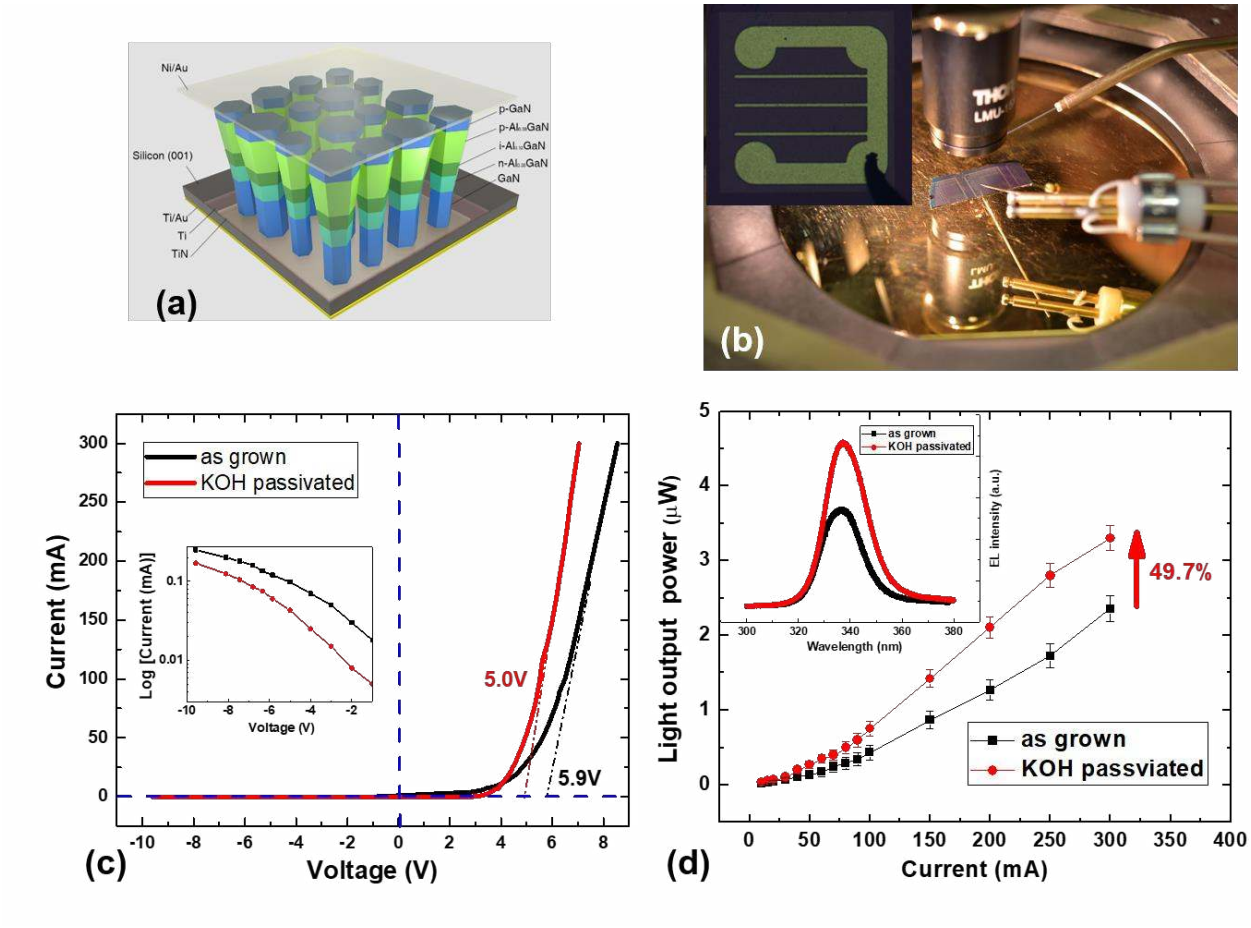
An effective and environmentally-friendly method to significantly remove surface oxidation and reduce surface states in MBE-grown AlGaN nanowires by using KOH solution and thus remarkably enhance the ultraviolet light output power.

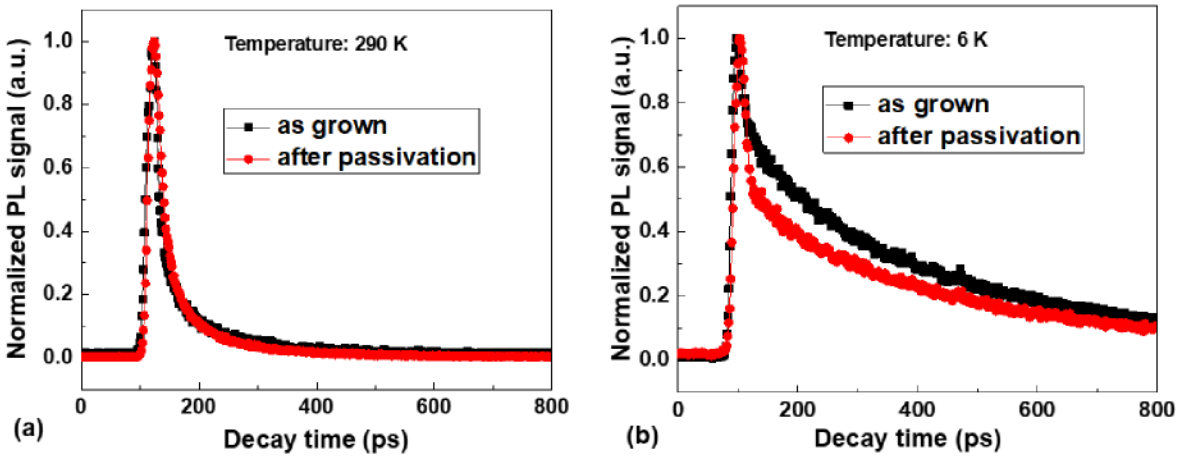

(a)
100nm
(b)
100nm
p-GaN
p
i
n
n-GaN
(c)
p-GaN
p
i
n
n-GaN
(d)
p-GaN
p-AlGaN
i-AlGaN
n-AlGaN
n-GaN
Ti-coated n-Si
(e)
(f)
100nm
(g)
100nm


6000
5000
4000
3000
2000
1000
0
PL intensity (a.u.)
200
250
300
350
400
450
500
Wavelength (nm)
94.5%
78.9%
40s
30s
20s
10s
as grown
Peak wavelength (nm)
336
334
332
0
10
20
30
40
KOH passivation time


Ga 3d
(19.9eV)
Al 2p
(74.4eV)
Ga 2p
(1117.7eV)
Intensity (a.u.)
16 18 20 22
68 70 72 74 76 78
1110 1125 1140
(a)
Binding Energy (eV)


Ga 3d
(19.3eV)
Al 2p
(73.1eV)
Ga 2p
(1117.0eV)
Intensity (a.u.)
16 18 20 22
68 70 72 74 76 78
1110 1125 1140
(b)
Binding Energy (eV)


Ni/Au
p-GaN
p-Al0.2GaN
i-Al0.1GaN
n-Al0.2GaN
GaN
Silicon (001)
Ti/Au
Ti
TiN
(a)
(b)
as grown
KOH passivated
Current (mA)
Log [Current (mA)]
Voltage (V)
5.0V
5.9V
(c)
Light output power (μW)
EL intensity (a.u.)
Wavelength (nm)
49.7%
as grown
KOH passviated
Current (mA)
(d)


Temperature: 290 K
as grown
after passivation
Normalized PL signal (a.u.)
Decay time (ps)
(a)
Temperature: 6 K
as grown
after passivation
Normalized PL signal (a.u.)
Decay time (ps)
(b)