# PAMBE growth of GaN nanowires on ZrN metallic buffer layers

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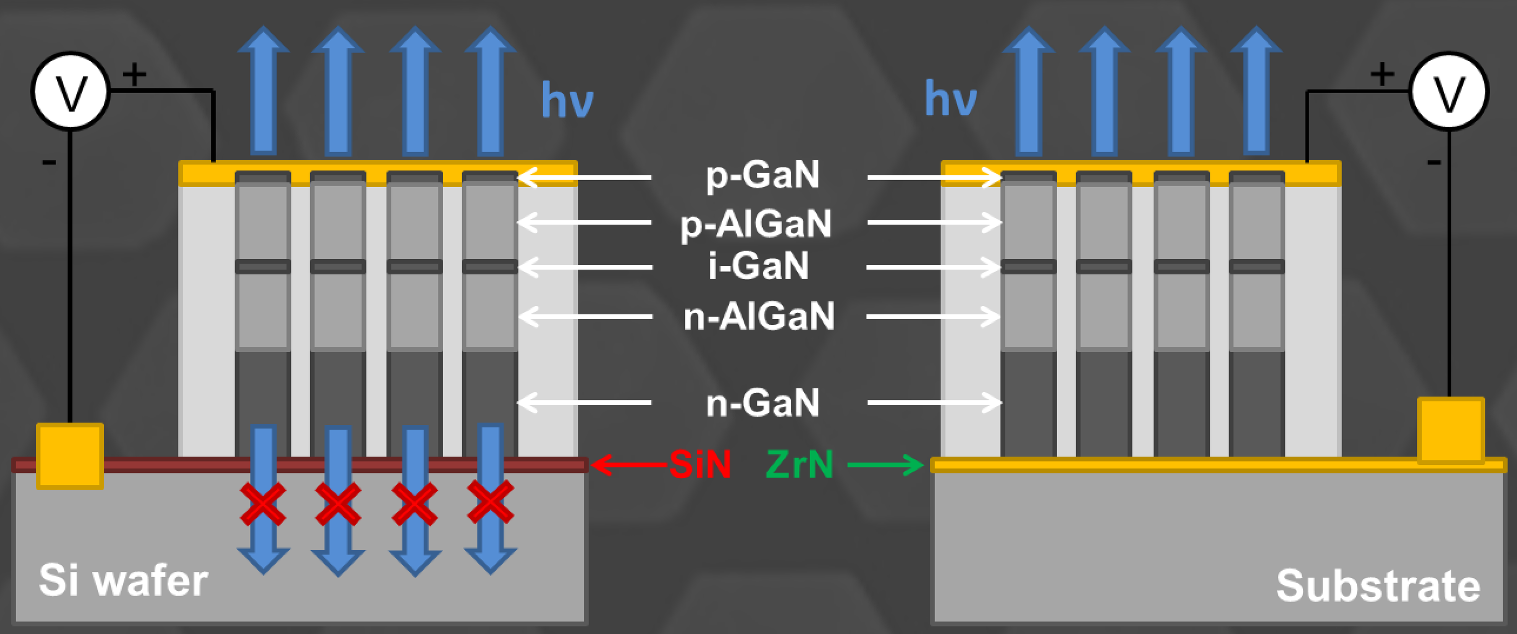
## Introduction

- Two factors limit expected high efficiency of a LED based on GaN NWs grown by Plasma Assisted Molecular Beam Epitaxy (PAMBE) on a Si(111) substrate:
  - ➢Part of the emitted light is absorbed inside the Si substrate
  - ➢GaN and SiN form a non-linear electrical contact

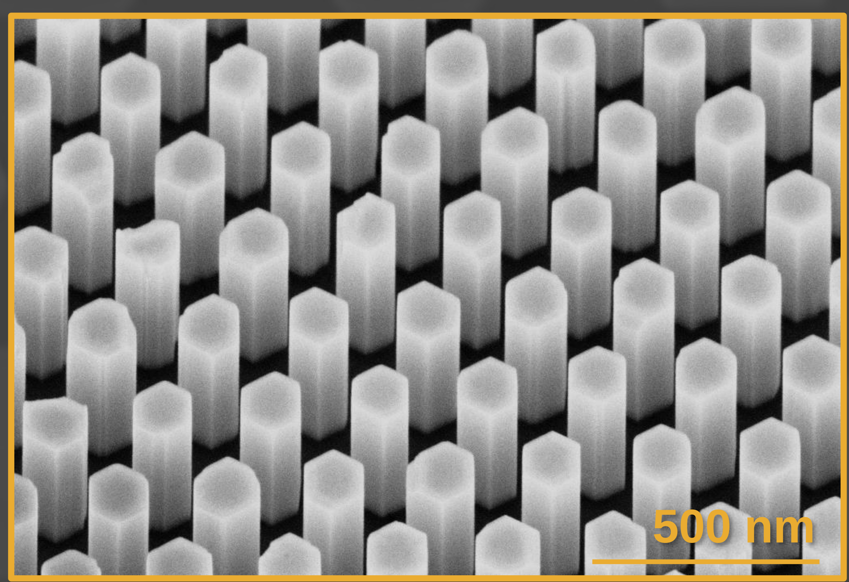


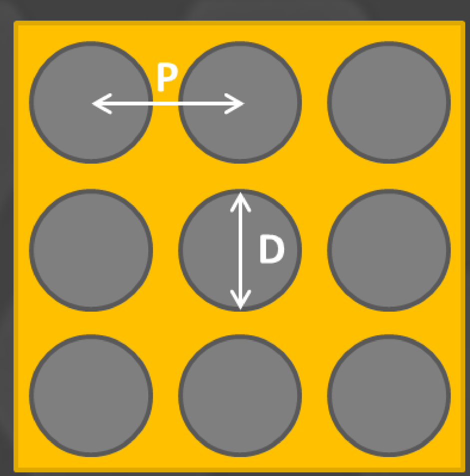

### Advantages of ZrN layer for GaN based LEDs

- High electrical and thermal conductivity, ohmic contact between ZrN and GaN
- Light emitted towards the substrate gets reflected back due to high reflectivity of the metallic layer (a buried mirror)
- Higher optical output and better electrical characteristics of LEDs expected

## Selective are growth of GaN NWs on ZrN mask

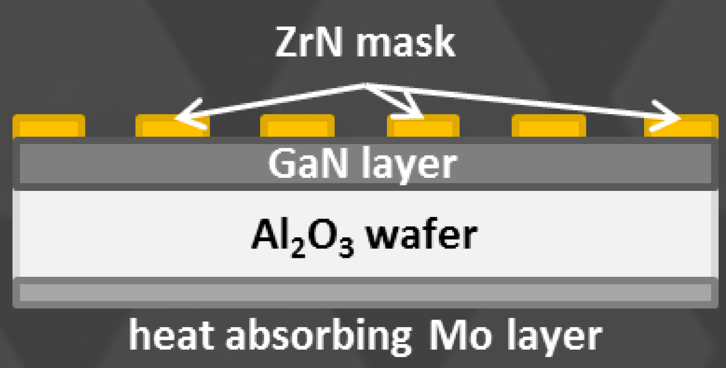
- For specific growth conditions (Ga/N flux ratio, substrate temperature) extremely long incubation times observed for nucleation of GaN nanowires on ZrN
  - ➢ZrN can be used as a mask for selective area growth (SAG) of GaN NWs

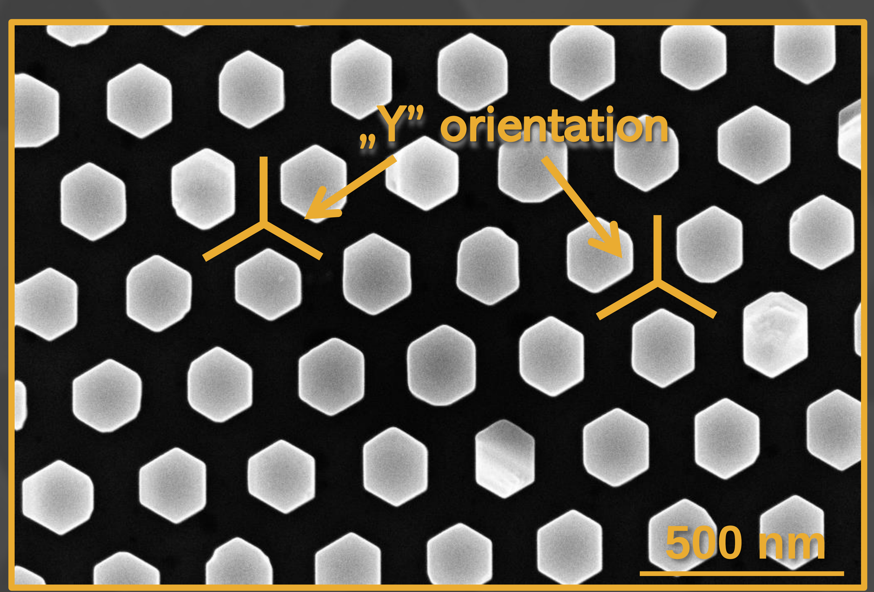


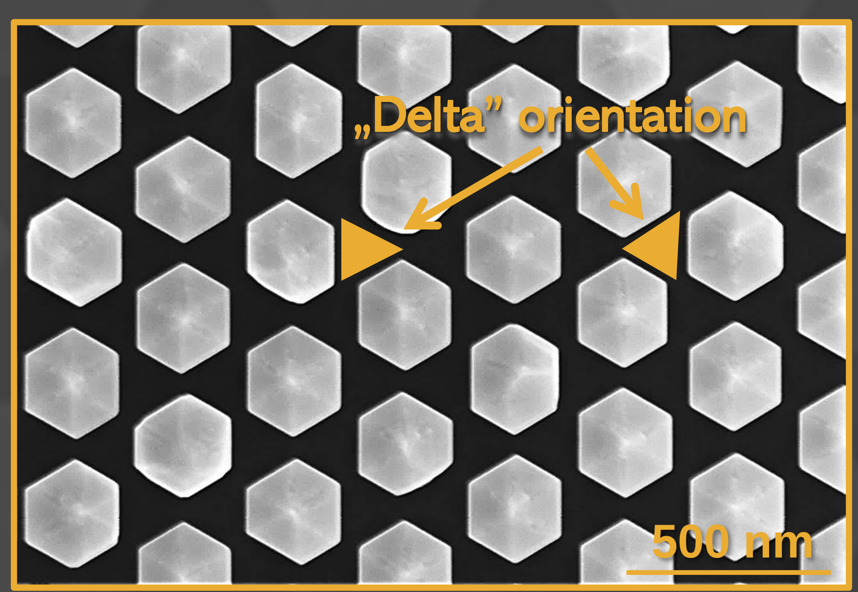




ZrN mask for SAG of GaN

- Thin (~7 nm) ZrN layer deposited on a GaN template (GaN/sapphire/Mo)
- Openings etched in the mask by e-beam lithography expose the GaN layer underneath
- Pattern of openings with different diameters (D) and pitch between them (P)
- Growth of GaN directly inside the openings leads to formation of hexagonal nanowires




- Full growth selectivity has been achieved (no growth of GaN nanowires by self-assembly directly on the ZrN mask)
- Two different orientations of NWs respective to each other found:
  - ➢Siedwalls of neighboring nanowires are parallel to each other („Y" orientation)
  - ➢Neighboring nanowires are aligned to their edges („Delta Δ" orientation)
- Y orientation is preferred for applications, easier top contact deposition
- Orientation of the nanowires can be controlled by aligning the mask pattern with the direction of the GaN layer miscut (measured by XRD)

## Summary

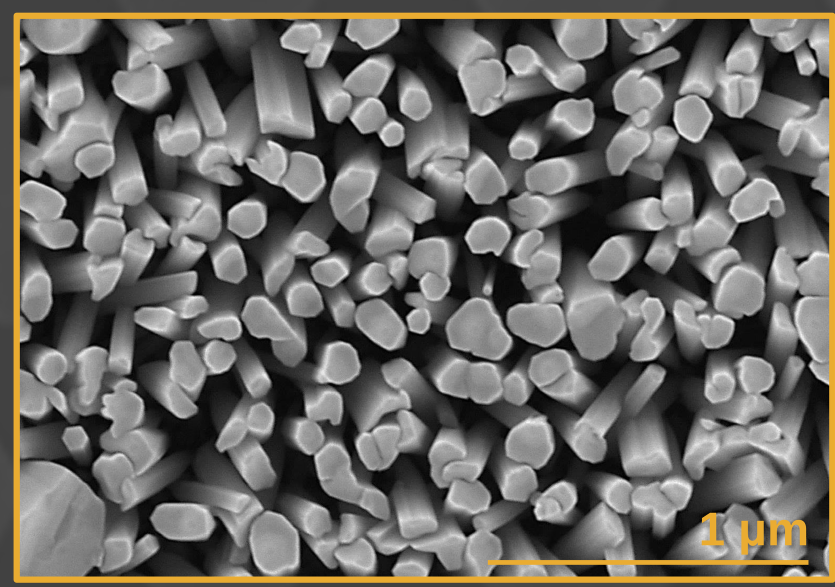
- GaN nanowires successfully grown by PAMBE on polycrystalline ZrN layers
- Unexpectedly small tilt dispersion of the nanowires observed in dense NW arrays
  - ➢The effect explained as being due to geometrical selection of nanowires
- At high temperatures ZrN reacts with Si substrate, damage to the layer surface observed
- $ZrN/Al_2O_3$ much more stable; allows growth of NWs at very high temperatures
  - ➢Higher crystalline quality and better optical properties of the NWs expected
- Twofold increase in conductivity of the ZrN layer observed after the growth
- GaN NWs grown on ZrN have uniform N-polarity unlike for other substrates (no mixed polarity effect)

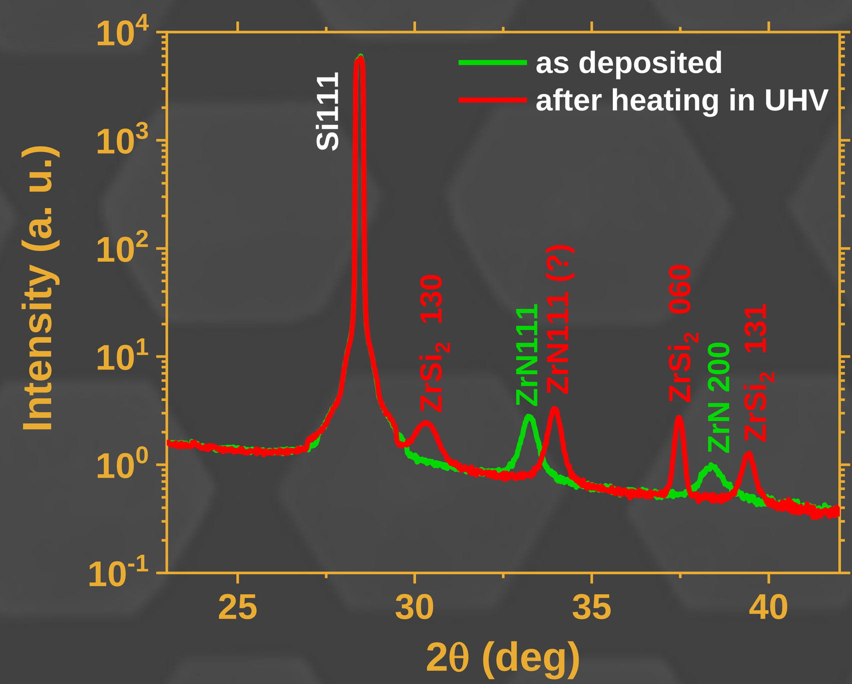
## Self-assembled growth of GaN NWs on ZrN

- ZrN layer are deposited on a substrate by DC sputtering from a ZrN target
- XRD measurements show that ZrN layers are polycrystalline with grain size ~ 15 nm
- Substrate temperature is calibrated for each specific substrate type and ZrN layer thickness by controlled melting of Al wires bonded to the substrate surface
- For self-assembled growth of GaN NWs ZrN layers are 100 nm thick

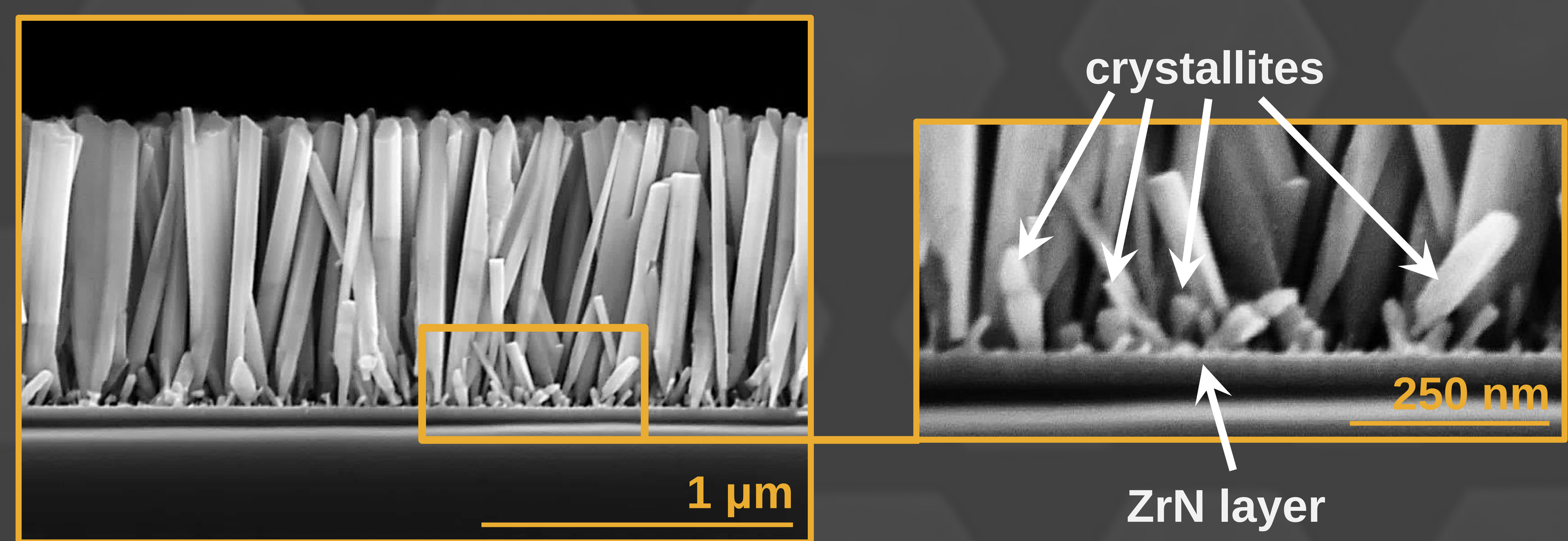
### GaN NWs grown on ZrN/Si(111)

- At high temperatures ZrN reacts with the Si substrate (XRD), which leads to surface roughening (AFM) and formation of voids at the ZrN/Si interface (SEM)
- No defoliation of the layer observed unlike for other metallic layers on Si reported in literature



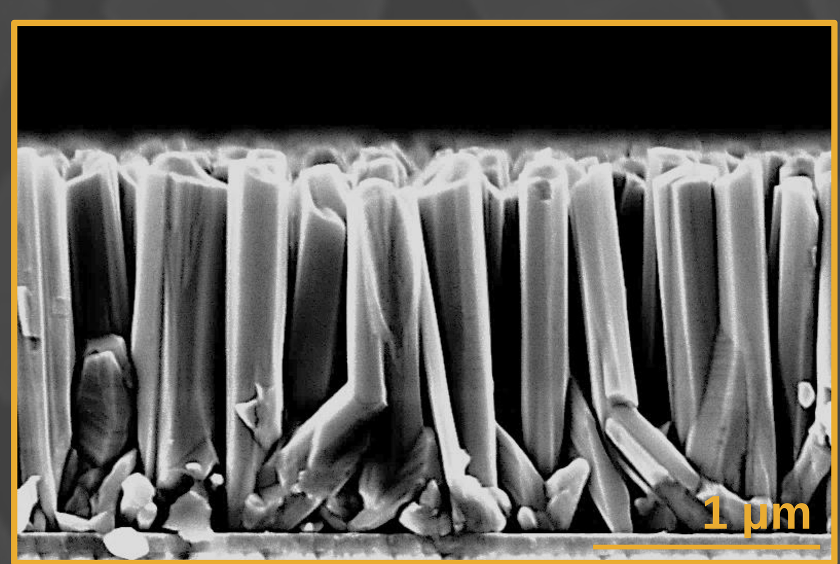

- Self-assembled GaN NWs can be grown on ZrN/Si(111) substrates by PAMBE
- NWs are epitaxially linked to the randomly oriented grains in polycrystalline ZrN layer
  - ➢ random orientation of the NWs expected
- Unidirectional supply of Ga in MBE favors NW growth in the direction of the gallium cell axis (tilted by 40° relative to the substrate normal)

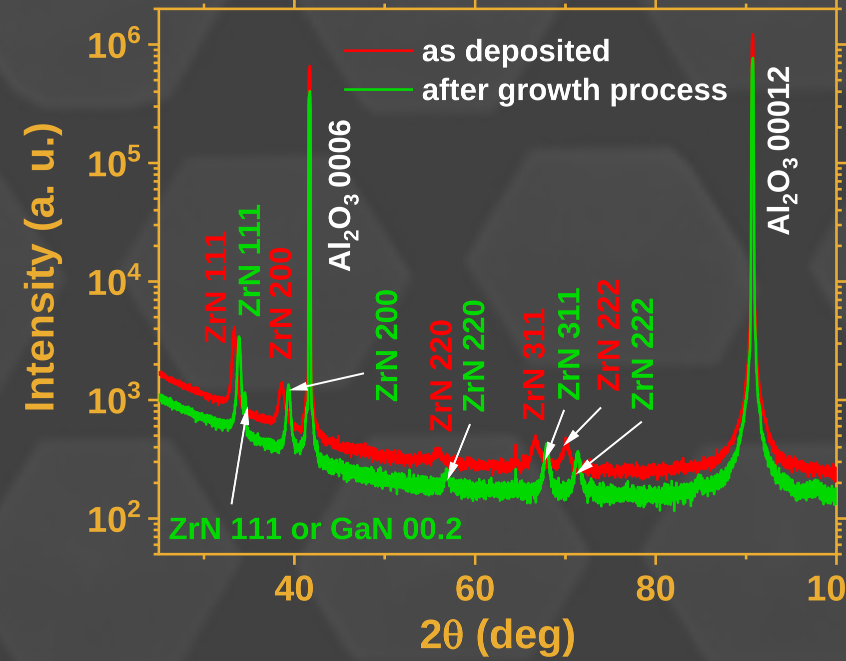



- This competition results in geometrical selection of vertical nanowires: due to rotation of the substrate NWs that are perpendicular to the substrate surface grow the fastest and overshadow strongly tilted ones, which remain on the substrate surface as small crystallites *Olszewski et al., Nanomaterials 2023, 13(18), 2587*
- As the result, ensembles of vertical, device relevant NWs on ZrN layers are obtained

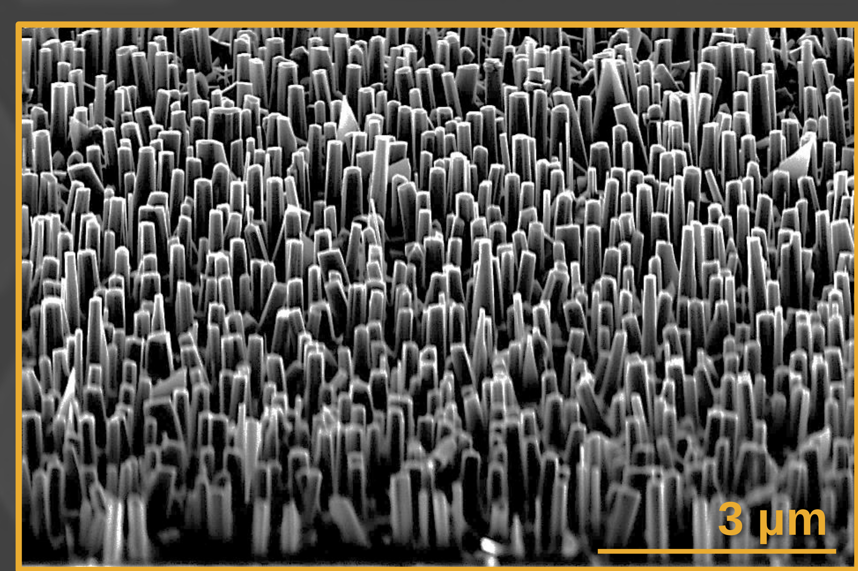
### GaN NWs grown on $ZrN/Al_2O_3$

- C-plane sapphire ($Al_2O_3$) used as an alternative host substrate for ZrN buffer
- No reaction between the sapphire and ZrN layer observed up to 1000°C




- Well aligned NWs obtained on $ZrN/Al_2O_3$ substrate due to geometrical selection principle as described for ZrN/Si(111)
- High stability of $ZrN/Al_2O_3$ substrates allows growth at very high temperatures > 850°C
  - ➢ higher crystalline quality of nanowires with improved optical and electrical properties
- After PAMBE growth twofold increase in conductivity of the ZrN layer observed

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