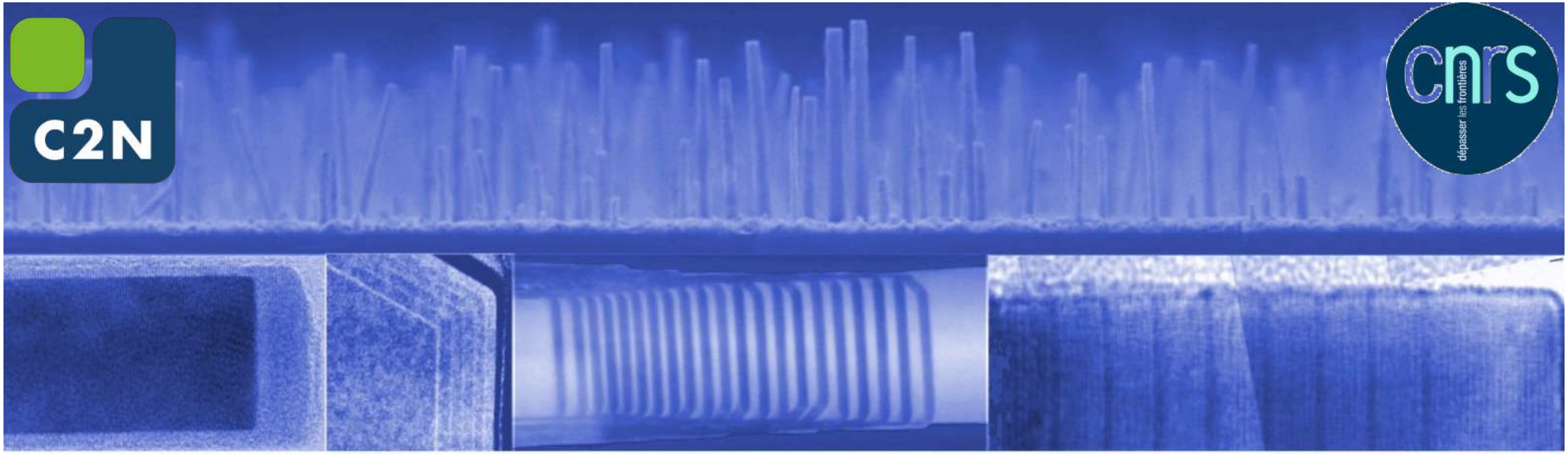


# Nitride nanowire light emitting diodes: from single wire properties to device applications

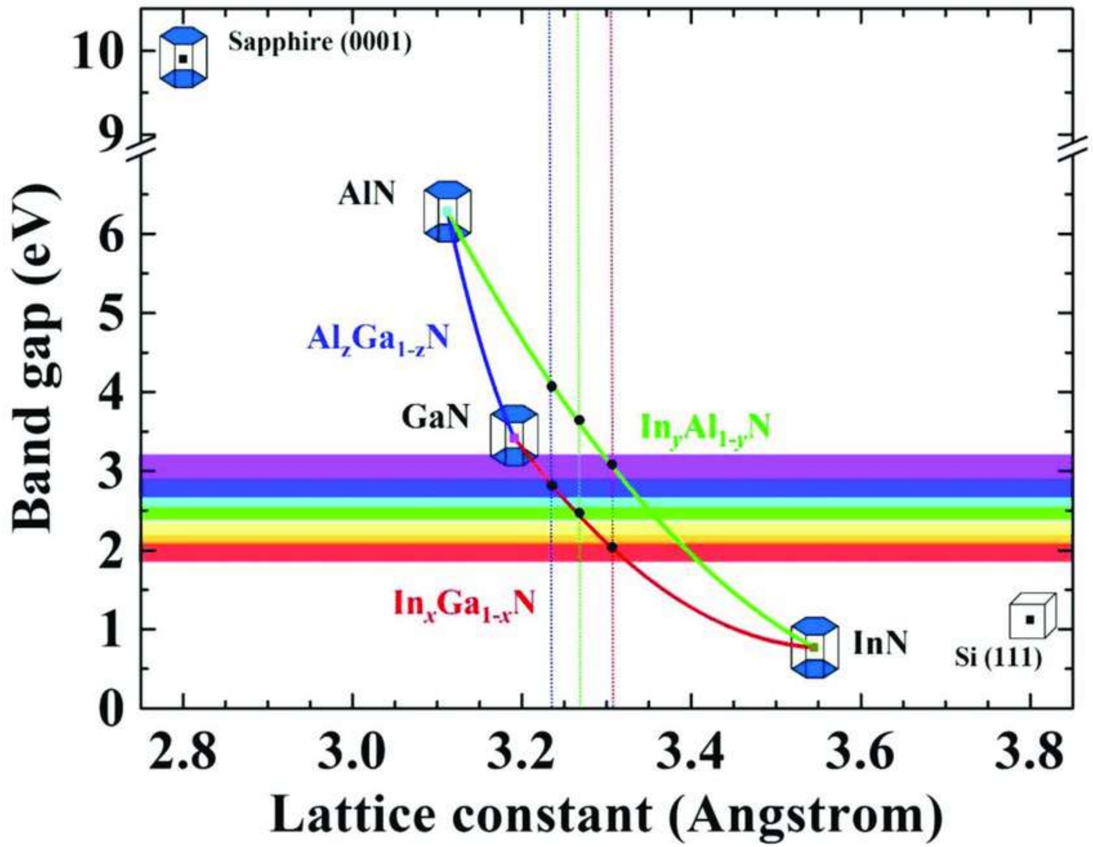
**M. Tchernycheva[1]**, N. Amador, S. Vézian, B. Damilano, J. Bosch, B. Alloing, J. Eymery, C. Durand

[1] *C2N-CNRS, University Paris Saclay, 91120 Palaiseau, France*

# Outline

- Nitride thin film LEDs and open issues
- Nanowires for LEDs
- From individual wires to array LEDs
- Flexible nanowire LEDs
- UV nanowire LEDs
- Nanoporous LEDs
- Summary

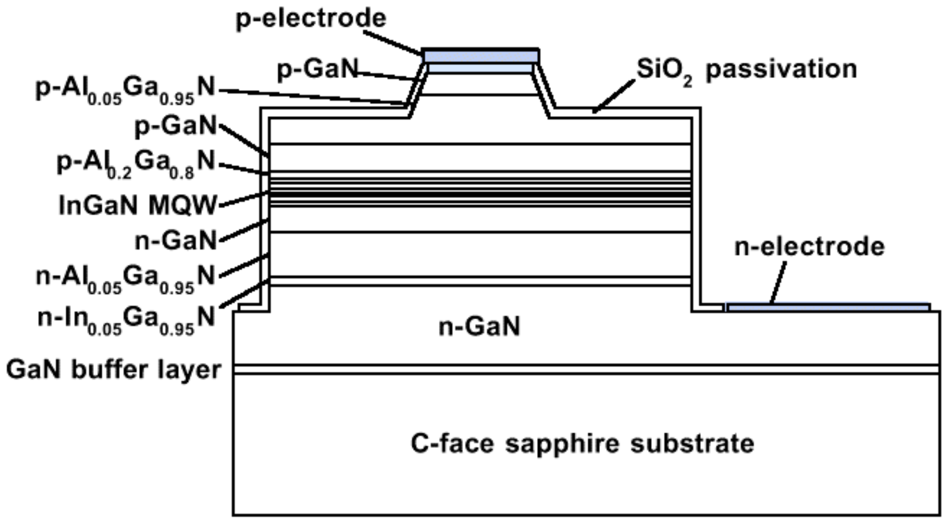
# Nitride semiconductor family

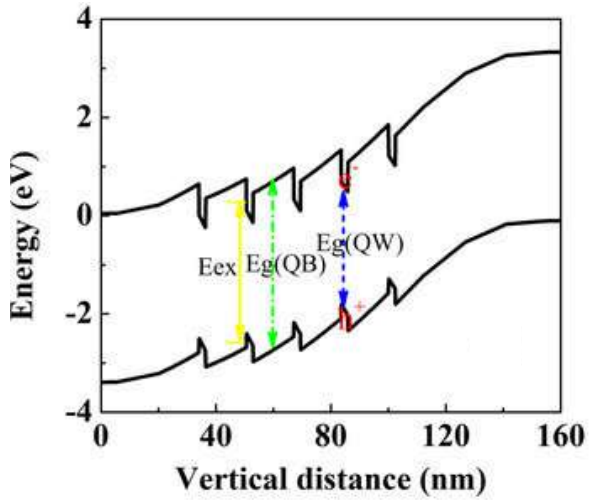



Direct badgap covering NIR – visible – UV ranges

- InGaN/GaN – visible
- GaN/AlGaN – UV

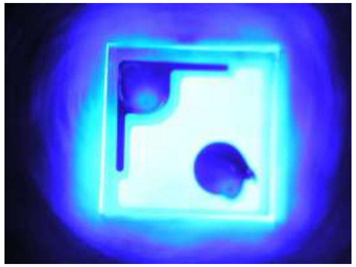
# InGaN/GaN light emitting diodes




Blue GaN/InGaN LED demonstrated in 1993

**Nobel Prize in Physics 2014** (Akasaki, Amano, Nakamura)

 +  = 

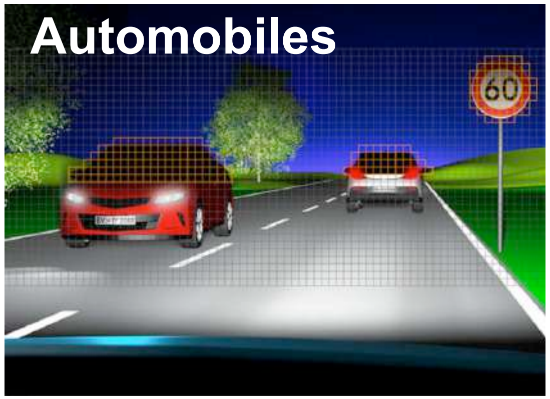
LED luminous efficacy >300 lm/W (incandescent lamp is ≈10-20 lm/W)

# Applications of visible LEDs


**Nitride white LED for lighting**

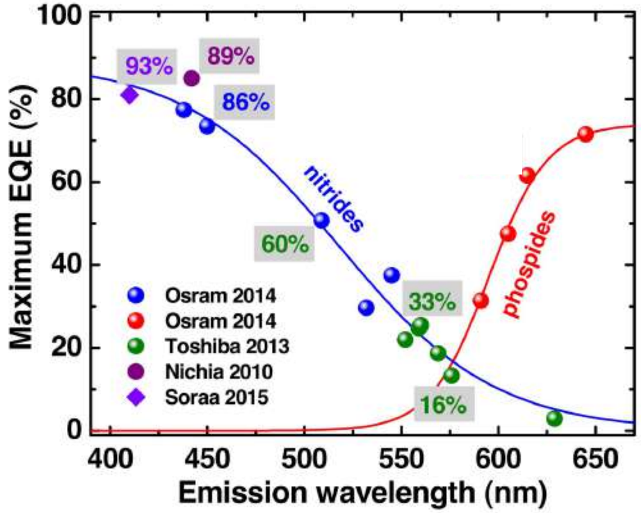
- Rapidly growing (70 billion $ market for nitride devices)
- Additional functionality of color tuning
- Eco-friendly and huge energy saving

**LEDs and micro-LEDs for displays**

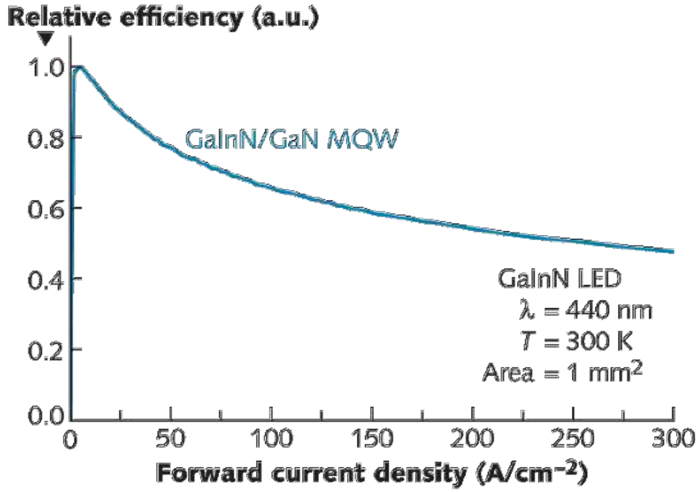




# Issues of thin film LEDs

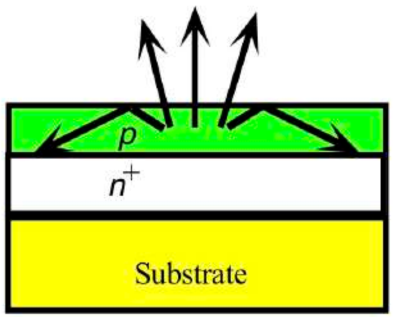
- Green gap



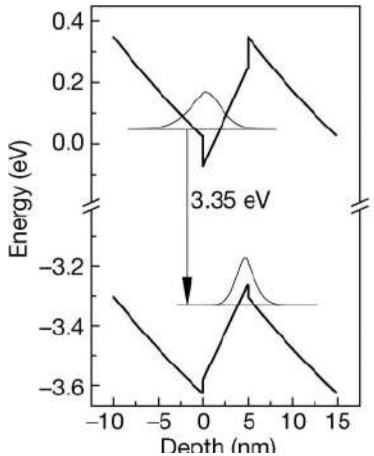

- Efficiency droop



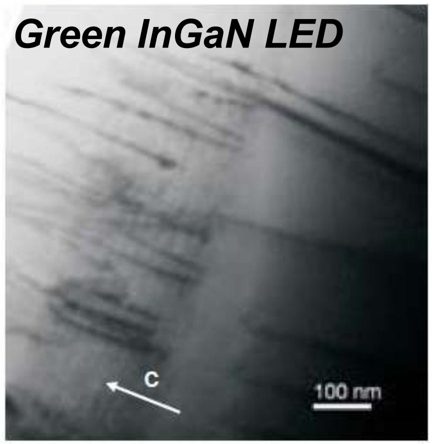

- Light extraction




- Internal electric field

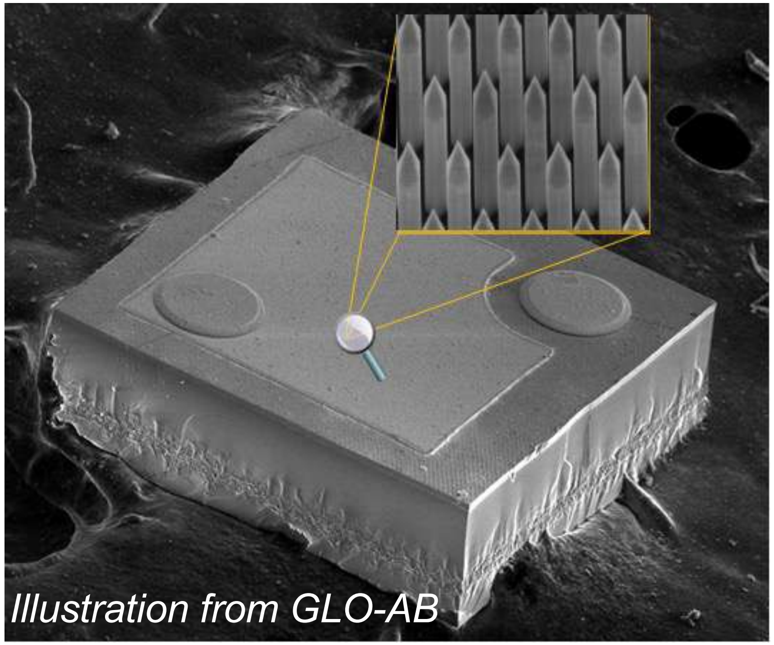



- Material quality



# Nanowires as a way to boost the LED performance or to bring new functionalities

## Nanowire LEDs




***Can we improve the performance using functional nanomaterials?***

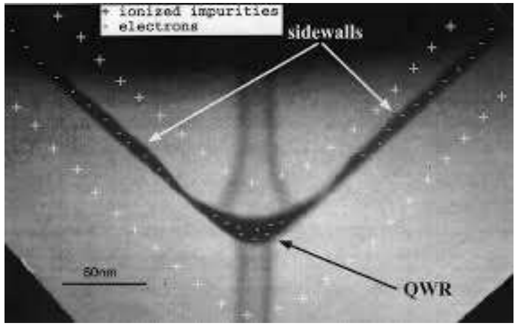
# Nanowires versus quantum wires

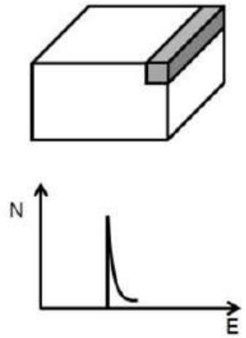
### Quantum wires

Example : V-groove QWire

Presents 1D quantum confinement

Embedded in a crystalline matrix




*Kapon, EPFL, 1988*

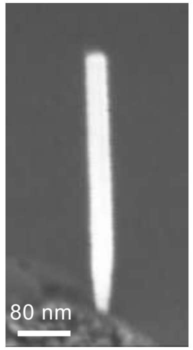
Incorporation of confining heterostructures (along the axis -- 0D, on the edges -- 1D, on the sidewalls -- 2D)

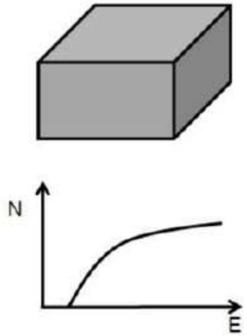
### Bottom-up nanowires

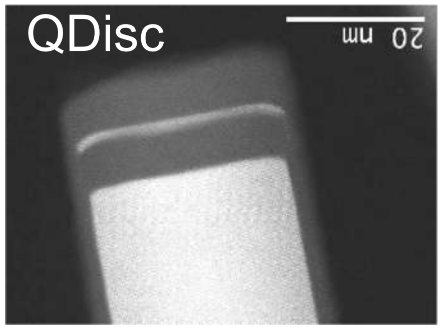
*Typical diameter 10 -- 1000 nm*

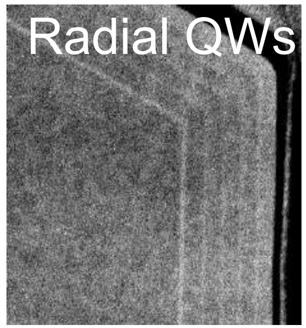
Not a quantum object

In ambient environment



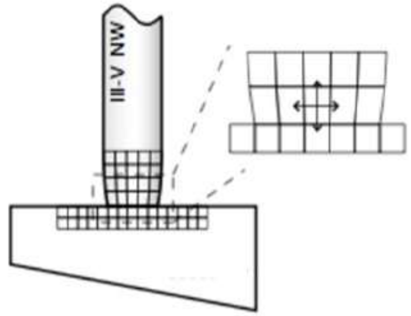



# Nanowires – new opportunities for material elaboration

**Strain relaxation**

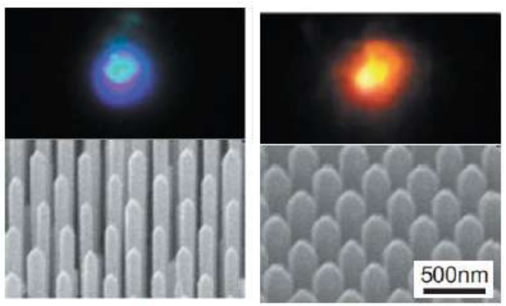
- Strain relaxation by the free surface – nanowires have an excellent crystalline quality independently of the lattice mismatch or thermal coeff. mismatch
- In thick NWs, if a dislocation is formed, it bends to join the lateral surface




➡ **Defect-free growth on cheap substrates (including Si, metals and non-crystalline materials)**

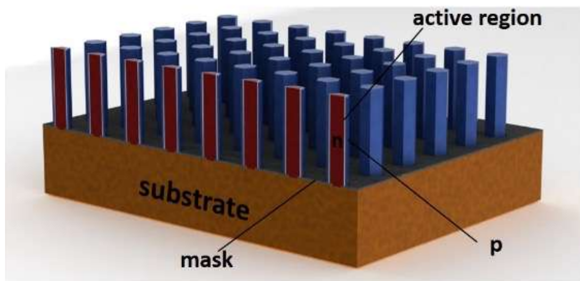
**New opportunities for synthesis**

- Control of composition by local environment



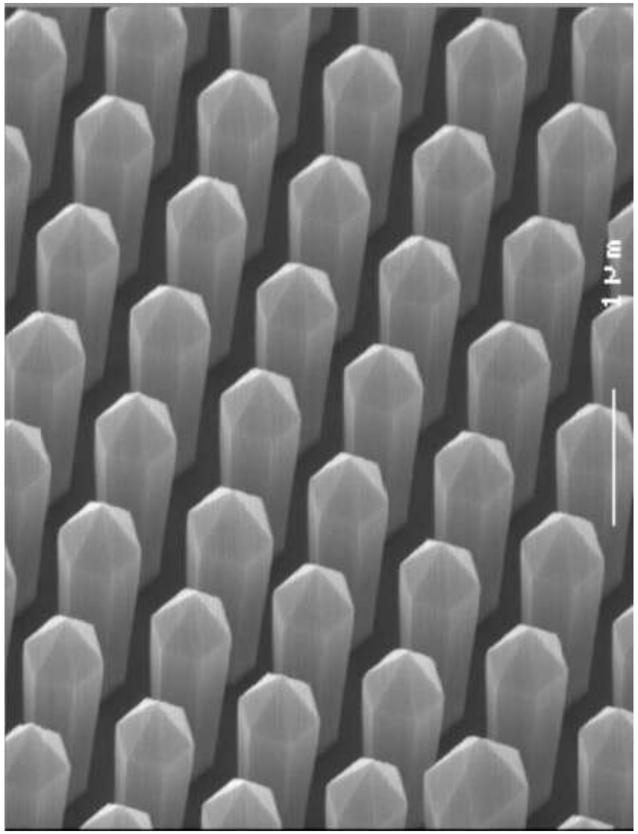

*Sophia Univ, Tokyo*

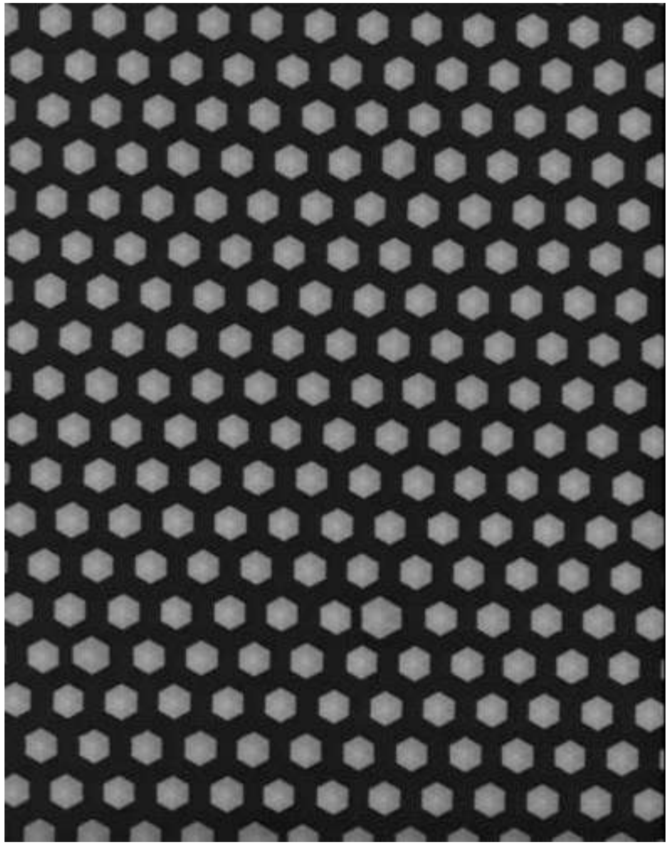
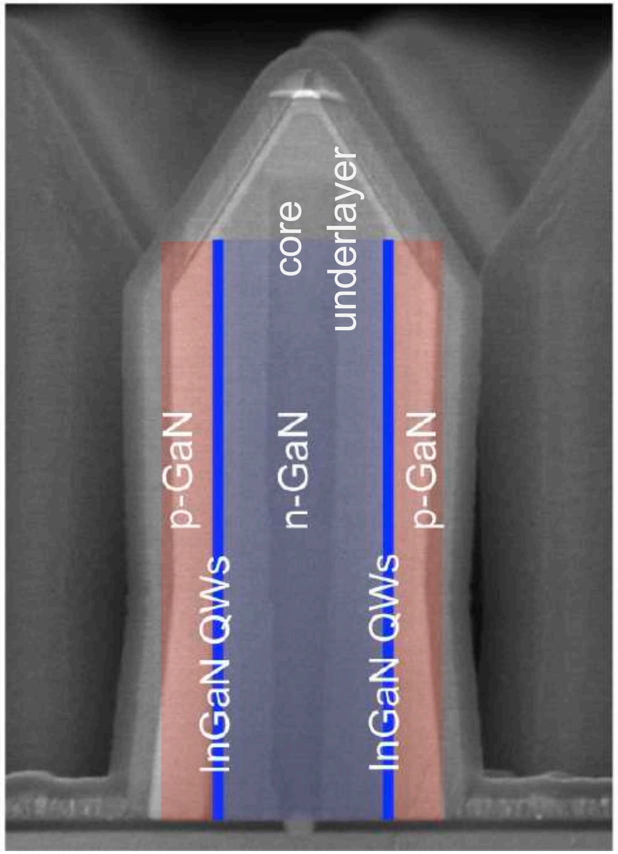
- New degrees of freedom (e.g. core/shell heterostructures – reduction of Auger effect)



# Organized LED nanowire arrays

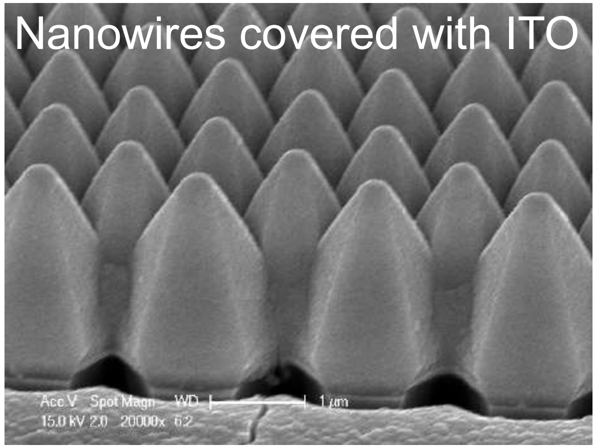
- MOCVD growth on nanopatterned substrates to control the wire homogeneity

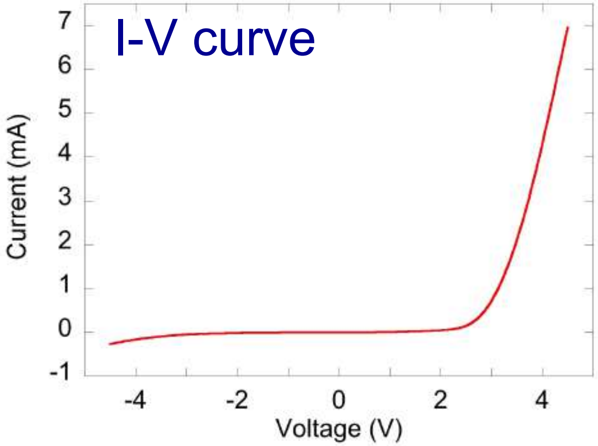


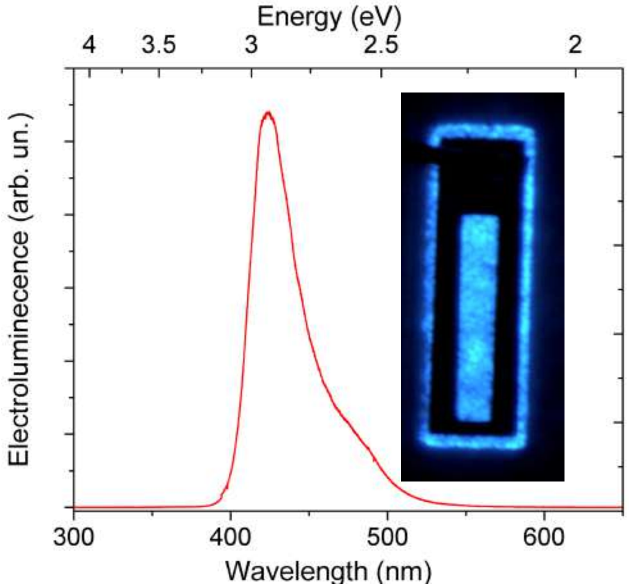




*MOCVD by GLO (O. Kryliouk, R. Ciechonski, G. Vescovi)*

# LEDs from organized nanowire arrays



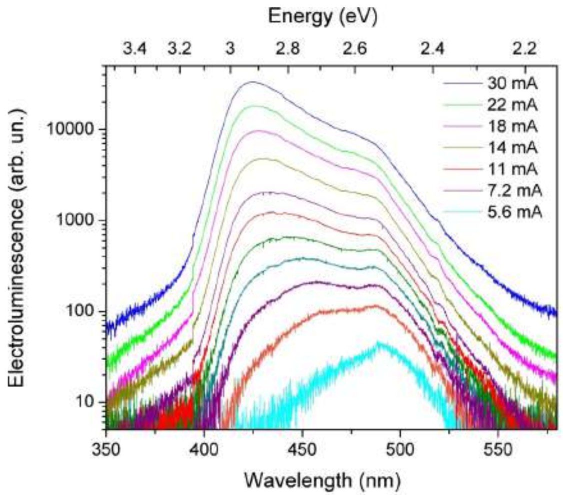



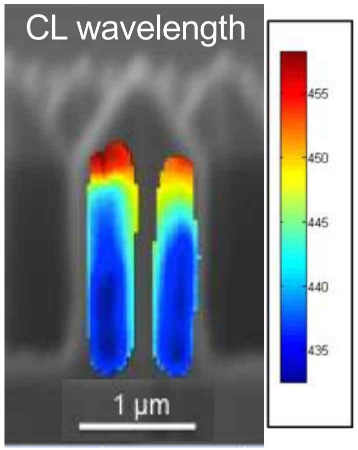

*MOCVD by GLO (O. Kryliouk, R. Ciechonski, G. Vescovi)*

## *Issues with NW LEDs*

**Optical inhomogeneity**

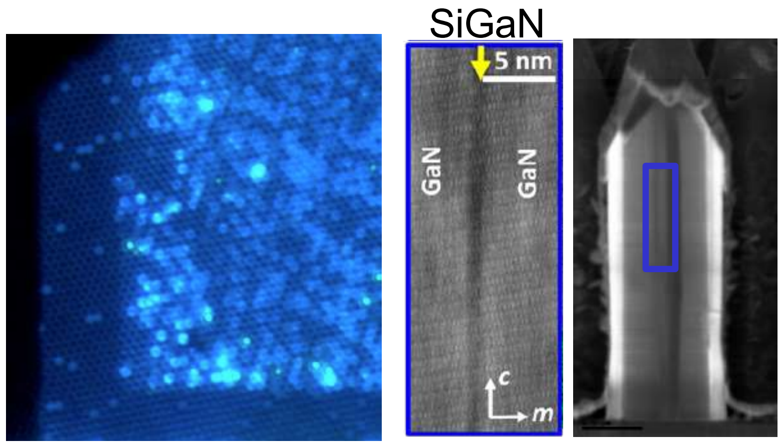
Color changes with injection




**Electrical inhomogeneity**

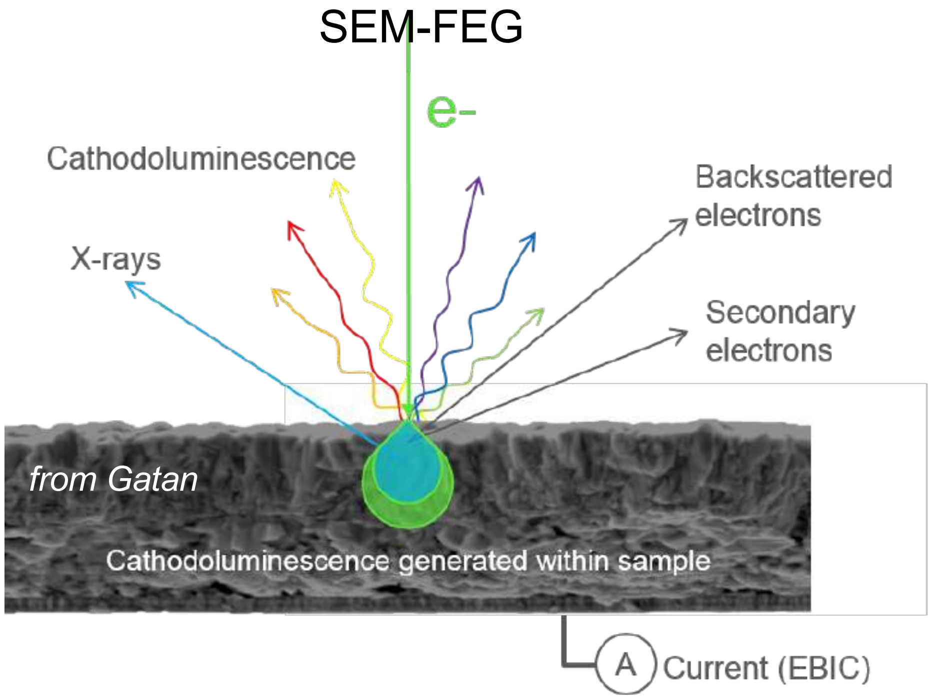
Strong intensity fluctuations



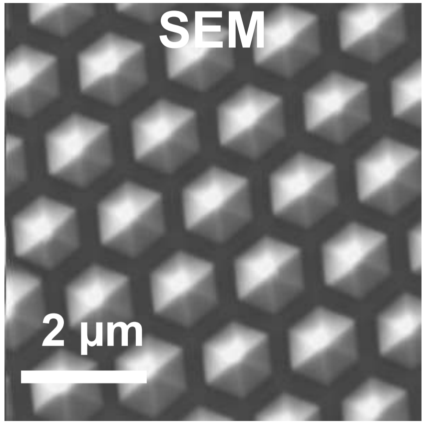

*H. Zhang, et al., Nanotechnology 2020; A. Kapoor et al, Appl Mat & Int 2020, J. Bosch et al., Crystal Growth & Design 2022*

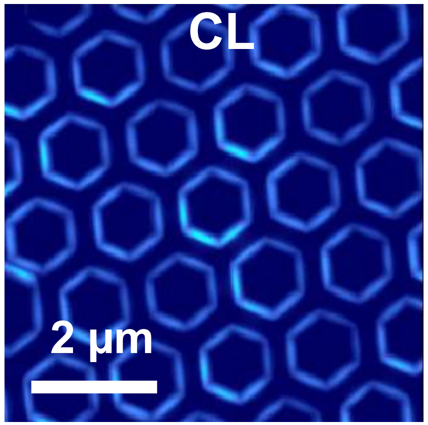
# Cathodoluminescence and Electron beam induced current microscopy

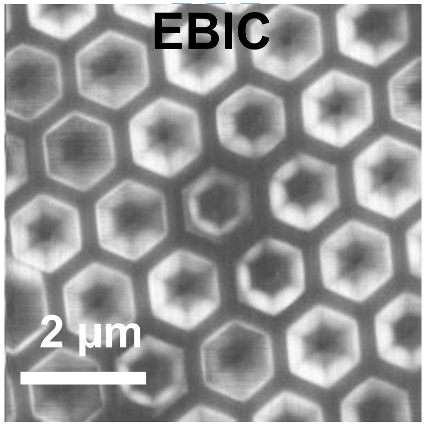
Signals generated during e-beam/matter interaction



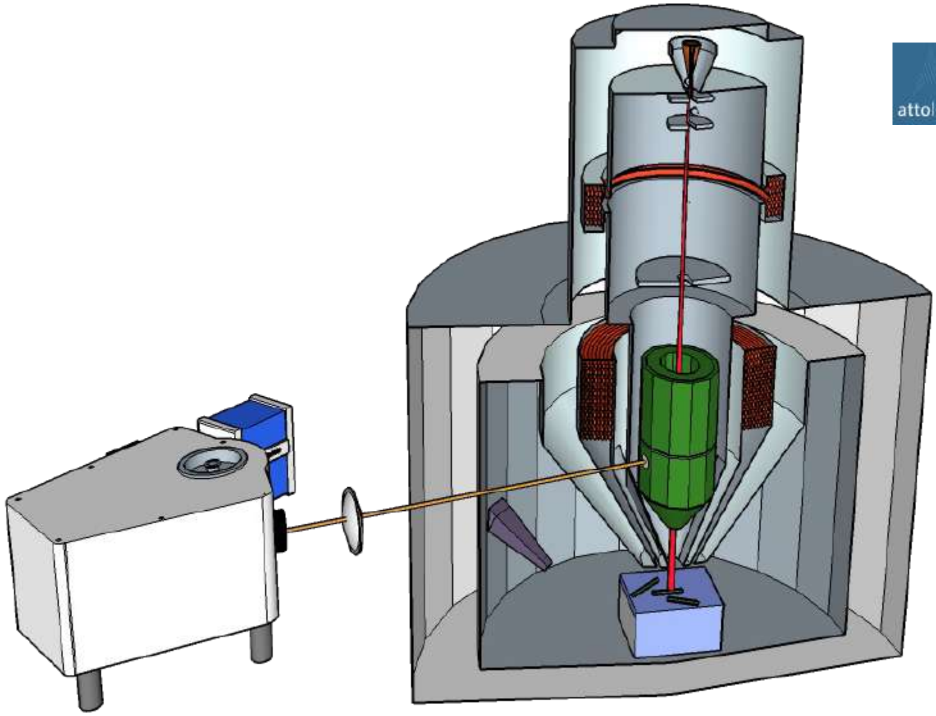

Nanowire LED



# Cathodoluminescence



Steady state and pulsed

(<10 ps) modes

1-100 electrons/pulse:

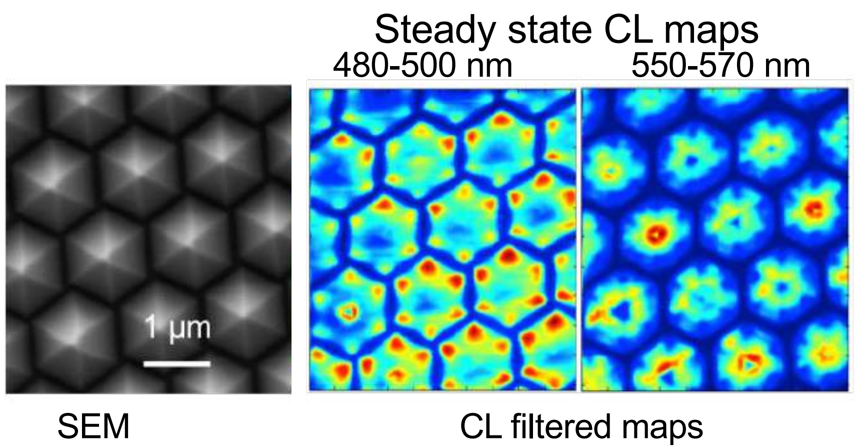
low excitation technique

From 4 K to 300 K

Acceleration voltage = 3-10 kV

**Luminescence spectrum versus beam position map**

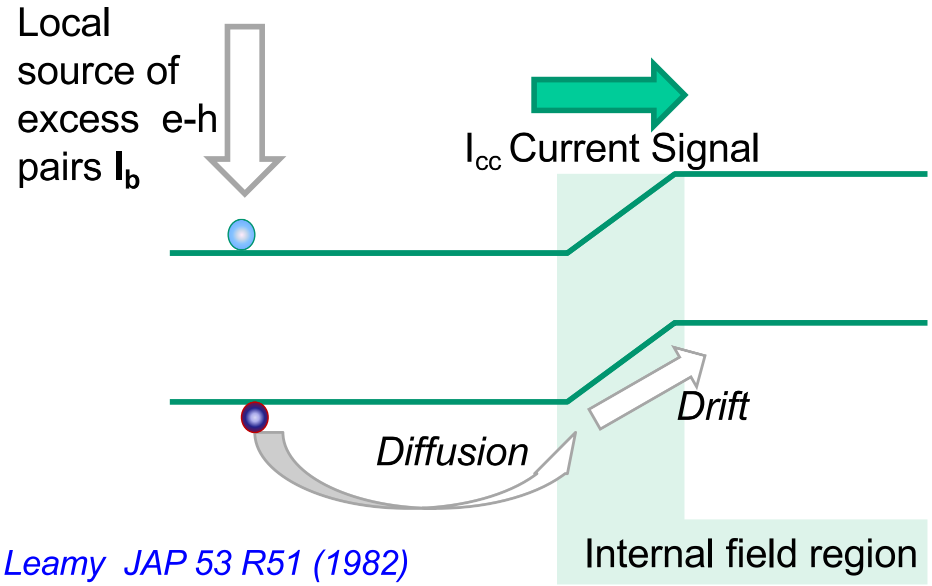
Nanopyramid LED



# Electron beam induced current microscopy

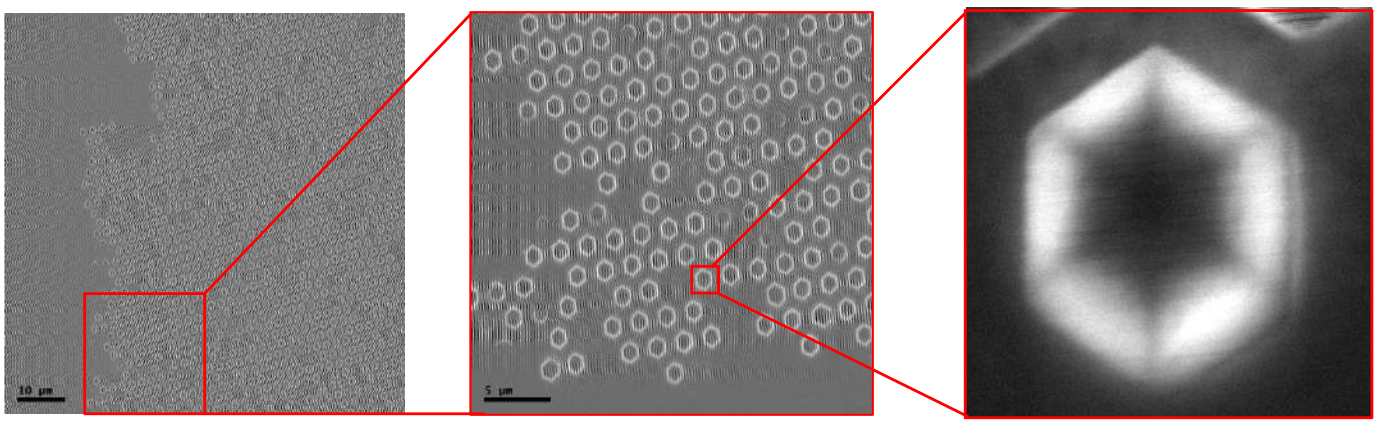
Hitachi SU8000
with Gatan control system
and Kleindiek 4 probes

$V_{acc}$=1-30 kV




*Leamy JAP 53 R51 (1982)*

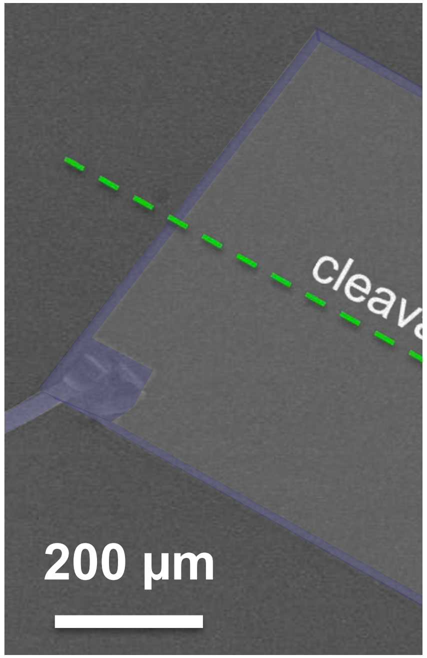
**Current versus beam position map of a nanowire LED from macro to nano scale**

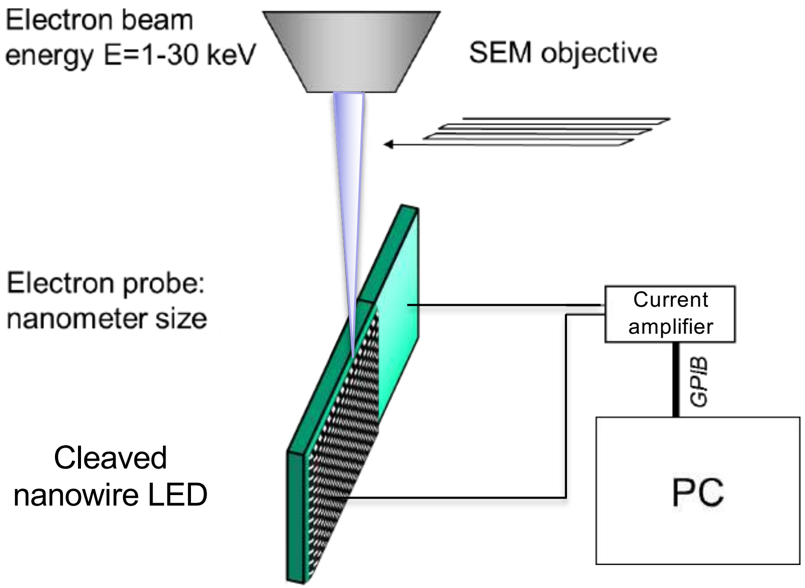


# Sample preparation for the cross-section EBIC and cathodoluminescence mapping

LED mesa device

SEM image of the cleaved edge

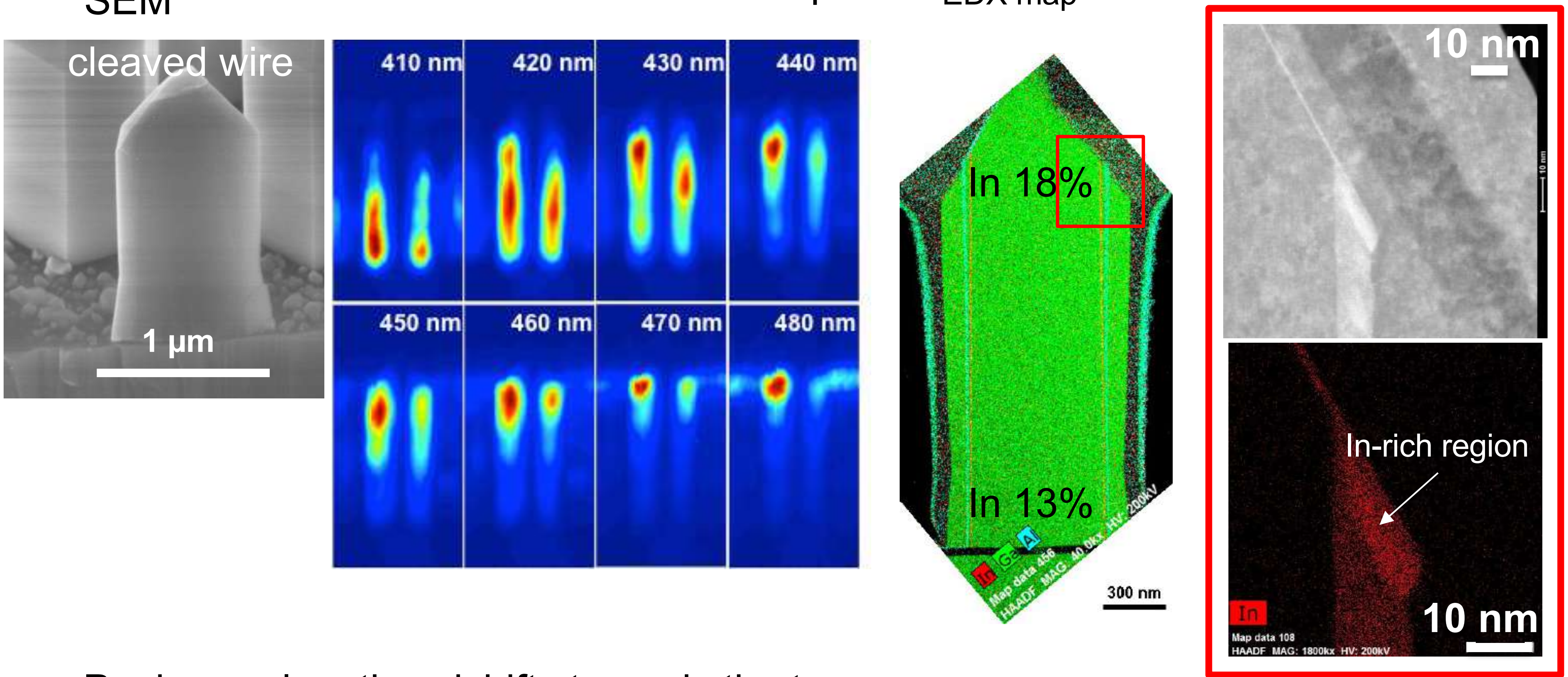



Possible to cleave some nanowires along their axis while preserving the electrical connection with the substrate and with ITO

# Compositional variation in the NW QW

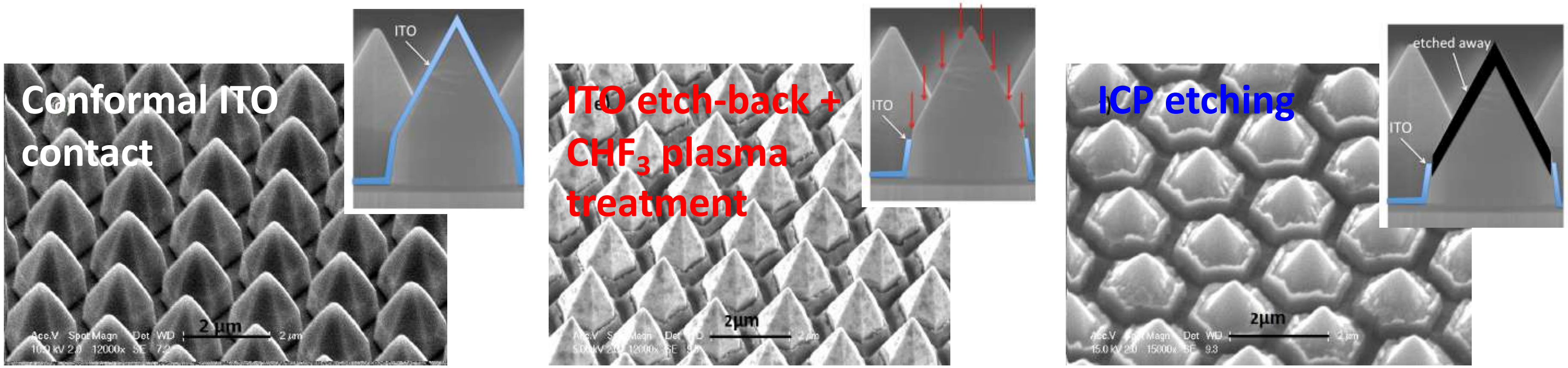
SEM | Cathodoluminescence maps | EDX map | STEM




- Peak wavelength redshifts towards the top
- Green emission for excitation at the m-plane/semipolar plane junction
- In-rich region in the QW at the m-plane/semipolar plane junction

*H. Zhang et al, Nanotechnology 2015*

# Post-growth treatment to tune the emission color

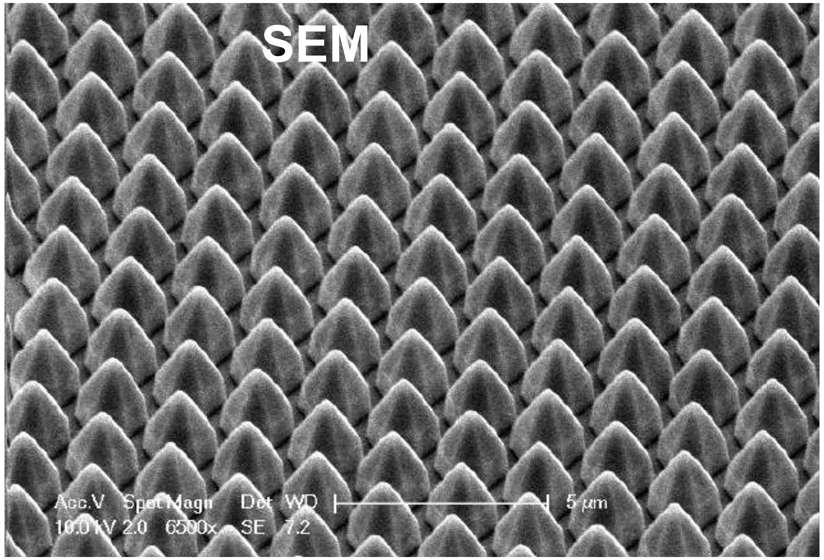


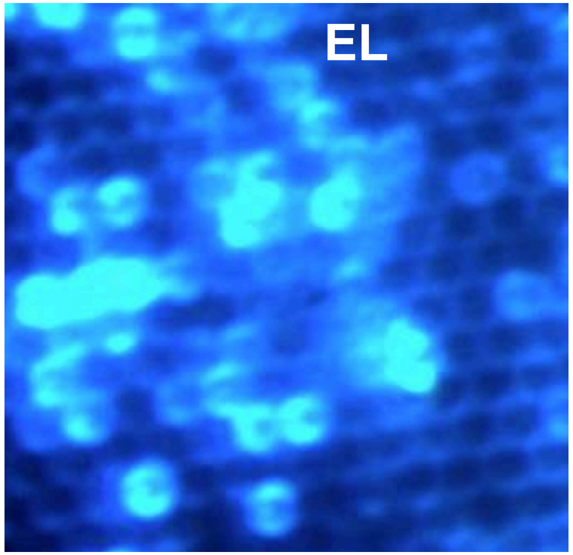

It is possible to control the NW LED color by a post-growth treatment
The price to pay is loosing a part of the active area



*H. Zhang et al, Nanotechnology 2015*

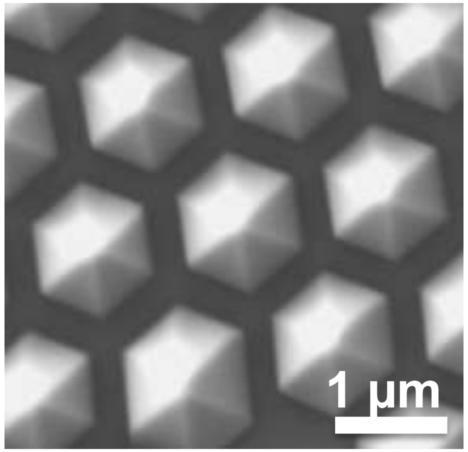
# Problem of the electroluminescence inhomogeneity : correlation between EBIC and EL maps



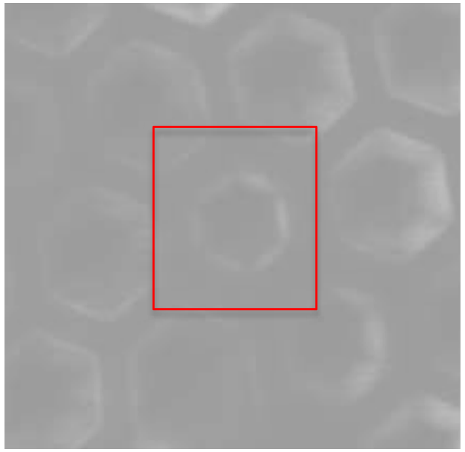



# Correlation between EBIC and cathodoluminescence

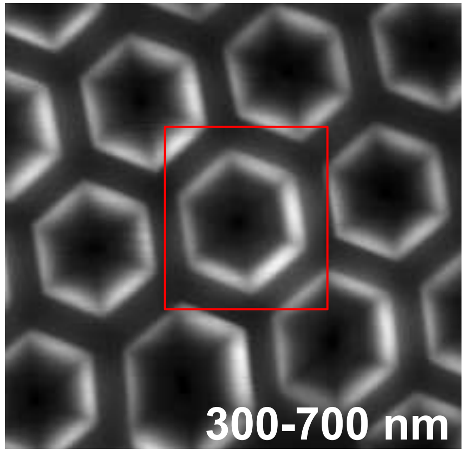
**SEM**



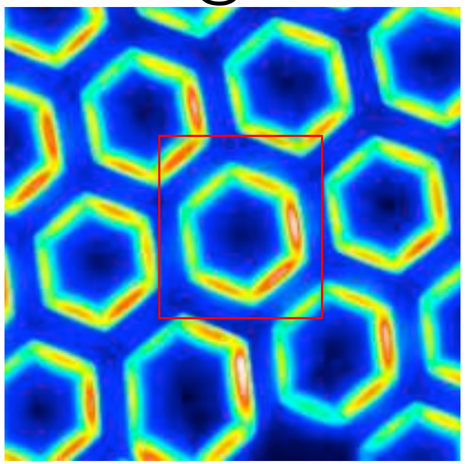

**EBIC**



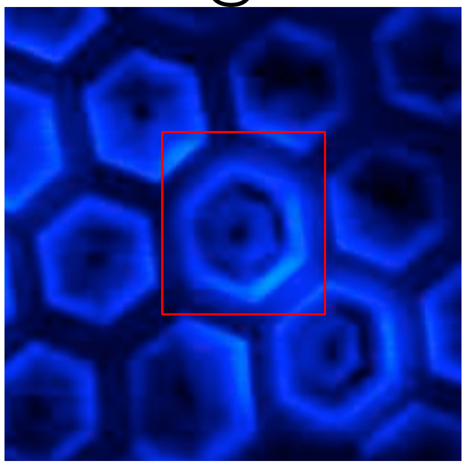
**Panchromatic CL**

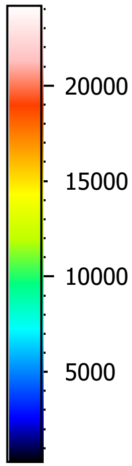



**CL @ 460 nm**

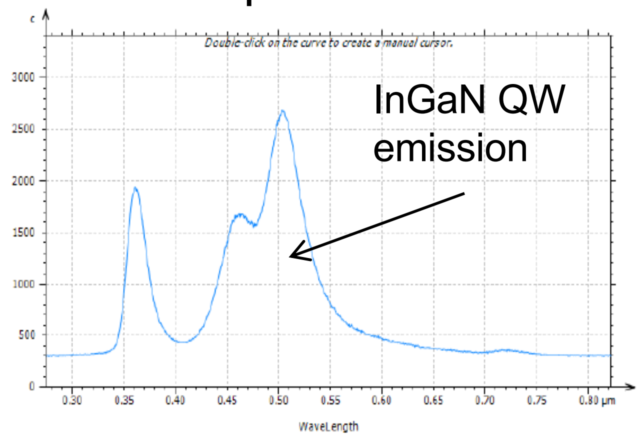


**CL @ 515 nm**





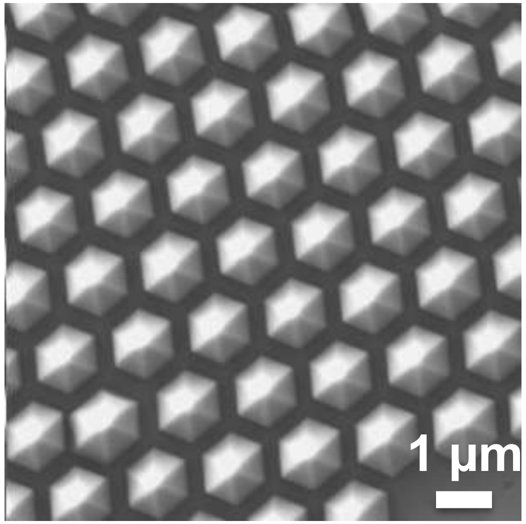

CL spectrum



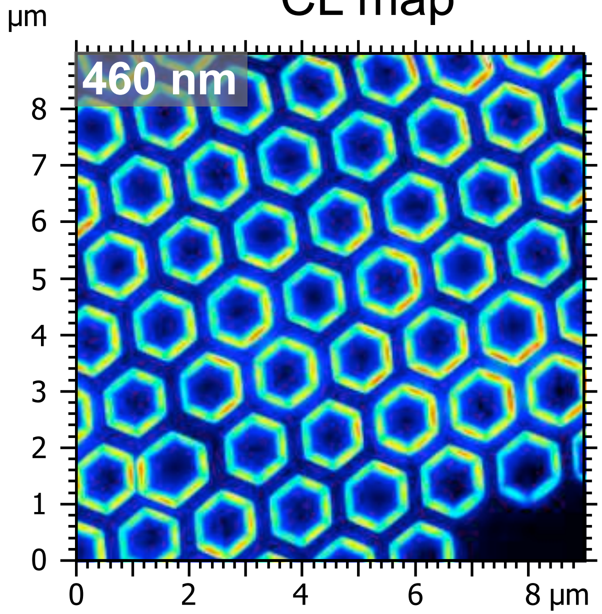

Both CL intensity and spectra for "abnormal" NWs shows no anomalies

# Good wire-to-wire homogeneity of the cathodoluminescence

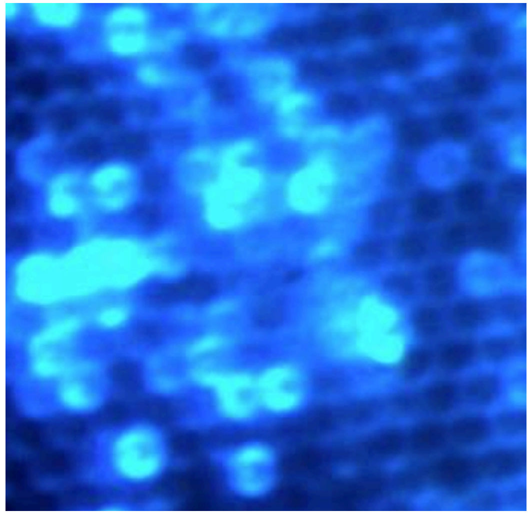
SEM




CL map




EL map (different region)



Cathodoluminescence is present in all NWs with almost constant intensity

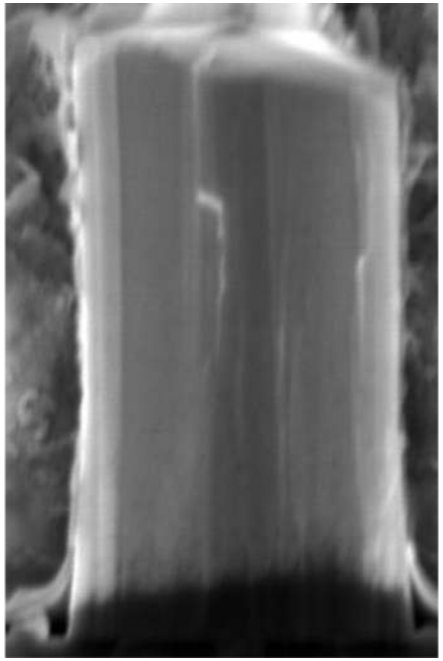
✓ QE of the InGaN QW is not affected (no pronounced non-radiative defects)

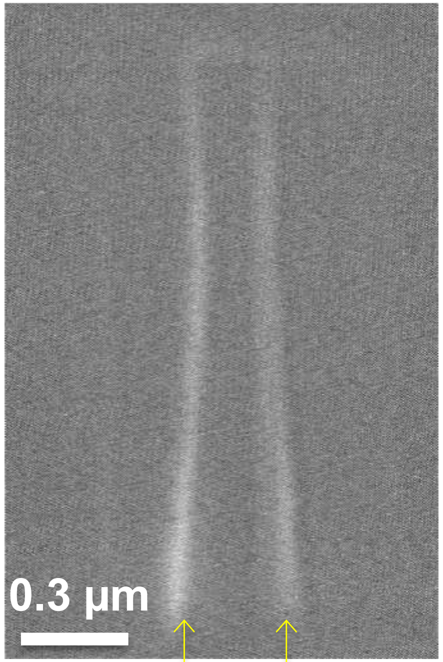
Electroluminescence is very spotty

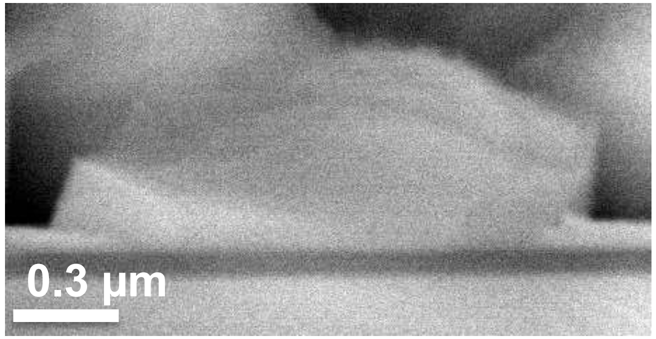
✓ Electrical properties should be questioned

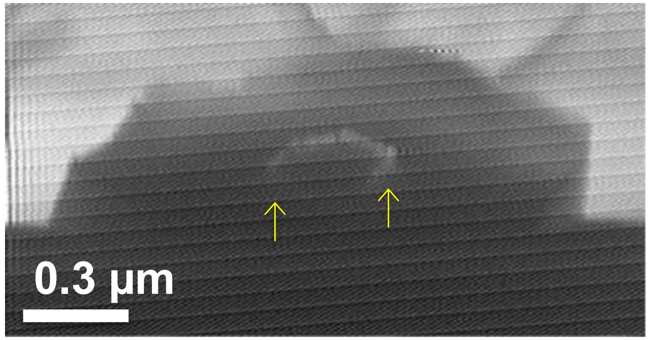
# Abnormal EBIC signal in cross-sectional maps

Signal is localized at the nanowire core



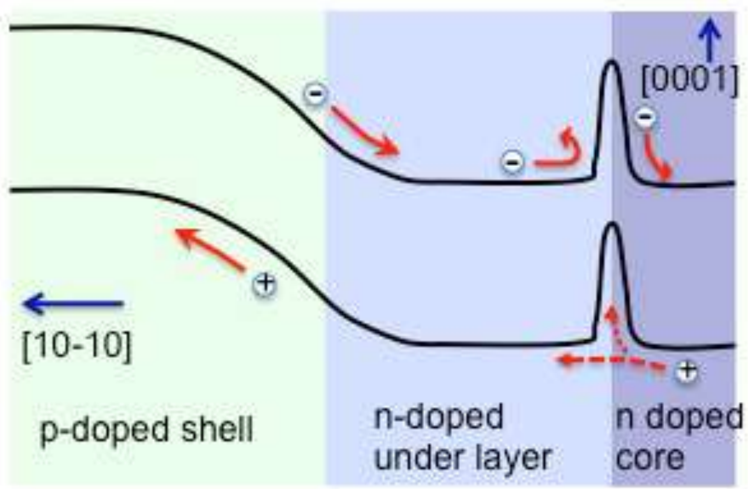


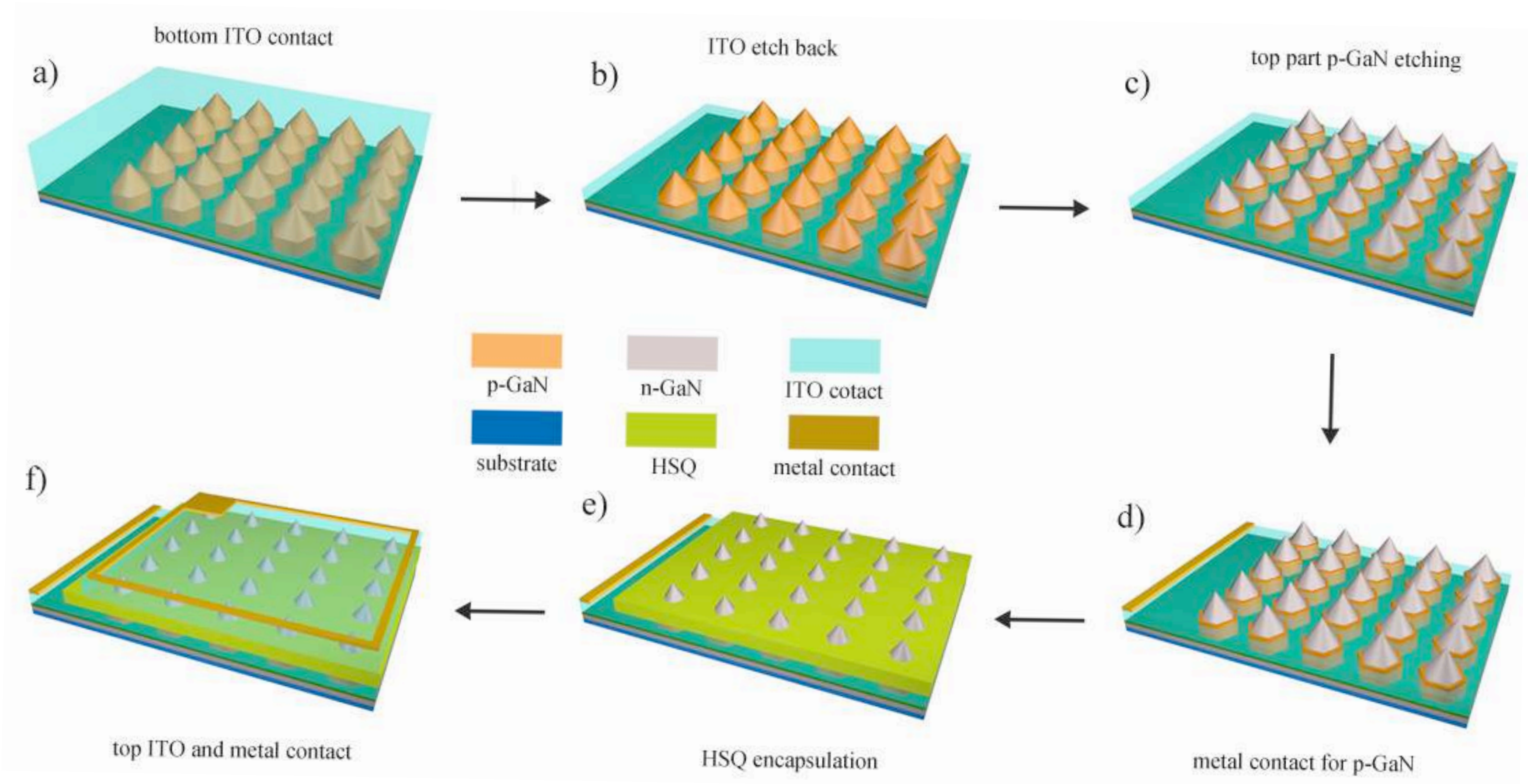

Charge traps at the core/ underlayer interface could lead to an inhomogeneous injection

Tentative explanation : formation of a discontinuous SiGaN layer due to high Si doping of the NW core

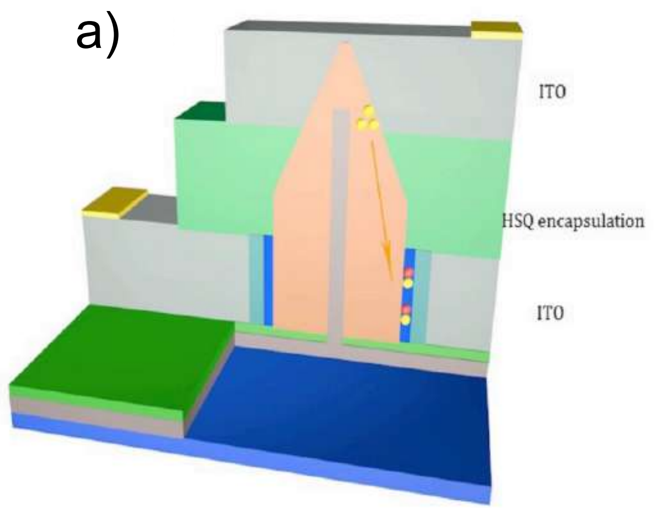


# Front contacting for direct electron injection in the underlayer

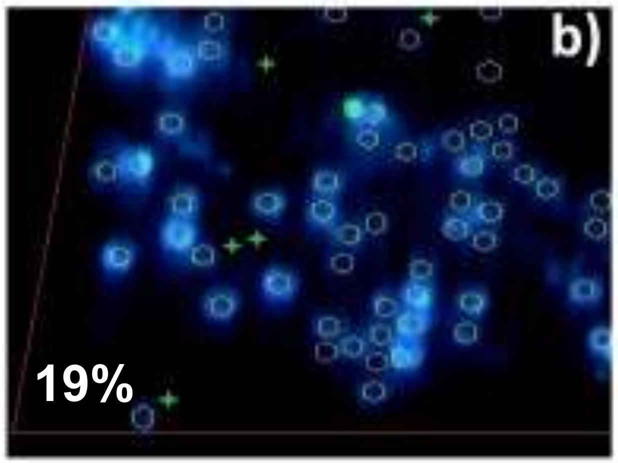
Inject electrons directly in the core avoiding the core/shell interface



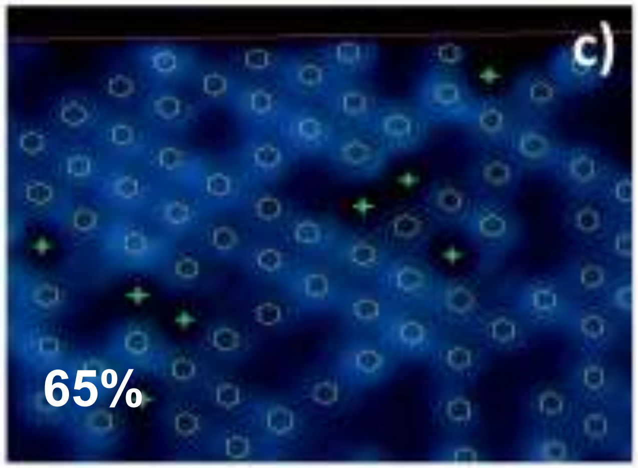
# Improved EL yield for front contacting process

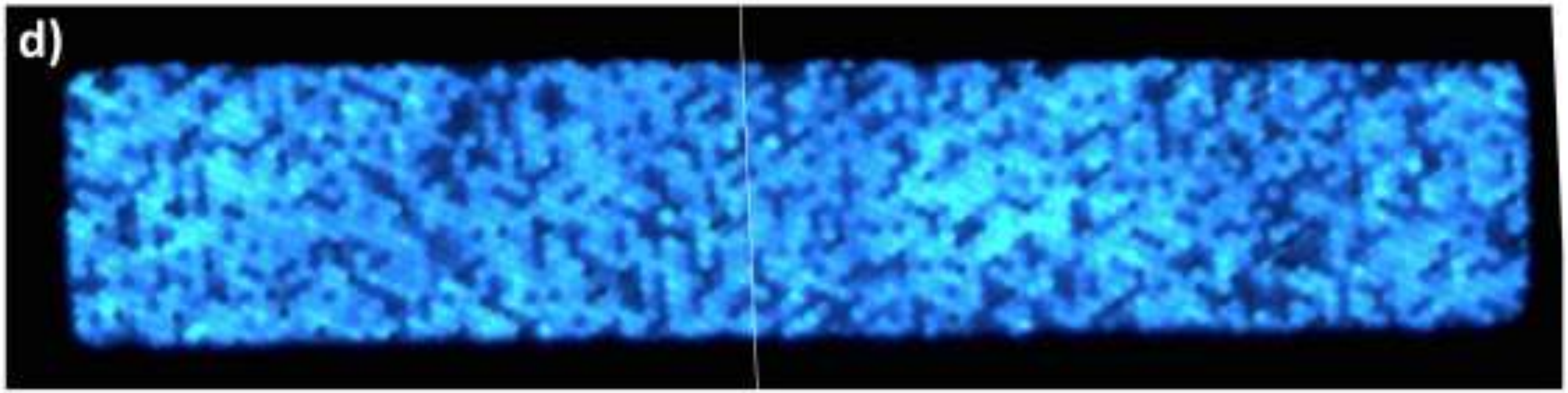



core e injection




underlayer e injection




Direct electron injection in the underlayer allows to increase the yield of EL NWs from 19% to 65%

*H. Zhang et al, Nanotechnology 2020*

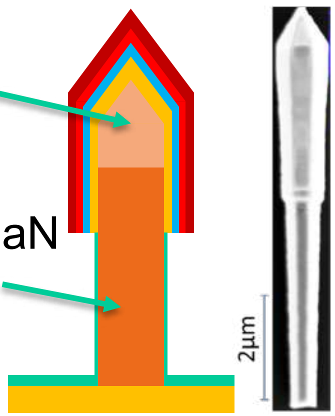
# Surface NW treatment to improve the growth homogeneity

*PhD of Julien Bosch*

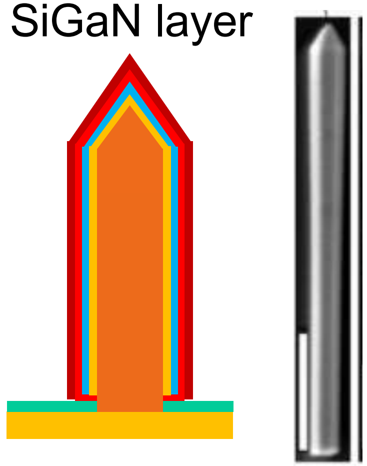
Previously adopted NW LED structure

**N.i.d.** GaN

Highly **n-doped** GaN with a SiGaN passivating shell



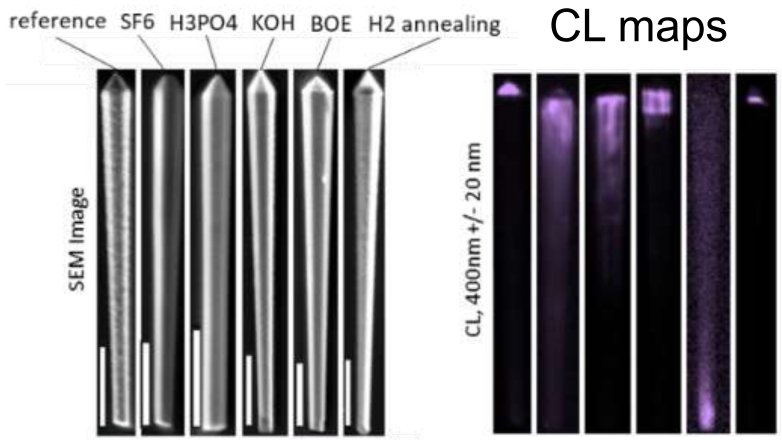

Remove n.i.d. part, achieve homogeneous QWs by etching the SiGaN layer



Remove the SiGaN shell by a chemical treatment

Investigation of different chemistries + regrowth of the QWs

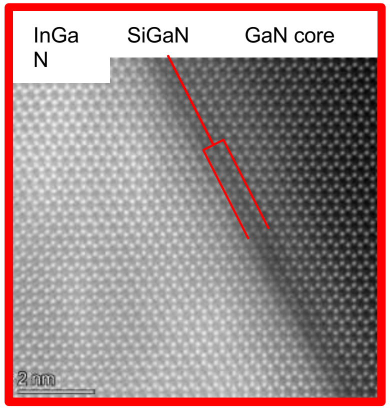
✓ Best optical results for $H_3PO_4$ etching

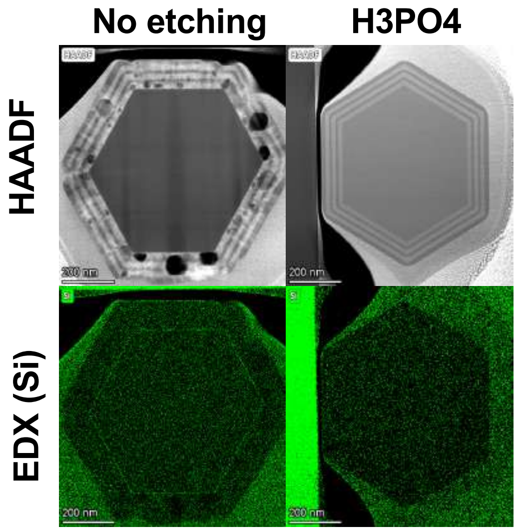



*J. Bosch et al, Cryst. Growth Des. 22, 9, 5206 (2022)*

# Analyses of the surface SiGaN passivating layer

TEM

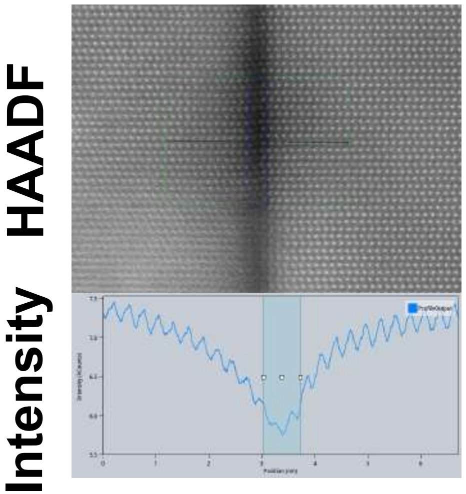


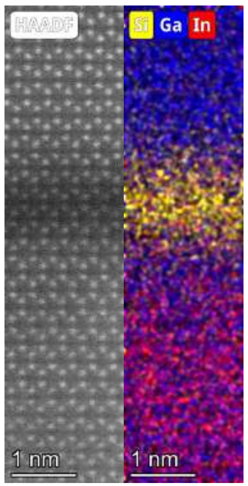

TEM confirms the removal of the passivation layer by the treatment and a better crystalline quality in H3PO4 sample

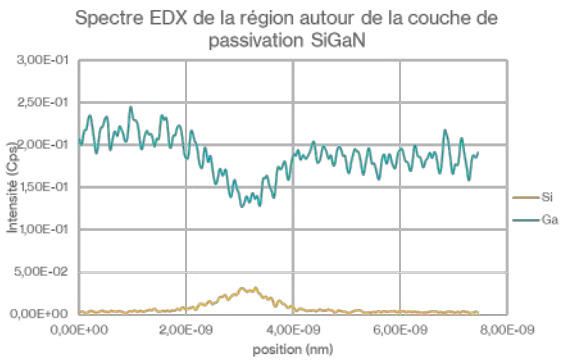
SiGaN passivation layer:
Constant thickness of 2 monolayers
Composition is close to $Si_3Ga_5N_9$

HAADF

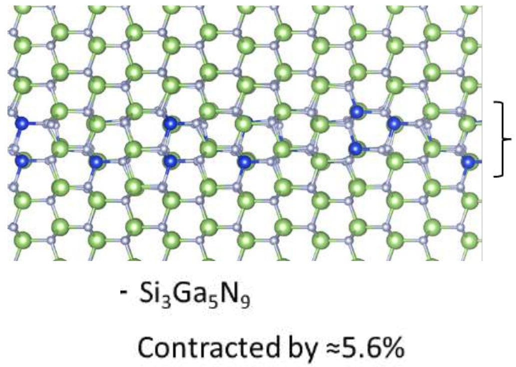



EDX study




Si/(Ga+Si) concentration of 1/3

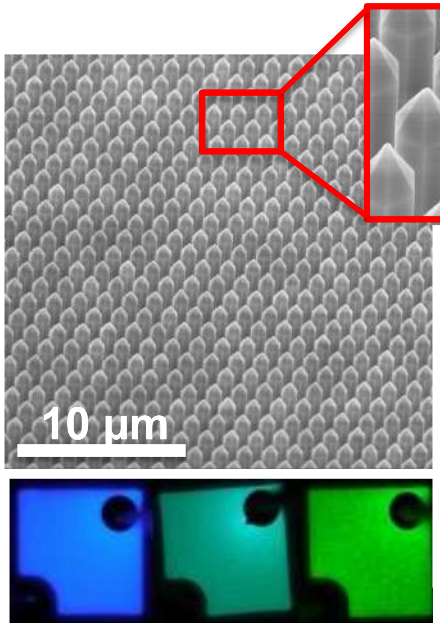


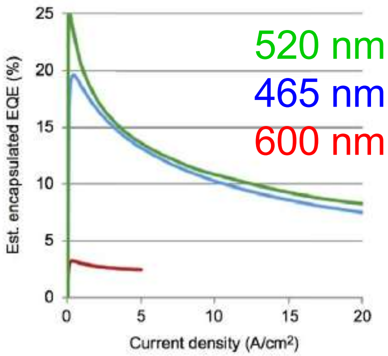

**SiGaN-vGa**

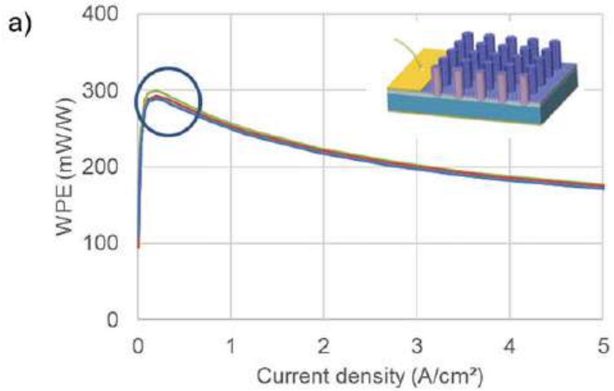


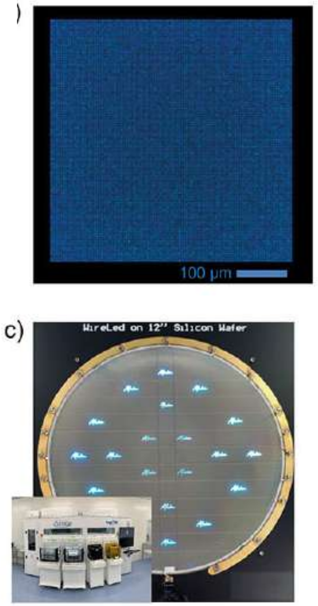
*J. Bosch et al, Cryst. Growth Des. 22, 9, 5206 (2022)*

# Present status of rigid nanowire InGaN/GaN LEDs




*P. Tchoulfian, Aledia, 30 % WPE*
*Compound semiconductor 2023*

*InGaN nanowire LEDs, GLO AB, 20 % WPE*
*Monemar et al. Semicond. & semimetals 2016; Nami, M. Sci. Rep. 2018*

Academic labs and start-ups are working hard to bring nanowire-based LEDs to maturity and make them enter the market

- Promising technology, however the WPE (30%) is still not competitive for lighting
- No interest for lighting, but good for alternative applications :

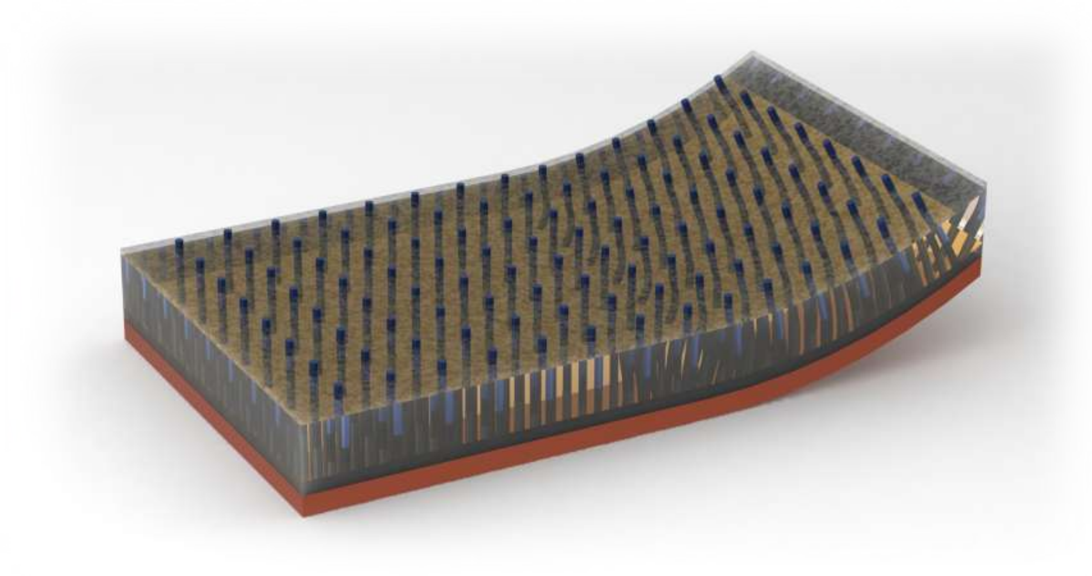
**µLEDs** **Li-Fi** **Flexible LEDs** **UV LED**

# Flexible LEDs based on nanowire / polymer membranes

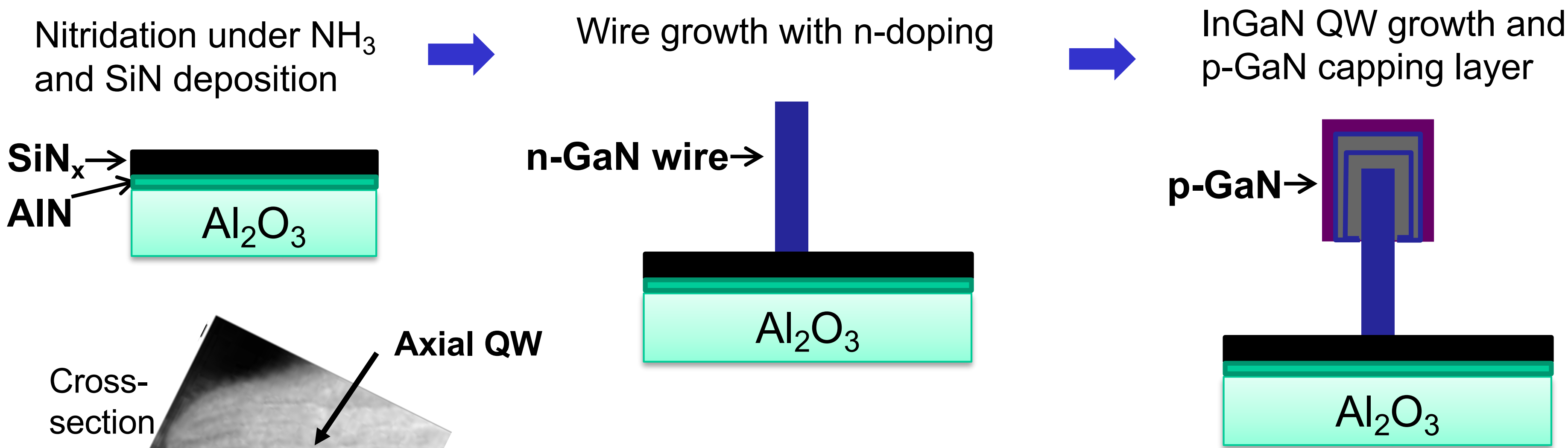
Replace organic semiconductor devices

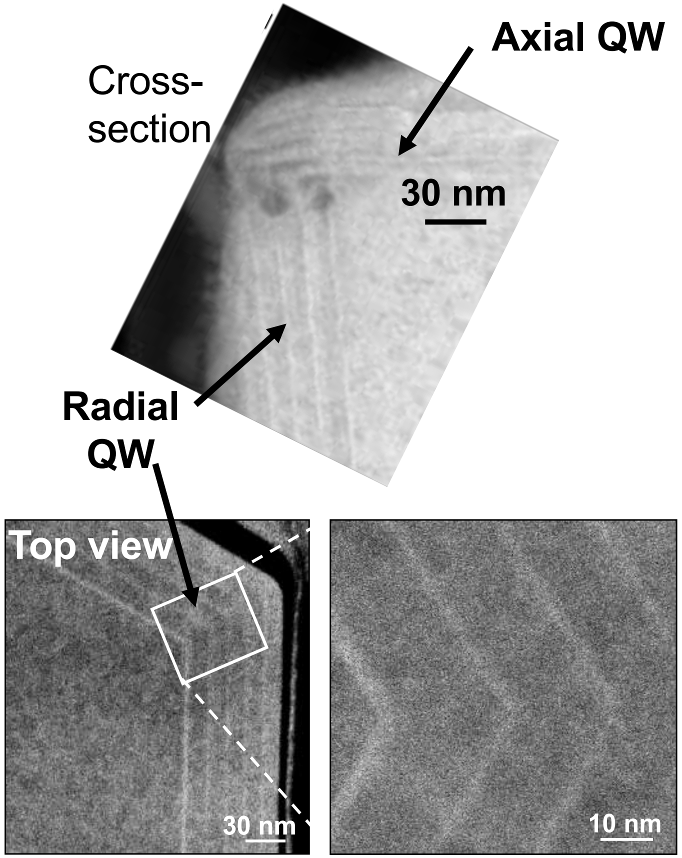
**Combine crystalline III-V materials with flexible polymers**

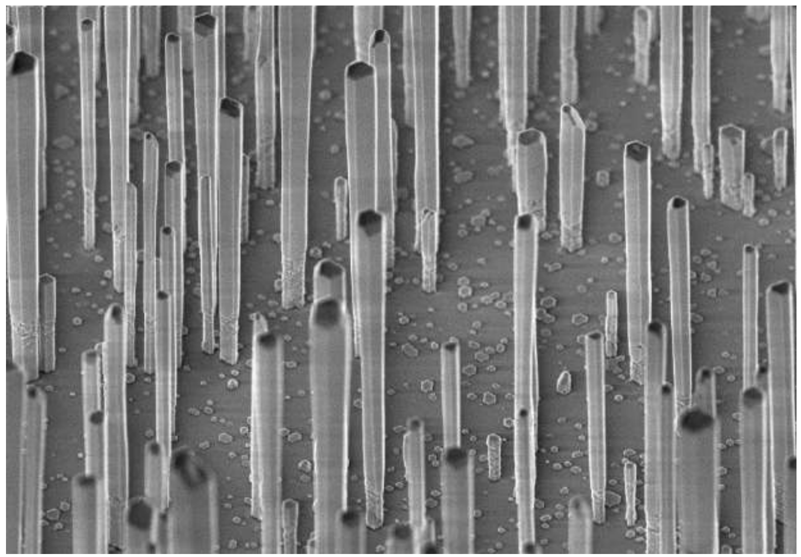
- ✓ Flexibility of polymers and high efficiency and long lifetime of crystalline materials
- ✓ Modularity – combination of "incompatible" materials



# Self-assembled nanowire LEDs

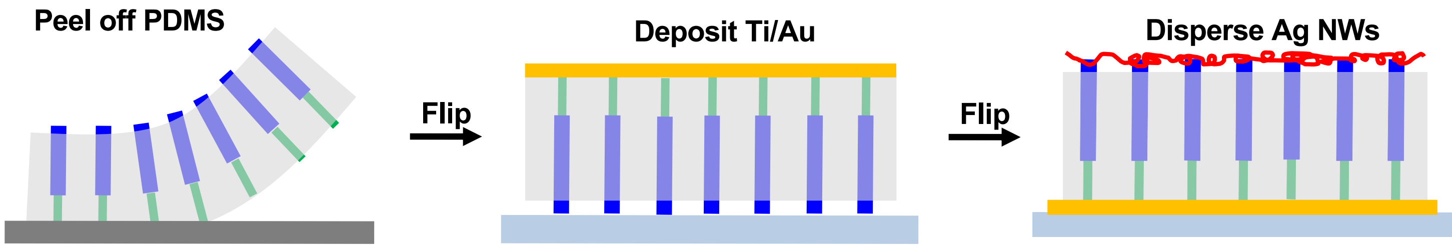


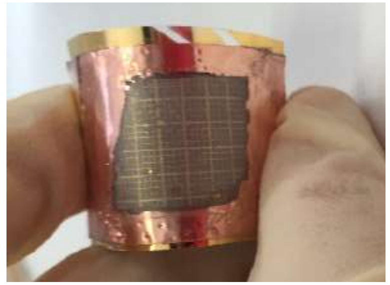



*MOCVD by C. Durand and J. Eymery (IRIG, Grenoble)*

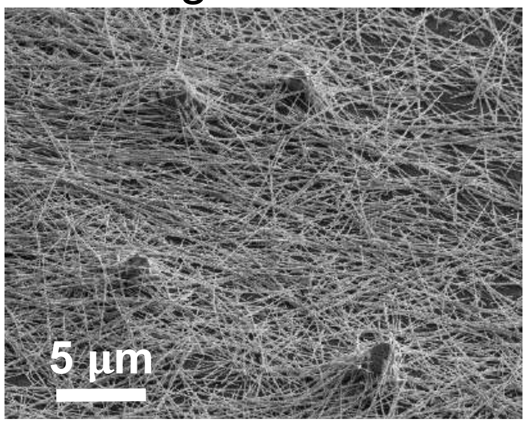
# Flexible blue LED



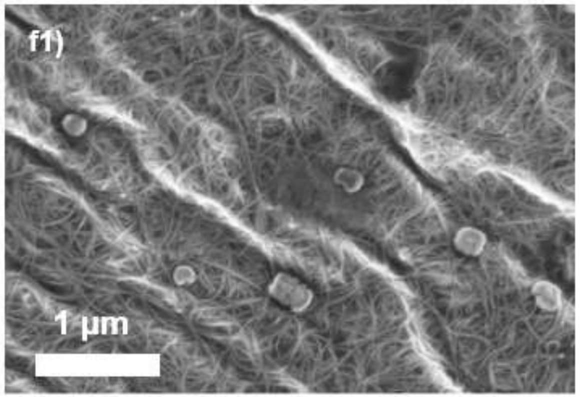



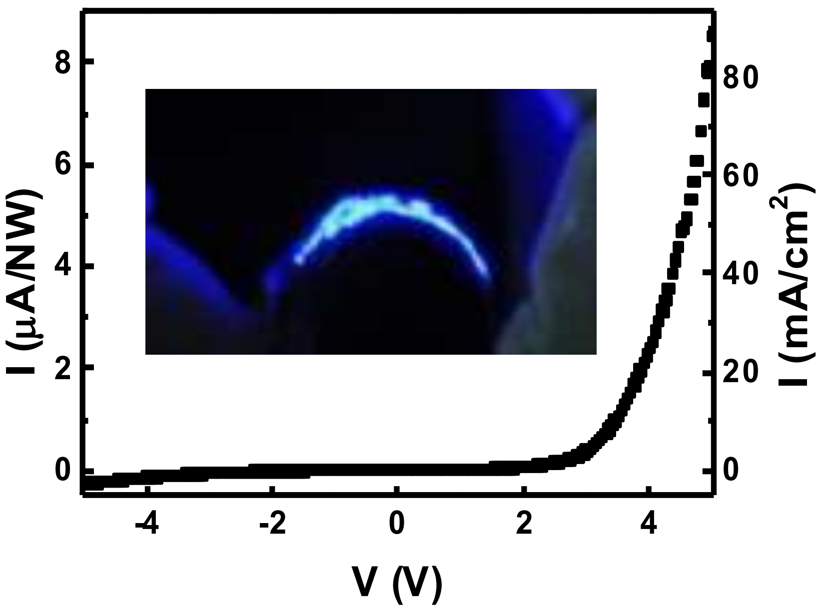
**Top contact**

Ag NWs




Carbon NTs



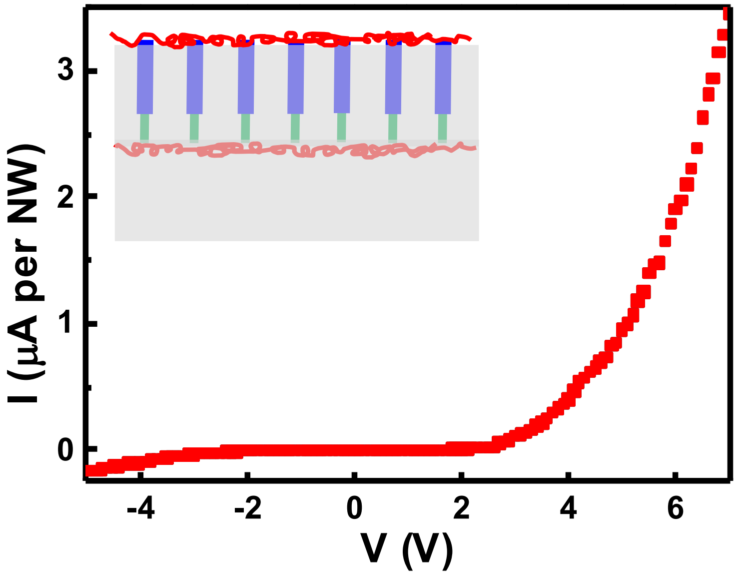




- Ag NWs and carbon nano-tubes both form a reliable contact to nitride NWs – no degradation after 10 bending cycles ($R_{bending} \approx 0.3$ cm)

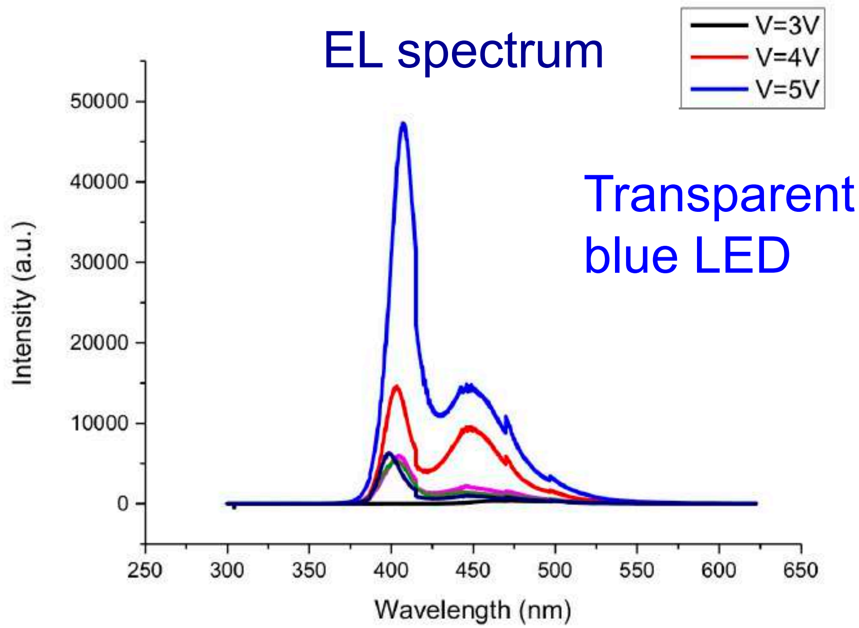
*D. Xing, et al., Nano Letters, 15, 6958 (2015)*
*N. Amador et al, submitted*

# Fully transparent LEDs

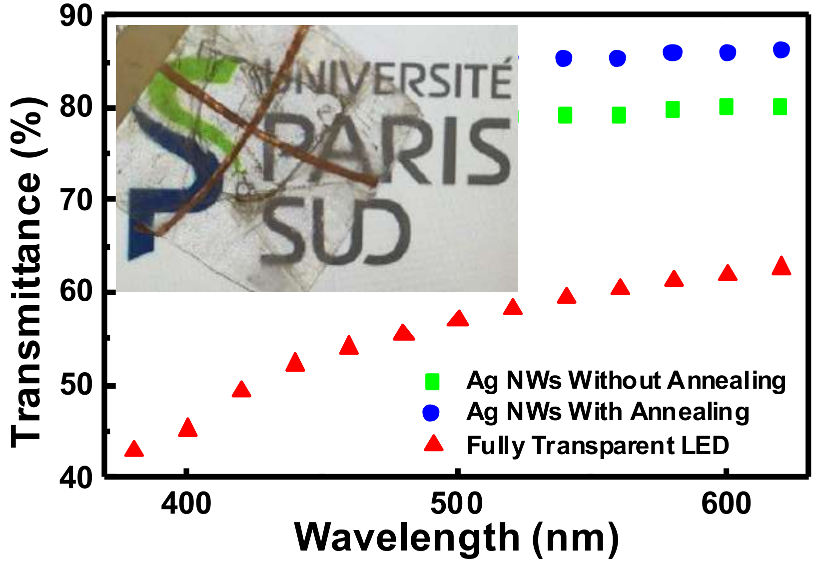
I-V curve




EL spectrum




Transmittance



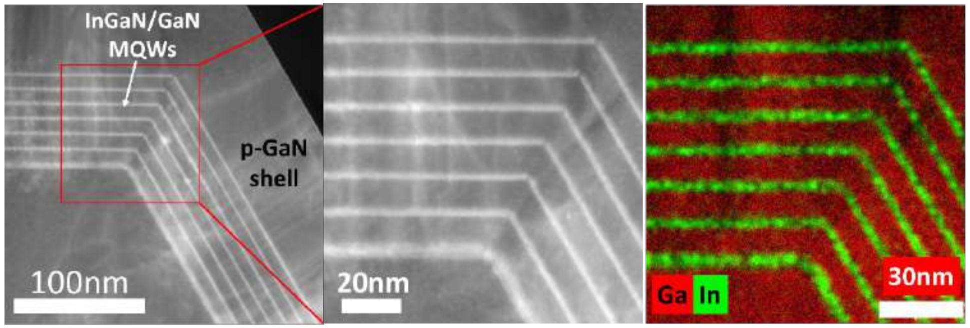

- Rectifying diode behavior
- Electroluminescence (V>3 V)
- Transmittance 60 % @ 550 nm

*D. Xing, et al., Nano Letters, 15, 6958 (2015)*

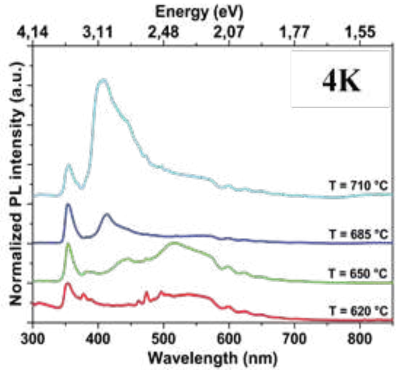
# Producing green emission: In-rich radial quantum wells

Growth of the QWs at different temperatures

**HAADF-STEM** **EDX**




**Photoluminescence**

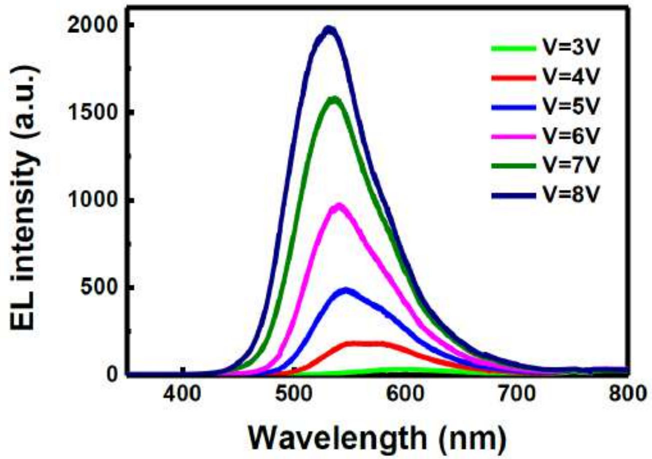



**Green emission for QWs grown at 650 C**

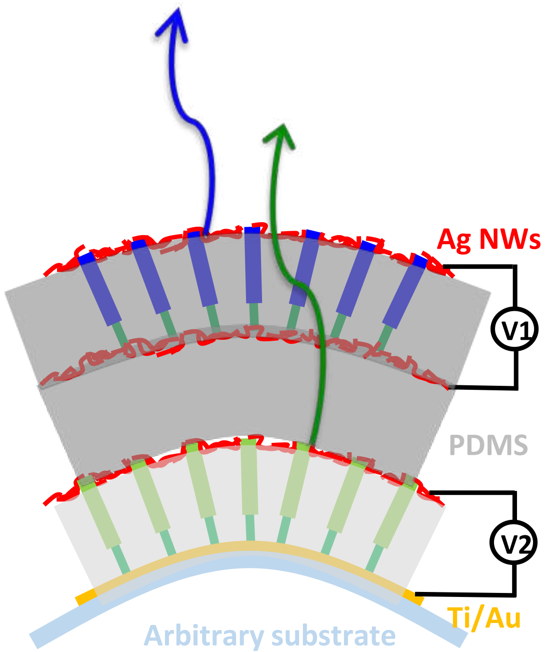
QW th = 6.7 nm
23% of In in m-plane QWs
In-rich regions with 35%

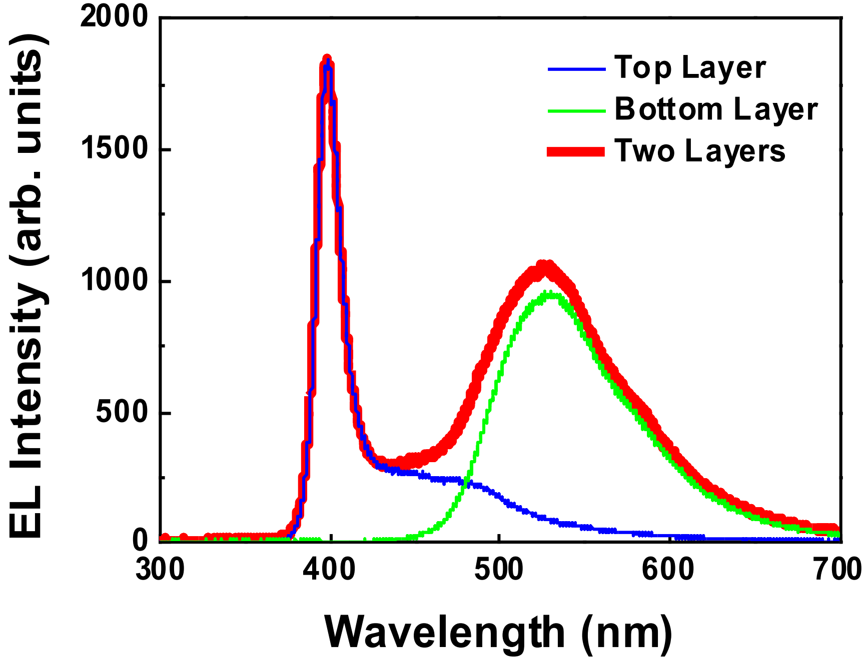
*A. Kapoor et al, ACS Photonics (2018)*
*A. Kapoor et al, Adv. Photonics Res. (2021)*

**Flexible green LED**



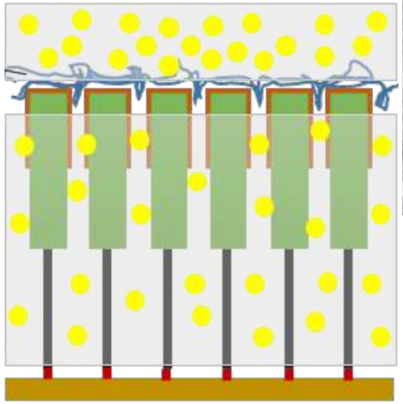
# Two-layer green-blue flexible LED

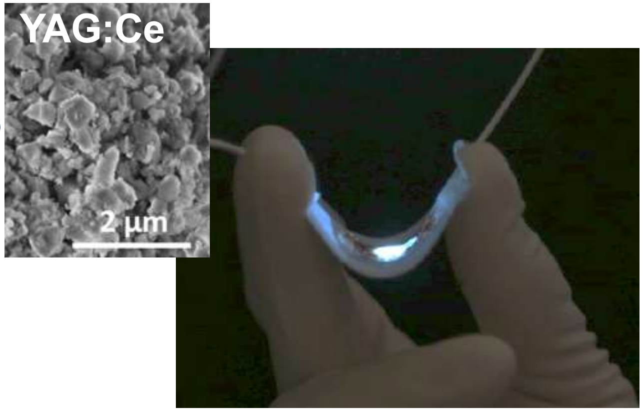


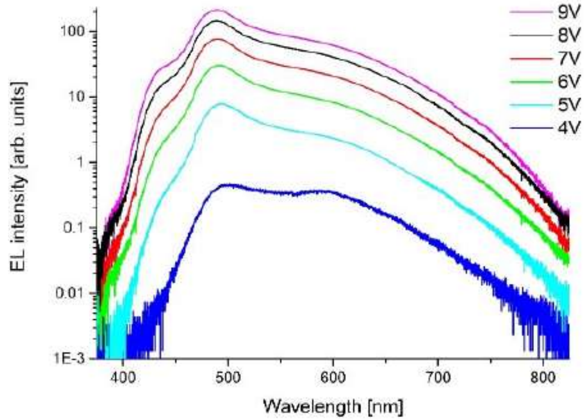

- Demonstration of 2-color stacked NW flexible LED
- Emission in blue and green spectral regions

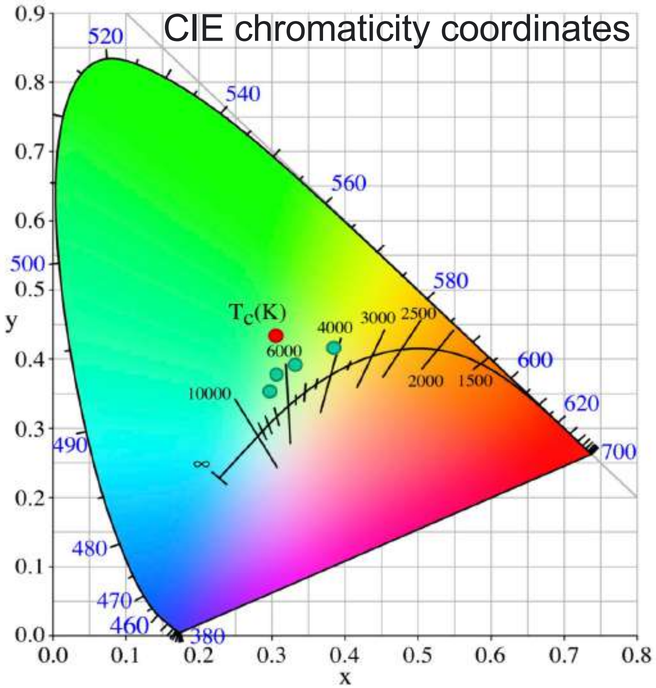
# Flexible LED color quality






CCT 6306 K CRI 54




Color optimization:

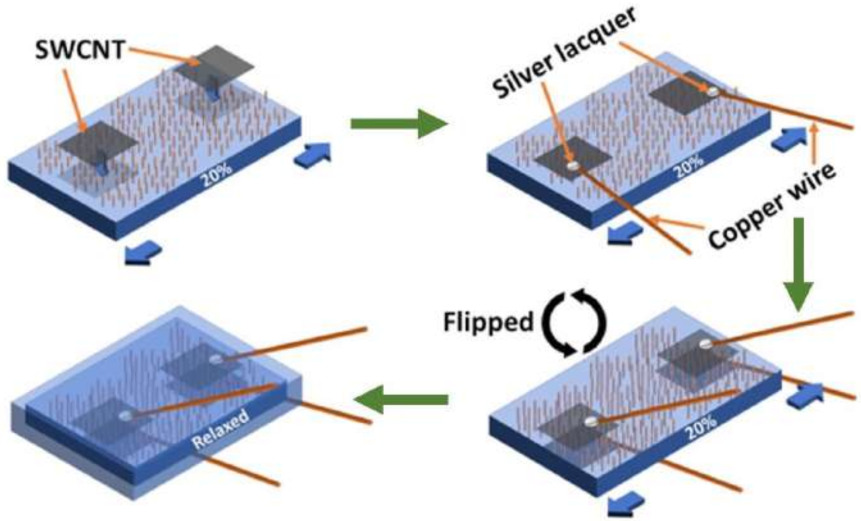
- Mass ratio of phosphor: PDMS increased from 1:20 to 1:10
- 2 different PDMS thicknesses
- 5 phosphors (yellow, orange, mixture)

After color optimization

- CCT 4000 – 5000 K warm white
- Best CRI 84

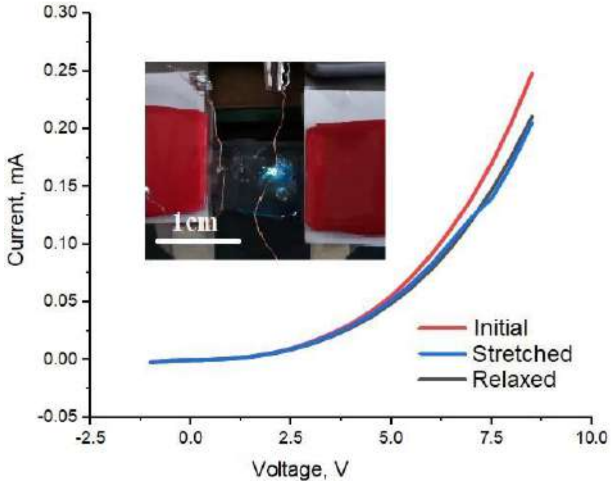
*N. Guan et al, ACS Photonics (2016); N. Guan et al, Journal of Physics: Photonics (2019); M. Abraham et al., Dalton Transactions (2021); K. Thejas et al., Applied Mat Today (2021)*

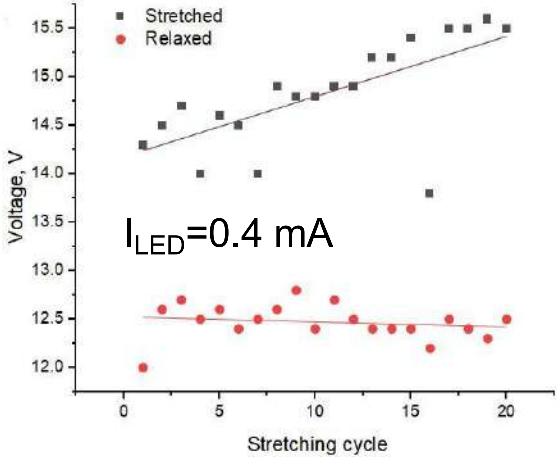
# Stretchable LEDs

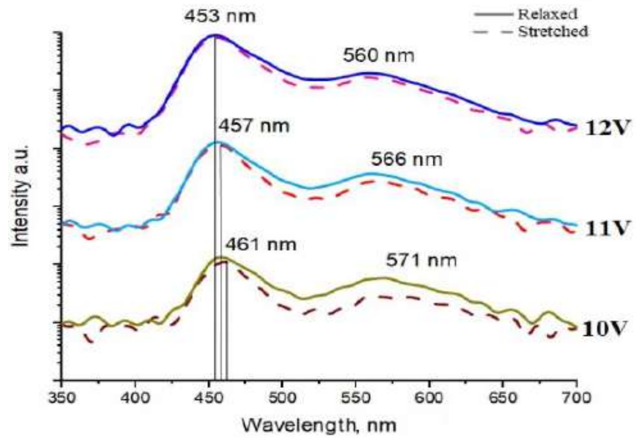



- Transparent contact using carbon nanotube mesh
- Transmittance 80% at 550 nm $R_{\square} = 20\ \Omega/\square$
- Membrane is pre-stretched prior to contact application

*Collaboration with Alferov University*



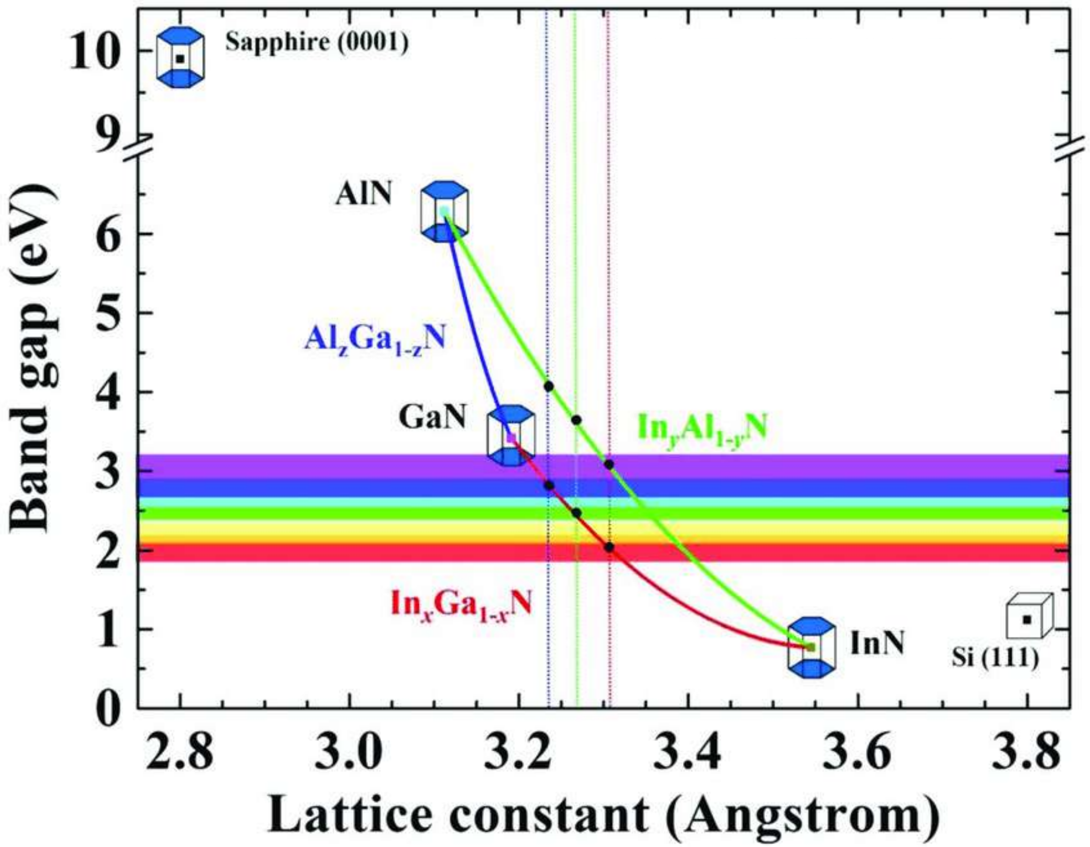




- 15% resistivity increase under 20% stretched conditions, no change in relaxed
- EL spectra show no significant change under stretching to 20%



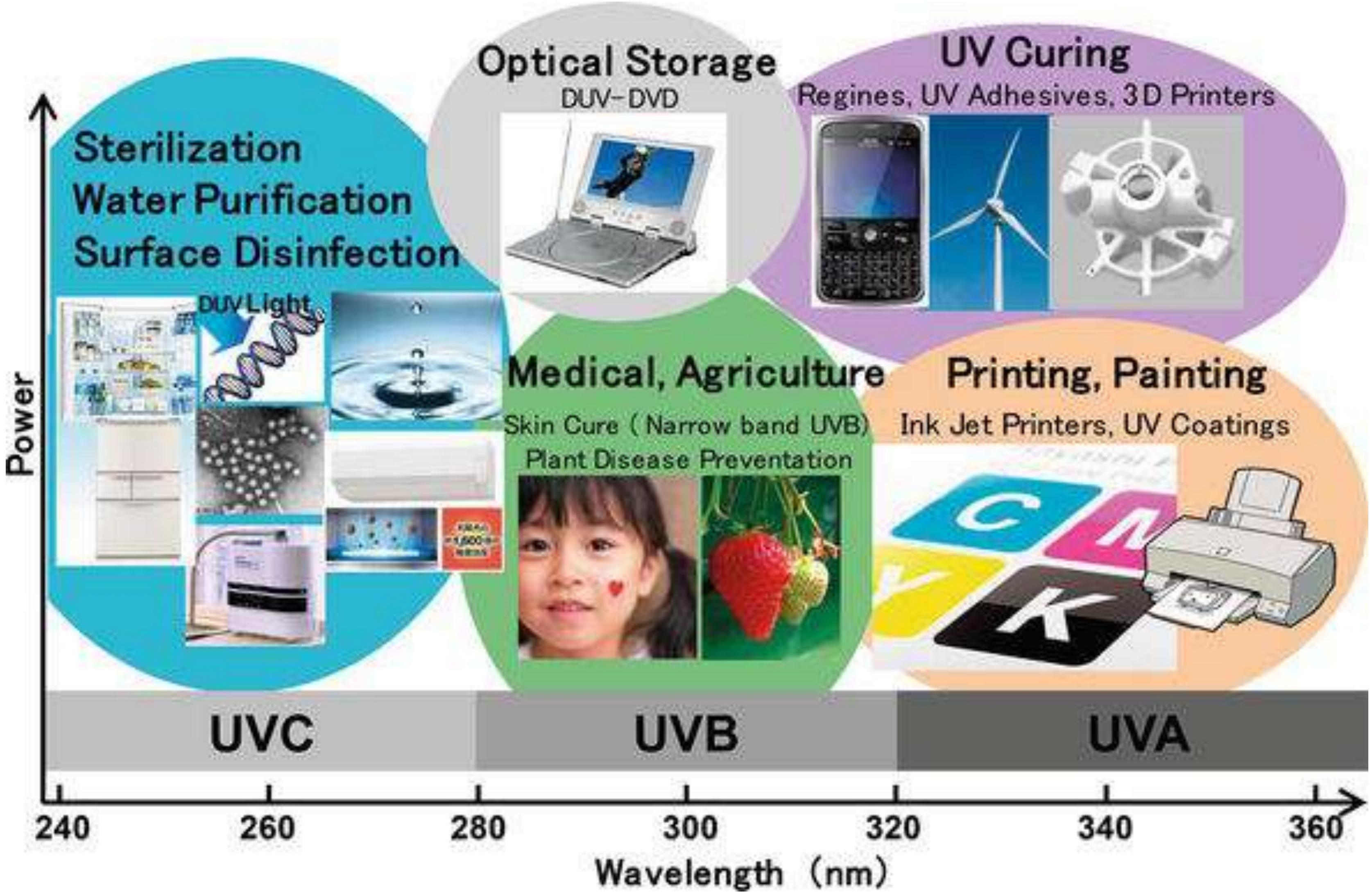
*Kochetkov et al., Nanomaterials 11, 1503 (2021)*

# UV LEDs : material




Replace InGaN/GaN by GaN/AlGaN quantum wells

# UV LEDs : applications

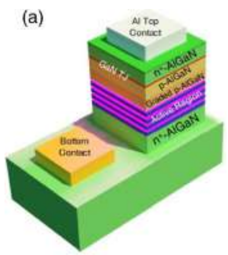


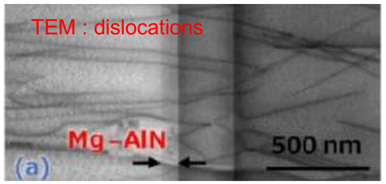

*H. Hirayama 2018 10.5772/intechopen.79936*

# UV LEDs : present issues

**Planar LEDs :**

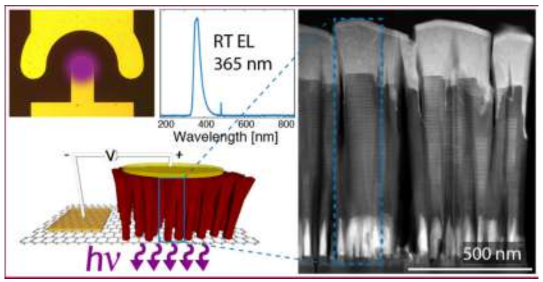
- Threading dislocations
- Issues with light extraction
- Doping



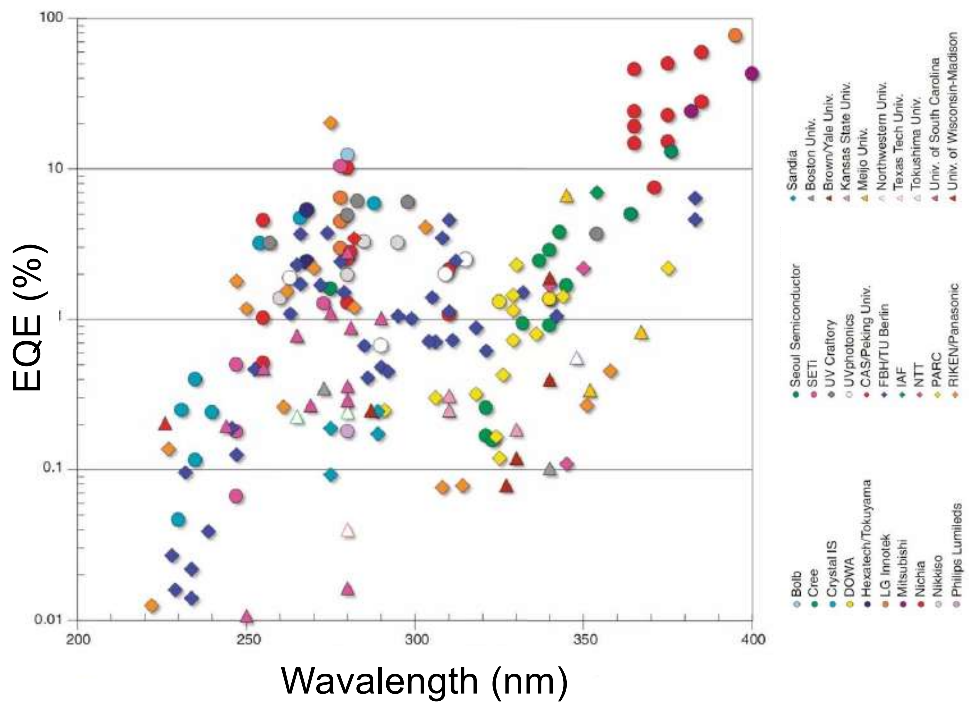




**NW LEDs :**

- No defects originating from the substare
- Easier light extraction
- Reports on higher doping




*EU project « SteriLED » CrayoNano*




*10.1002/admt.202101502*

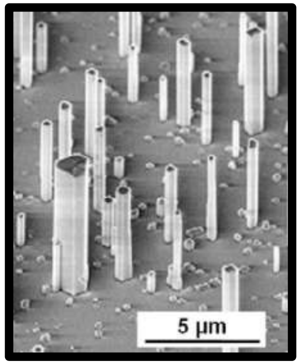
## Applications of UV LEDs on non-planar surface

➡ Water/air disinfection processing in flexible tubes
➡ Medical applications (skin care, implants…)
➡ UV pump for visible emission in flexible LEDs/displays

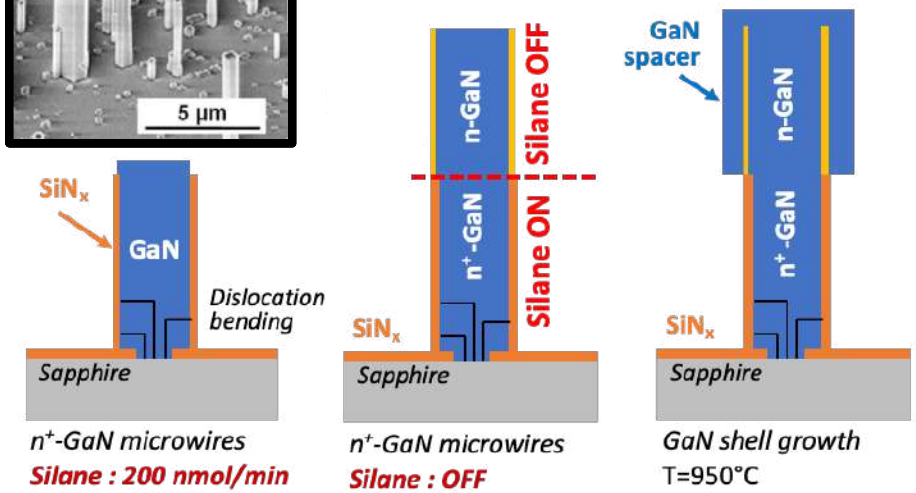
# MOVPE growth of core-shell UV nanowires

**GaN nanowires as templates for core-shell UV multi-quantum wells**

## Step 1: Nanowire growth by silane assisted method

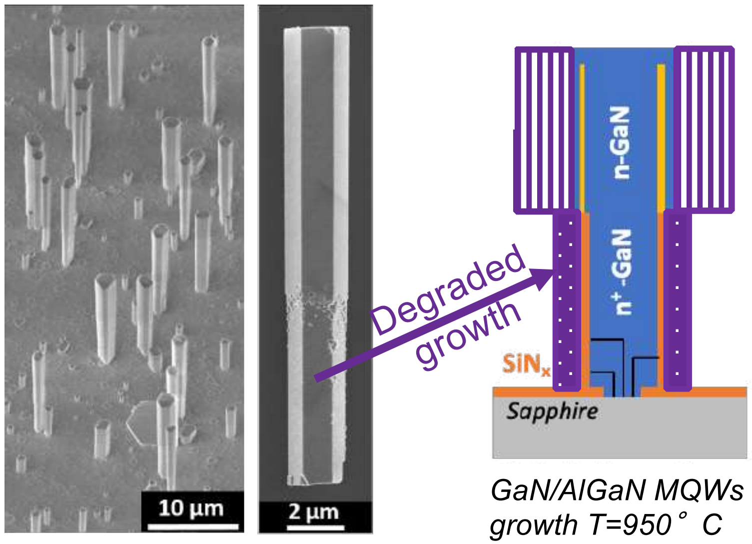



*L= 10-25 µm*
∅ = 500 nm-2 µm




*Koester et al. Nanotechnology, 21, 015602 (2010)*
*Kapoor et al. ACS Appl. Mater. Interfaces 12, 19092 (2020)*

## Step 2: Growth of core-shell GaN/AlGaN MQWs



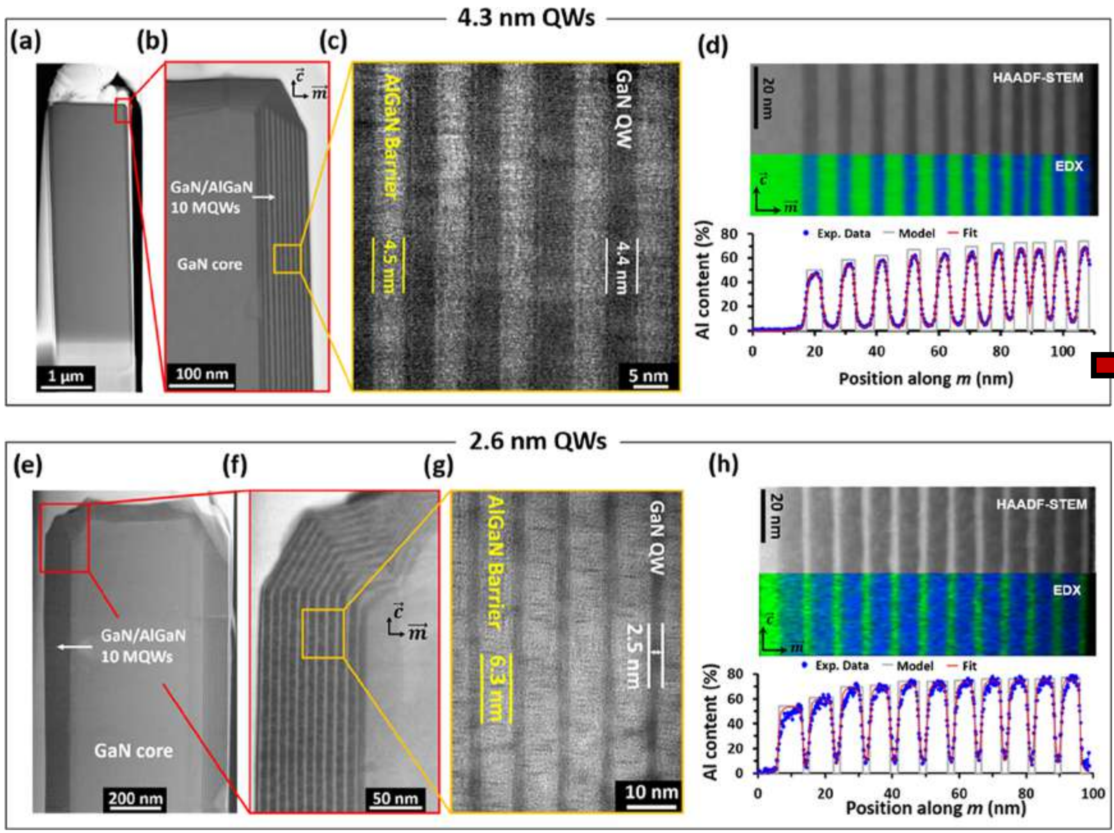

*GaN/AlGaN MQWs growth T=950° C*

➡ **Smooth growth of GaN/AlGaN MQWs on upper part with the GaN spacer**

*Grenier et al., ACS Appl. Mater. Interfaces 12, 44007 (2020)*

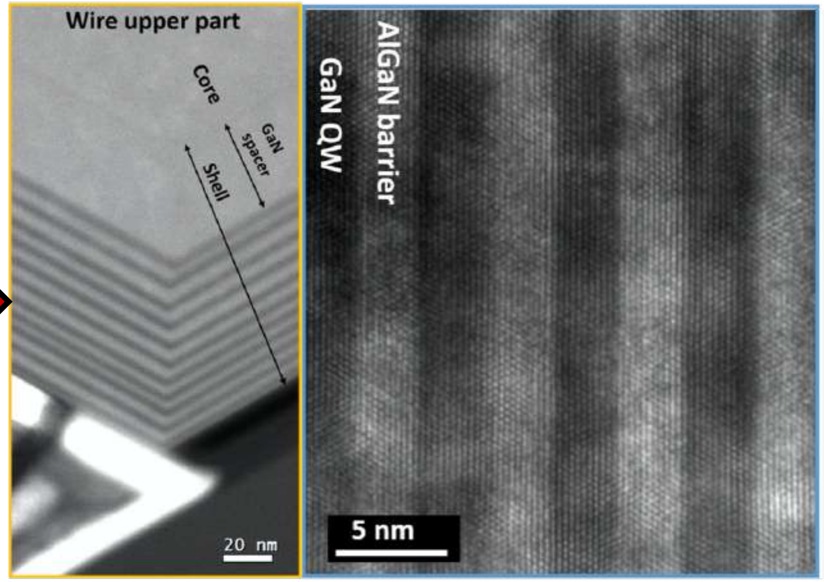
# Structural analyses of core-shell GaN/AlGaN multi-quantum wells for UV-A emission

Cross-sectional images




*Grenier et al., ACS Appl. Mater. Interfaces 12, 44007 (2020)*

Top-view images

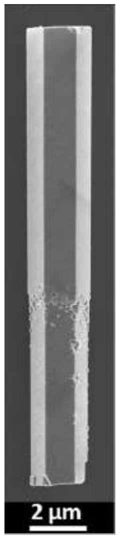



➡ **Core-shell GaN/$Al_{0.3}Ga_{0.7}N$ QWs**

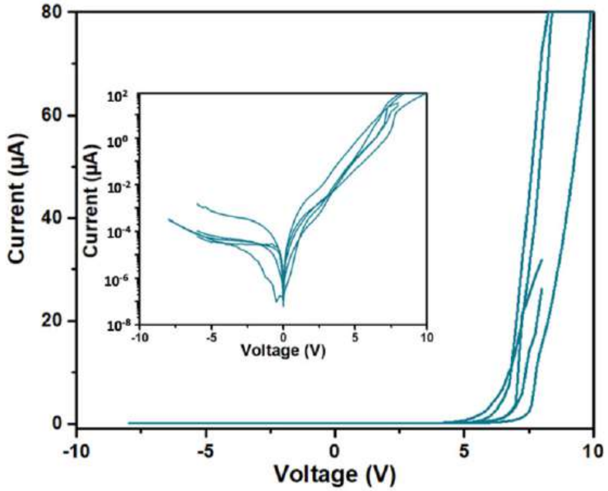
➡ **High quality growth on *m*-plane sidewalls**

# UV-A single NW LED

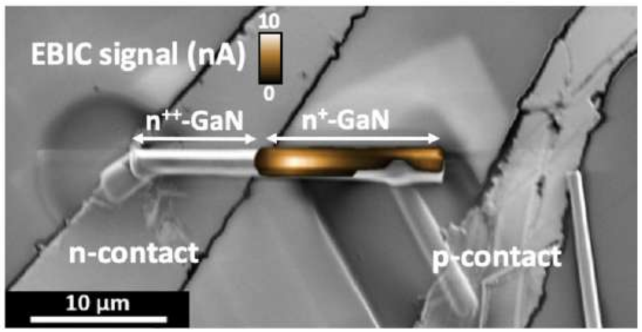
NW detached
from the substrate



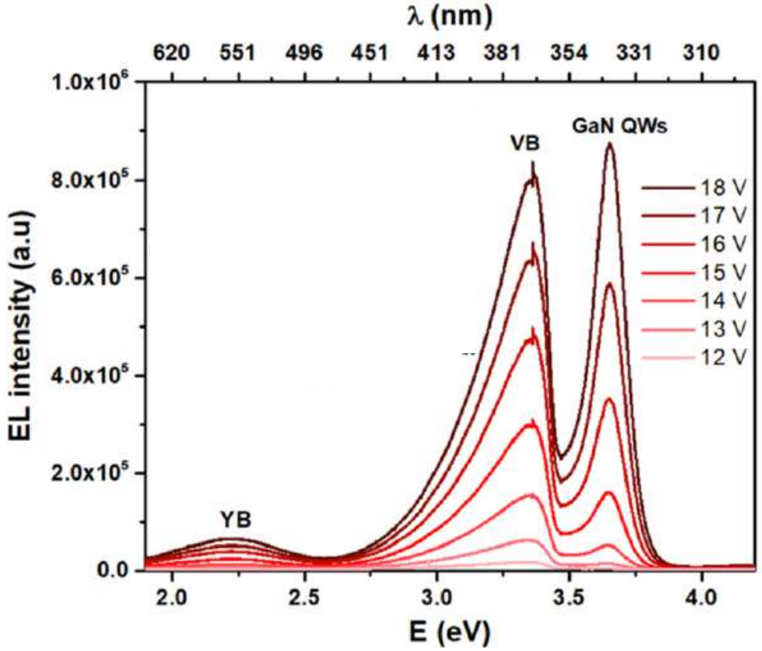

I-V curve




SEM+EBIC map




EL spectra

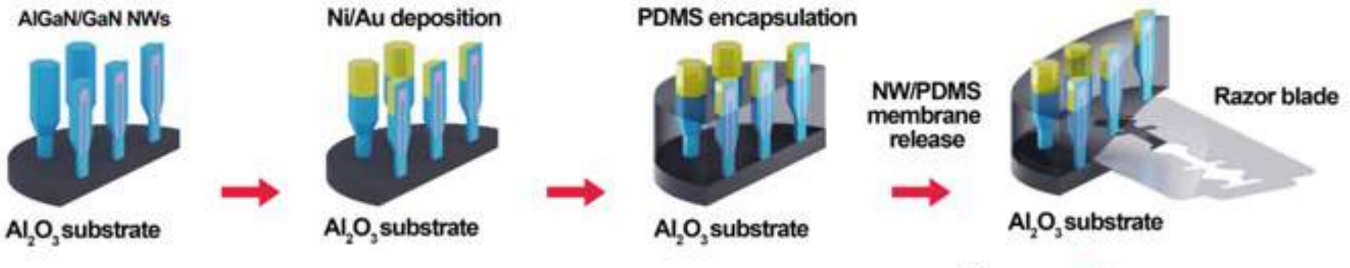


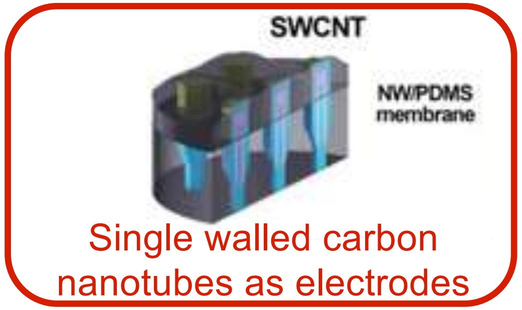

➡ **Core-shell n-p junction evidenced by EBIC**

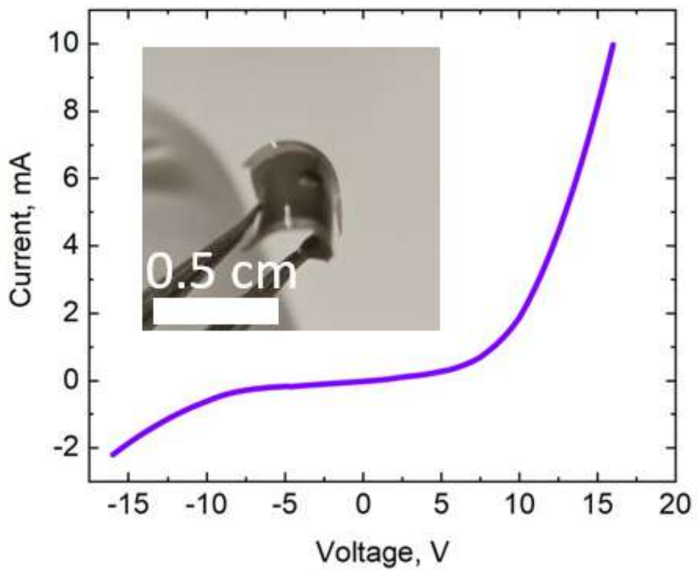
➡ **EL emission at 340 nm at room temperature**

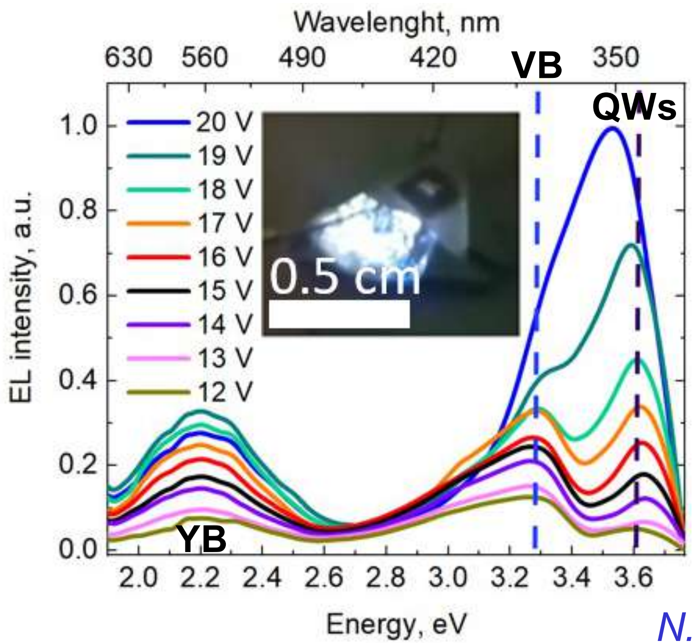
*V. Grenier et al., Appl. Phys. Lett. 121, 131102 (2022)*

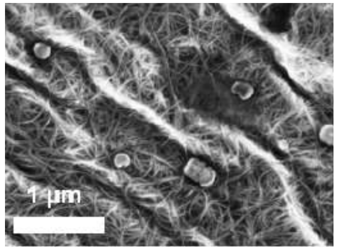
# Flexible macroscopic UV-A LEDs



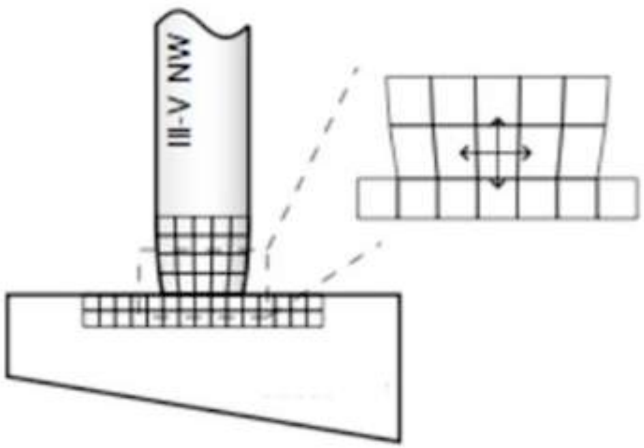

*N. Amador et al., ACS Applied Materials & Interfaces, submitted*

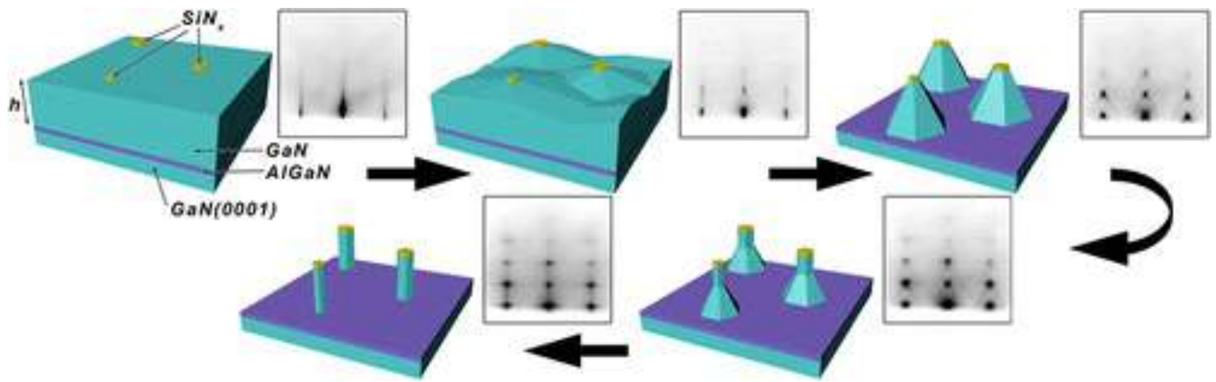
- Diode-like rectifying IV curve
- At low bias EL from VB, at high bias the dominant EL emission from MQWs at 345 nm

# Other ways to eliminate dislocations
# Top down approach – nanoporous LEDs

- <u>BOTTOM-UP: </u>Nanowires
- Relax by lateral surface
- Improved light extraction
- *Increase of the emitting surface*
- *Lateral non-polar m-plane*

- <u>TOP DOWN</u>: Etching structure
- Relax by lateral surface, *after growth*
- Improved light extraction
- *Adapt thin film technology*



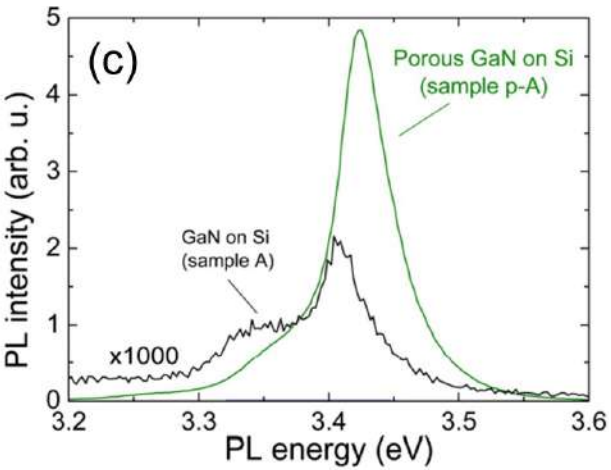



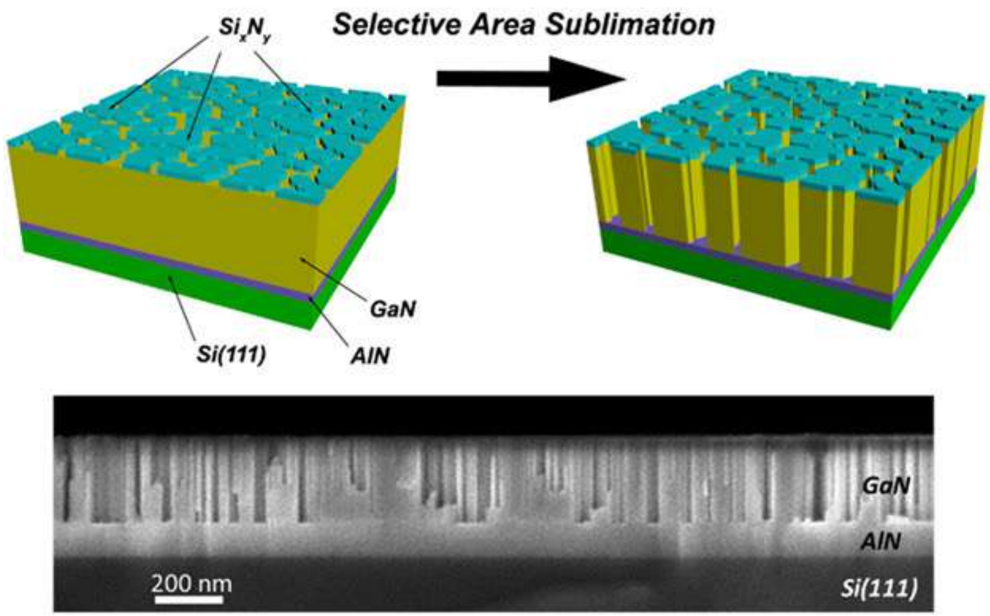

"Napoli"

*Porosification by sublimation, B. Damilano*

# Selective area sublimation applied to nitride LEDs

1. After the growth of the LED structure, in-situ partial coverage with an SiN layer
   – SiN coverage of the surface protects the material beneath
   – Self-organization: dislocations covered later than defect-free areas
2. Sublimation of unprotected regions
   – UHV (MBE chamber)
   – >1000 °C
   – AlN as stopping layer



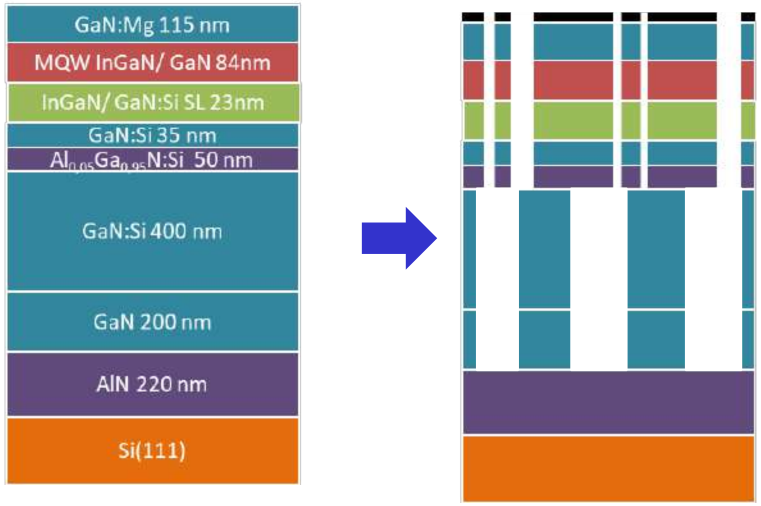



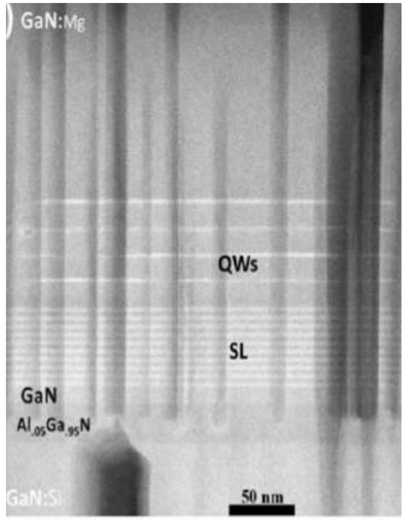

B. Damilano

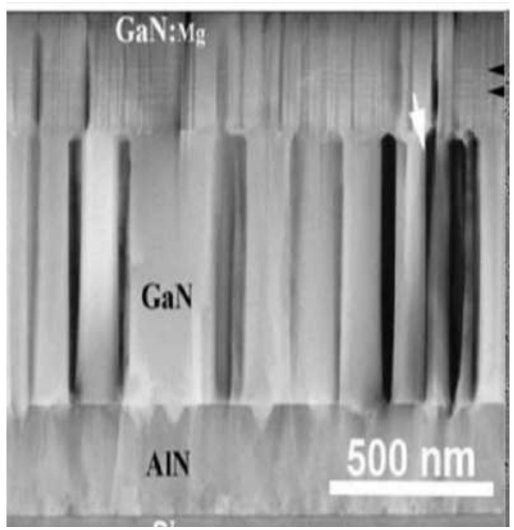
More than x1000 increase of PL intensity

B. Damilano et al, JAP (2022)

# Porosified LED fabrication

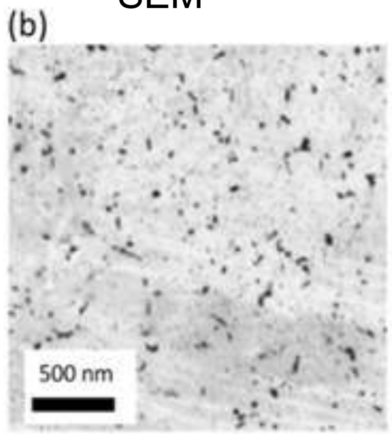


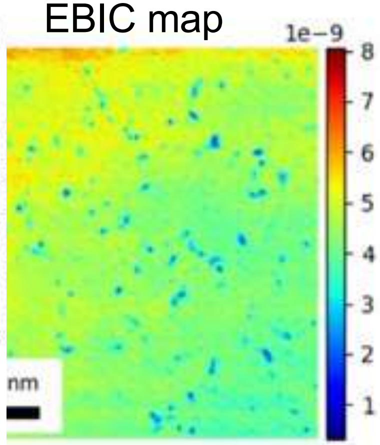




- Electrical insulation of pores to avoid short-circuiting
- Deposition of a 2 µm thick layer of parylene-C onto the top surface
- Plasma etching to uncover the p-GaN top surface
- Lithography and ITO contacting

SEM



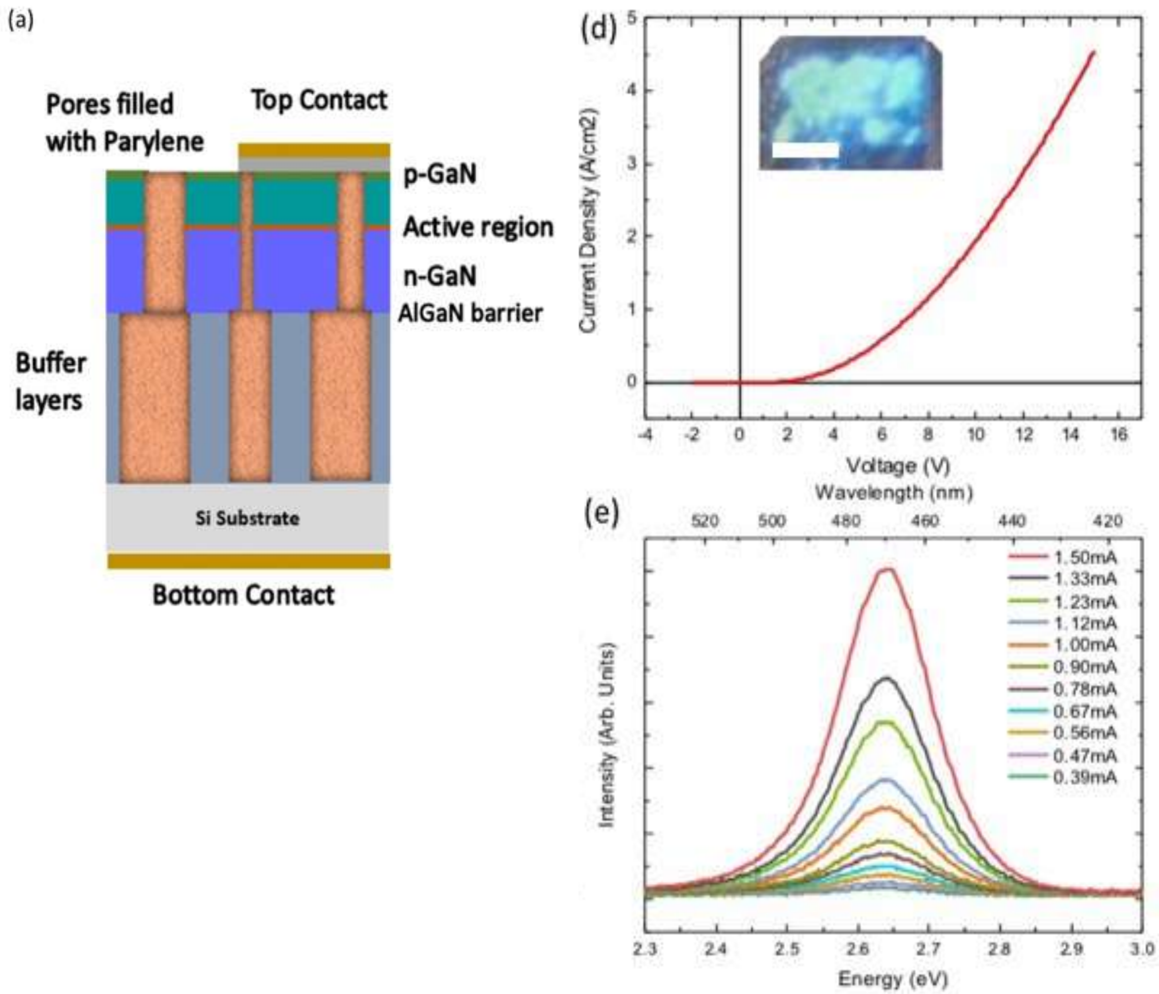

EBIC map




*N. Amador et al., ACS Photonics (2022), B. Damilano et al, JAP (2022)*

# Nano-porous LED demonstration

- Diode-like I-V characteristic with low reverse leakage
- The EL is peaked at 2.635 eV with a FWHM of 170 meV
- Low blueshift compared to standard non-porous LEDs is -- reduction of the internal electric field in the QWs thanks to porosification
- Intensity fluctuations attributed to electrical inhomogeneities of the top contact




*N. Amador et al., ACS Photonics (2022)*

# Summary

- Nanowires can potentially solve a number of thin film LED issues
- Variation of properties of individual NWs impacts the device properties on a macro scale (e.g. injection homogeneity)
- NW LEDs are still behind the mature thin film technology, but they have promise in niche applications
- NWs are good for mechanically flexible devices and can give new functionalities (e.g. stretchability)
- NWs have promise for UV emission
- Other approaches to nanostructuration to eliminate defects: top-down porosification

# Acknowledgments


- ***C2N research members***

  *N. Guan, M. Morassi, L. Mancini, N. Amador, D. Xing, H. Zhang, F. H. Julien, L. Largeau, N. Gogneau, J.-C. Harmand*

- ***Growth and characterization***

  CEA Grenoble — *A. Kapoor, C. Bougerol, J. Eymery, C. Durand*
  CRHEA Valbonne — *B. Damilano, S. Vézian, B. Alloing, J. Bosch*

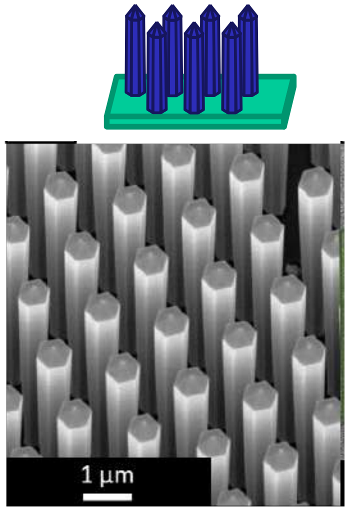
- ***Structural characterizations***

  CIMAP - Ensicaen — *P. Ruterana*

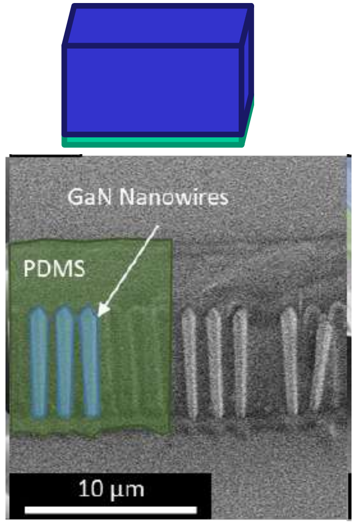
Financial support: Labex GaNEx, ANR “Napoli”, ITN “INDEED”, ERC “NanoHarvest”, franco-indien CEFIPRA

# Flexible LEDs

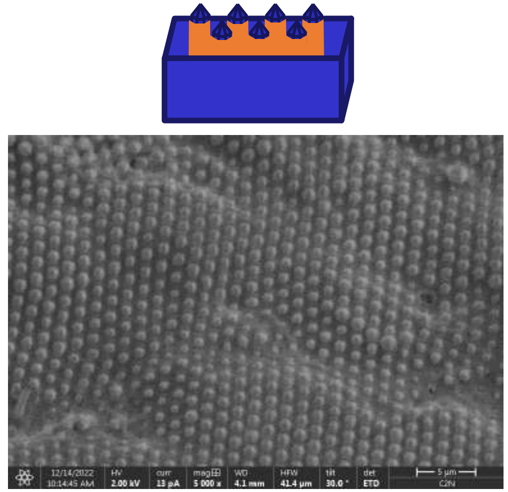
Densely packed short NWs

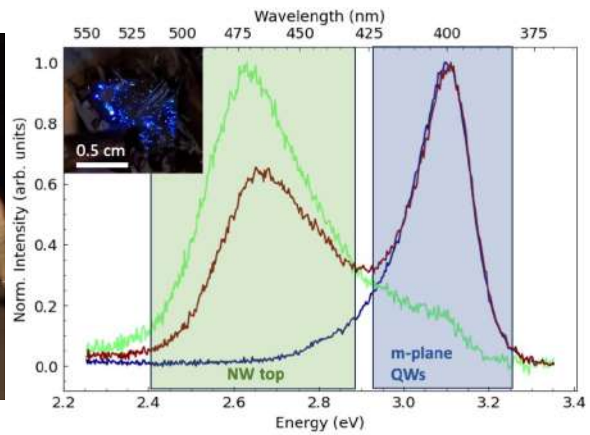



PDMS encapsulation




Thin membrane manipulation





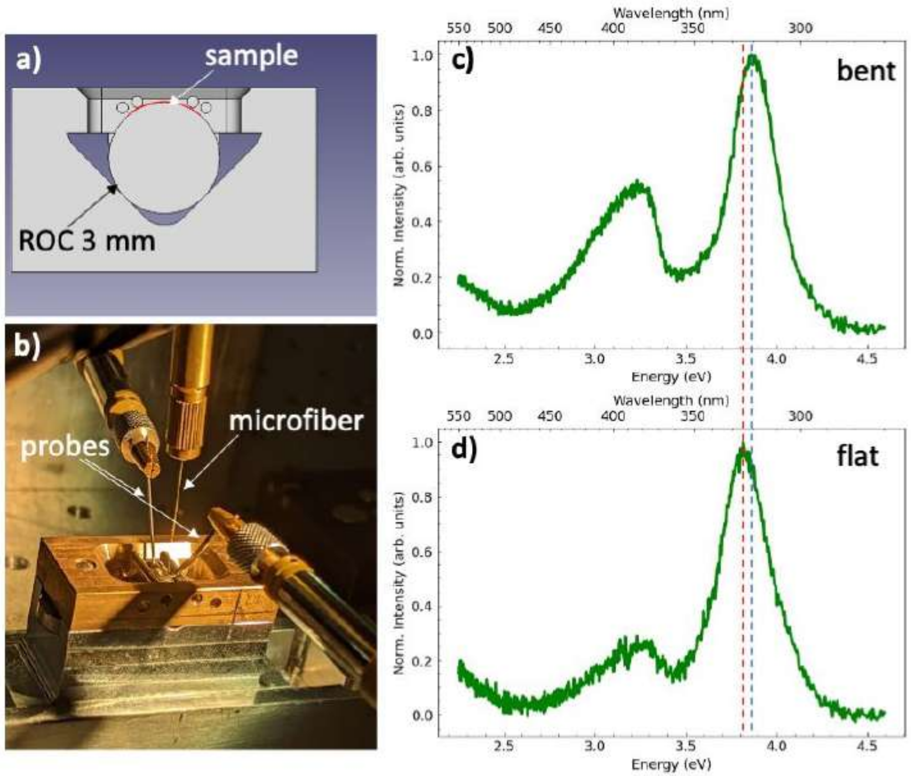

Flexible LED demonstrated and tested under 0.3 cm bending

Further optimization of

- Leakage
- Emission homogeneity
- Current injection

*J. Bosch et al, in preparation*

# Bending of UV LEDs



# Nitride nanowires

*Semiconductor nano-objects with a diameter < 1µm << length*

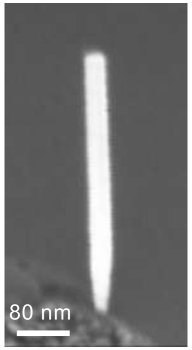
Large surface but a small footprint

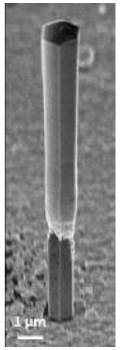
Fundamental interest :

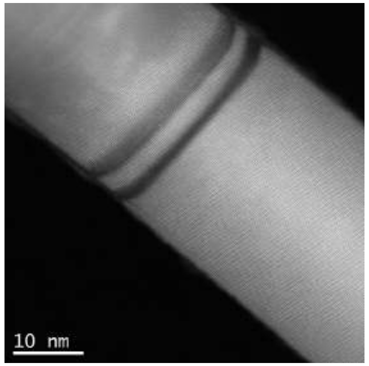
- ✓ Study of quantum confinement in quantum discs
- ✓ Study of quantum transport

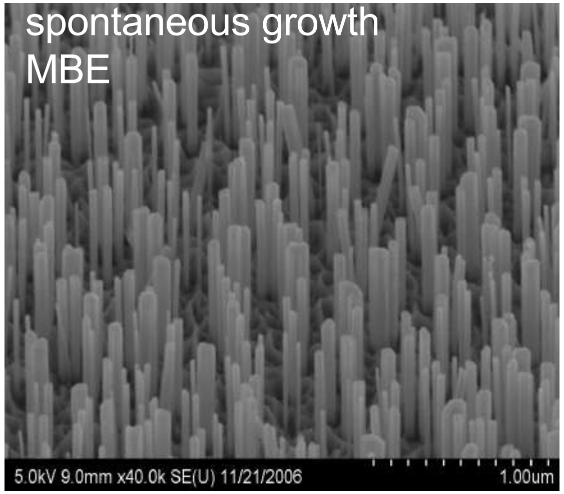
Nano-scopic and macroscopic devices

Bottom-up approach : self-assembled and organized nanowire arrays

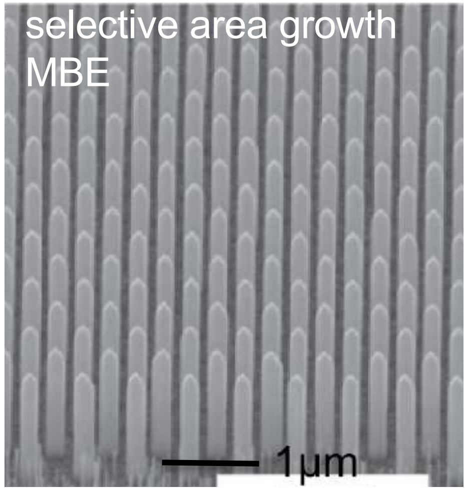


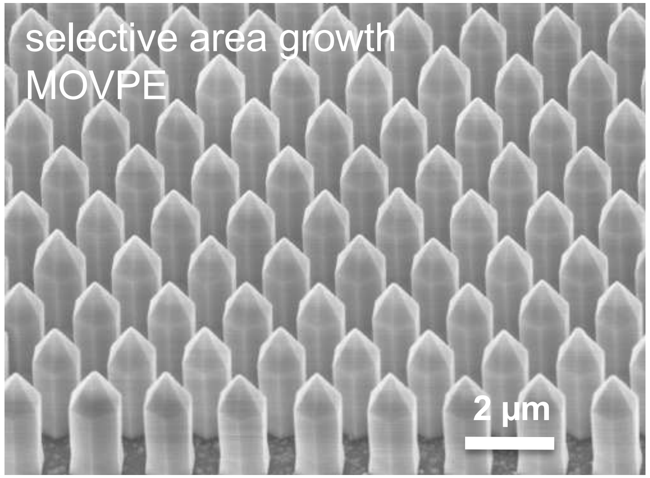




*M. Tchernycheva et al., Nanotech. 2007*



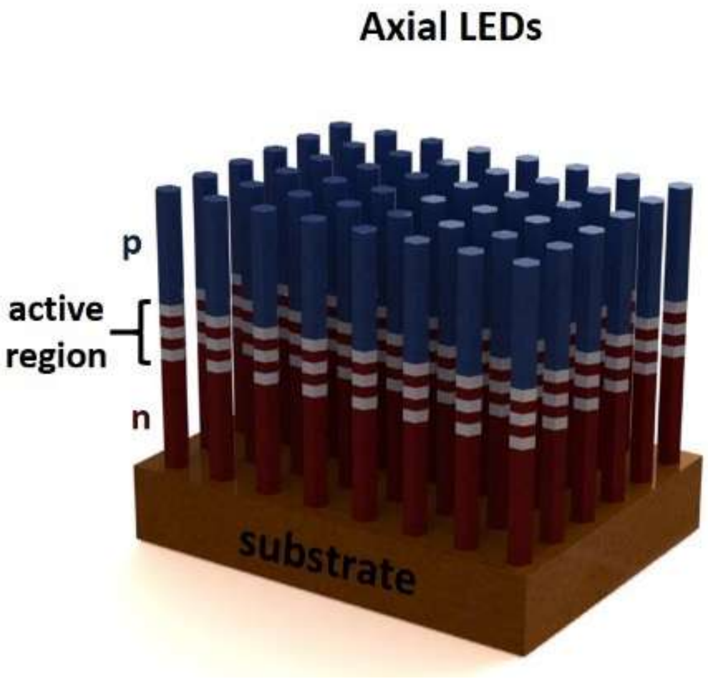

*Kouno, et al., Opt. Exp. 2009*

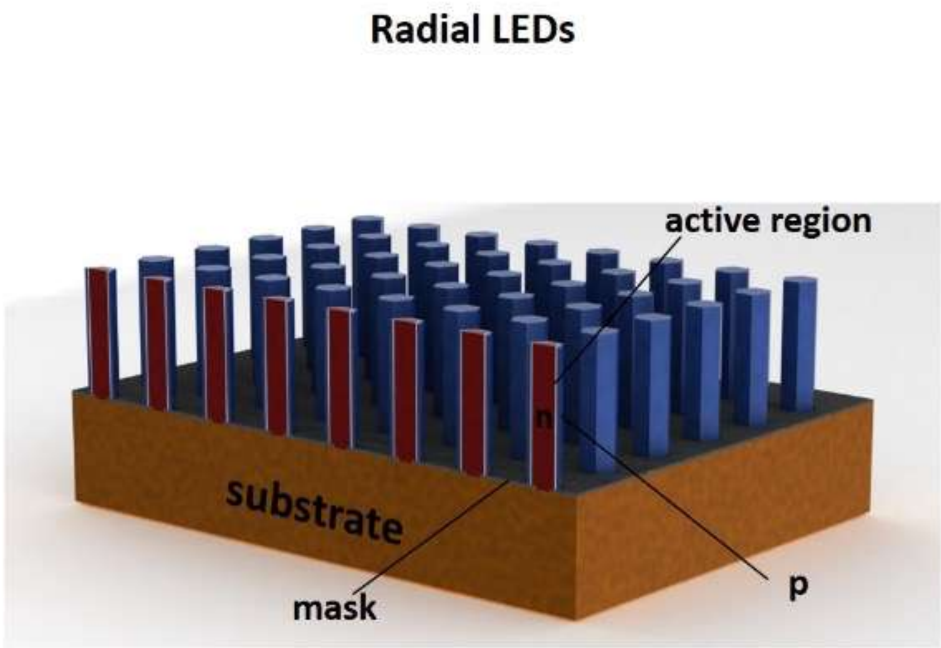



*Tchernycheva et al. NanoLetters 2014*

# Potential benefits of nanowire-based LEDs

Efficient strain relaxation – **defect-free nanocrystals**, higher QE
Growth on **low-cost substrates**



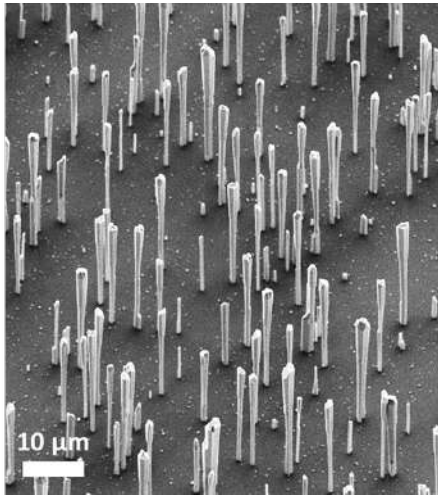



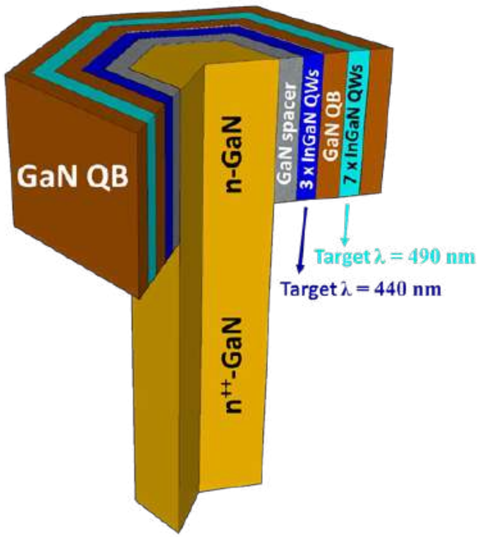

Dislocation free highly mismatched active region (e.g. In-rich InGaN/GaN QDiscs to cover the **green gap** )

Increase of the emitting surface - decrease of current density – **reduction of droop**
Lateral surface is non-polar – **no field**

# Monolithic integration of two colors

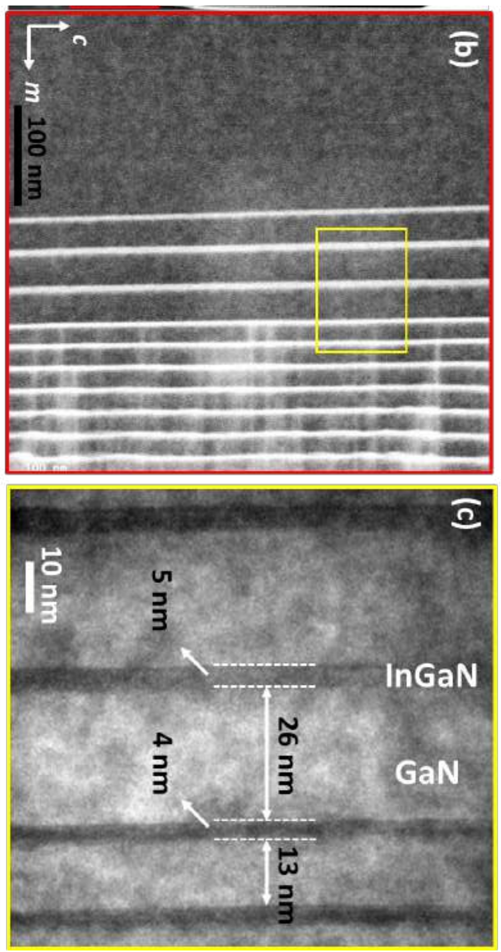
**Core-shell wire growth with bleu and green QWs**




| QW number | Target In-content | QW temperature | QB temperature |
|---|---|---|---|
| 3 | 15 % | 720 ° C | 900 ° C |
| 7 | 20 % | 680 ° C | 835 ° C |

**STEM-HAADF images**

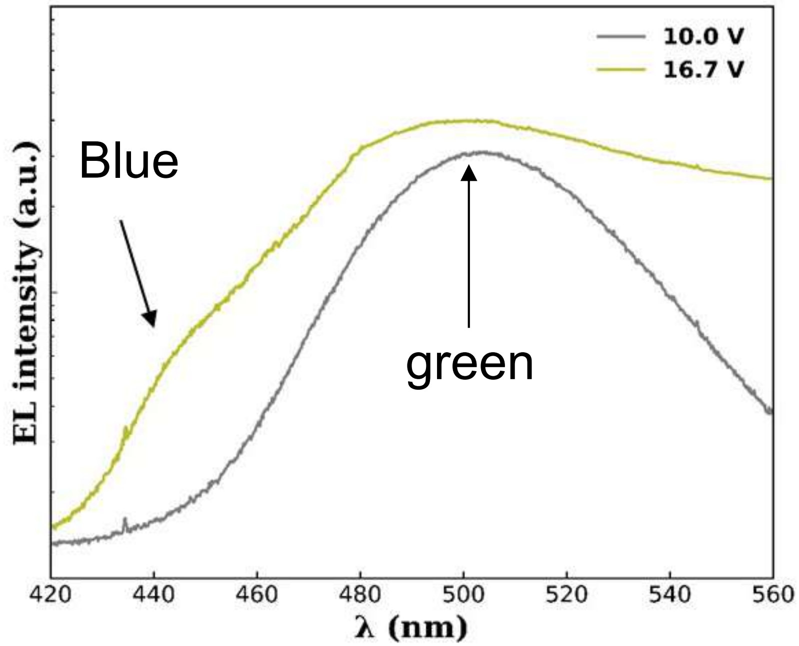



- Blue and green emitting QWs are integrated within the same core/shell LED structure

*A. Kapoor et al, Adv. Photonics Res. (2021)*

# Flexible two color LED

**Electroluminescence at RT**



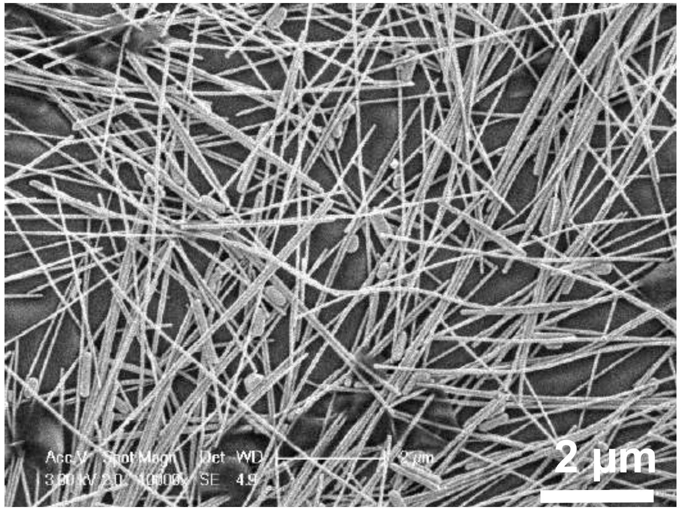

- EL spectra present a broad emission dominated by the green color
- Blue emission around 445 nm appears at higher injection

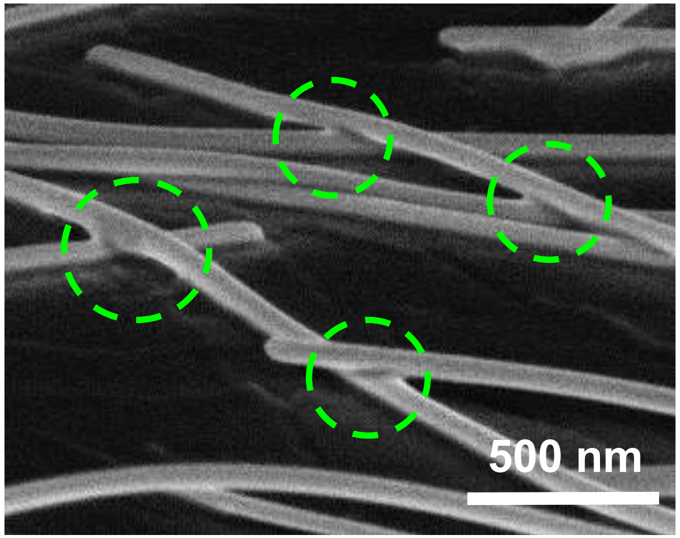


*A. Kapoor et al, Adv. Photonics Res. (2021)*

# Ag nanowire contact properties

## Silver NW mesh on PDMS




**Silver nanowire mesh fabrication :**

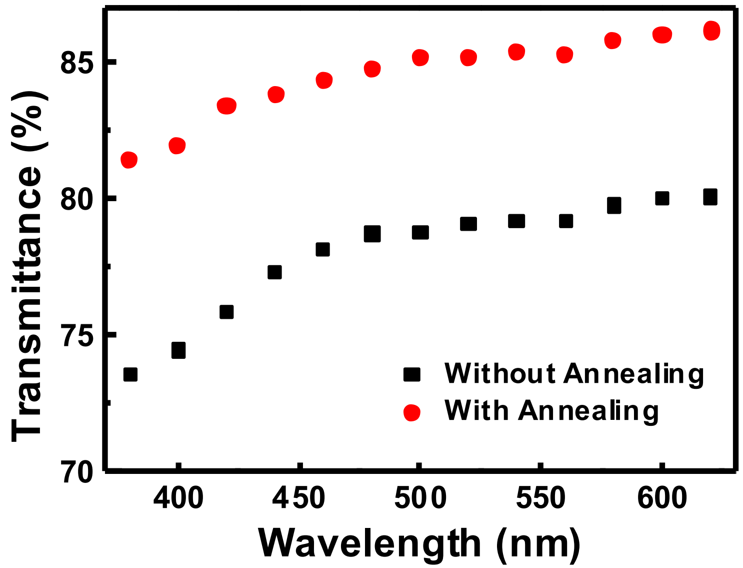
- Spin coating of Ag nanowires
- Baking for 20 min @ 200 ° C

**Sheet resistance after bending:**

- Unbaked Ag NWs $R_\square$ = 40 Ω/□
- Baked Ag NWs $R_\square$ = 18 Ω/□
- ITO (no bending) $R_\square$ = 5-100 Ω/□

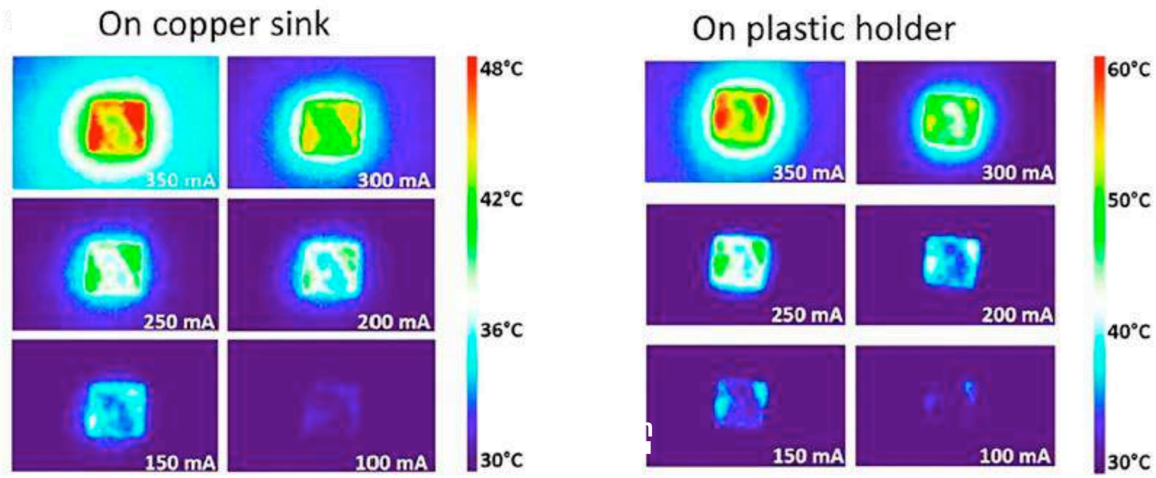
**Transmittance :** 80-85%

**Aging:** 5% $R_\square$ increase after 1 y. storage

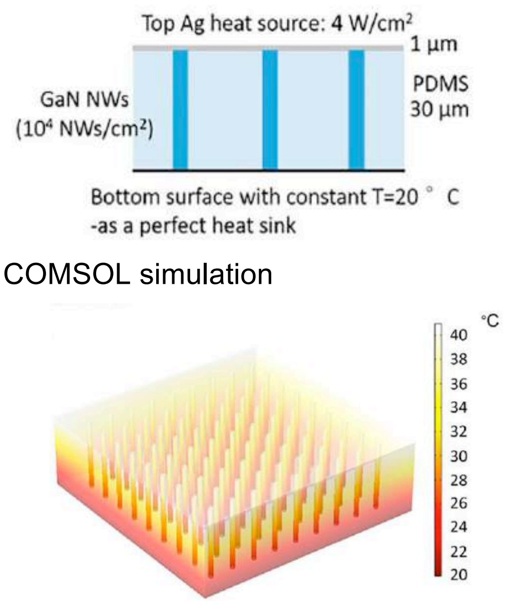


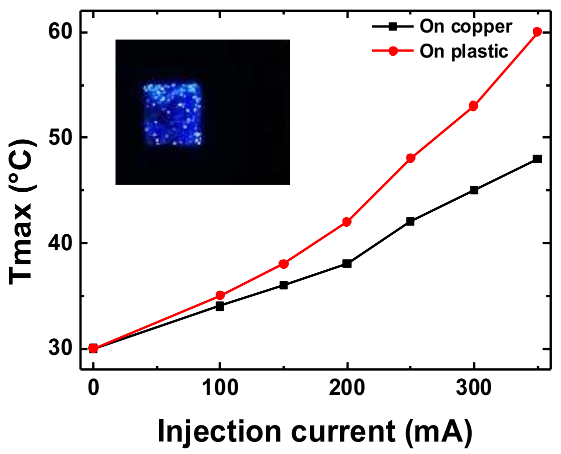
# Thermal studies: self-heating

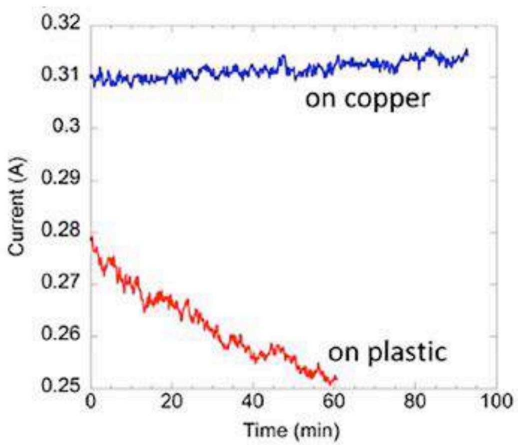
- PDMS is a bad thermal conductor
- Device can operate for 90 min at high injection without degradation
- NWs extract the heat to metal contact




**Simulation of T distribution**




*N. Guan, et al. Nanomaterials 10(11) 2020*