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Acid-based Crystallographic Chemical Wet Etching of GaN Nanostructures

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Abstract

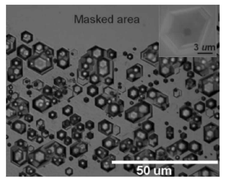
It has been previously reported that strong acids (H_3PO_4) and bases (KOH) can be used to smoothly etch non-polar and semi-polar facets in GaN. In conjunction with a two-step top-down fabrication process developed at Sandia National Laboratories, we investigate the effect of H_3PO_4 etching on high aspect ratio GaN nanowires.

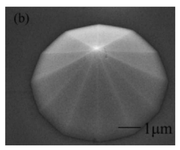
Motivation

Anisotropic wet chemical etch processes are highly sought after for semiconductor technologies where facets and facet-defined geometries dictate device properties for which III-nitrides are suitable materials. Optoelectronics (deep UV emitters and nano-lasers), MEMS, and even targeted drug delivery systems require precise shape control for successful devices. As GaN is a highly chemically inert material, a fundamental understanding of etch kinetics is necessary to utilize this material for novel devices.

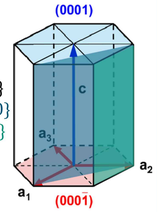
Background

- Group III-nitrides crystallize in a stable wurtzite structure with polar (*c*-), non-polar (*m*-, *a*-) and semi-polar plane directions





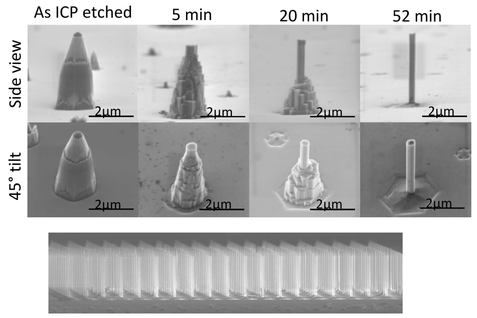
c- {0001}
m- {10$\bar{1}$0}
a- {11$\bar{2}$0}



- H_3PO_4 etching of Ga-face (0001) GaN results in dislocation decorating by forming *m*- oriented, stepped, hexagonal etch pits
- Concentrated H_3PO_4 etching of N-face GaN yields dodecagonal pyramids which form around threading dislocations

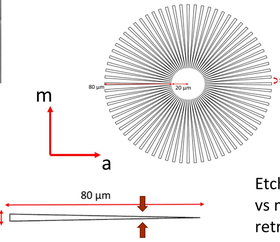
Keller at al., Semicond. Sci. and Tech., 11, 113001, 2014. Han et al., J. Electrochem. Soc., 157, D60, 2010.

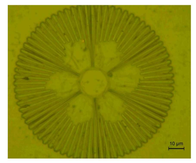
Anisotropic Etching of Vertical Nanowires in Hot (65°C) KOH-based Solution

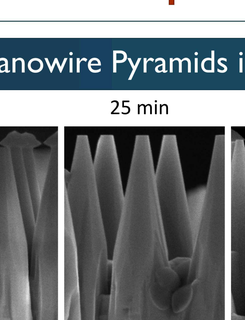


Yields atomically smooth, high aspect-ratio nanowires with cross sectional shape control

- Morphology defined by '*c*-' (horizontal) and '*m*-' (vertical) plane facets with ~nm/min etch rates
- Studies show that '*m*-' plane facets etch more rapidly than '*a*-' plane, thus defining a $(1\bar{1}00)$ orientation of nanowires





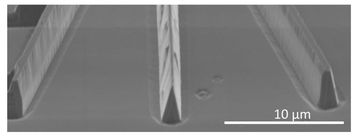


Etches laterally (⇩) at 100 nm/min vs measured distance of wedge retraction at 6.7 μm/min

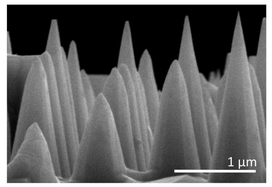
G. Wang et al., OMVPE-18, 2017

Anisotropic Etching of Vertical Nanowire Pyramids in Hot (93-96°C) H_3PO_4

Wagon wheel in H_3PO_4, 120°C, 5 min



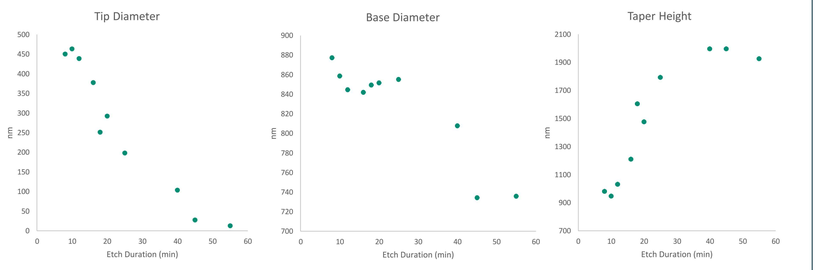
- Unable to measure lateral etch rates due to semi-polar etching



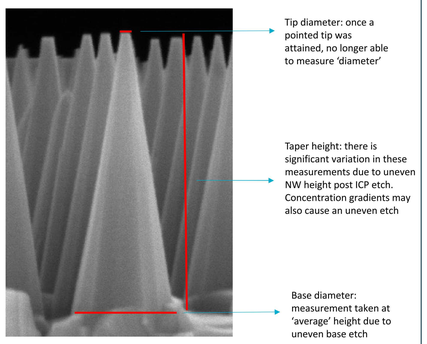
55 min

- H_3PO_4 etching adds an inclined facet to resulting structures → NOT seen in KOH based etch
- Additional complexity in characterization as the etch profile now becomes a function of angle and '*l*' miller index
- Overetching present beginning at 45 min

Nanowire Pyramid Etch Evolution

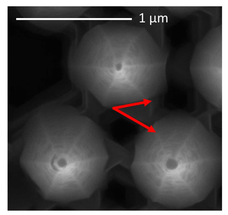


- Tip diameter: decreases with etch time
- Base diameter: decreases until V_t slows down, then stays relatively consistent with etch duration
- Over-etched NW average base diameter measured to be ~720 nm, supporting etch evolution theory
- Taper Height: Increases until V_t slows down and over-etching has not begin yet

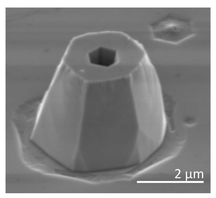


Concave vs Convex Etch Geometry Observed

- Nanowire facets are 30° rotated from etch pit facets in GaN
- Annular shapes confirm concave planes etch with '*m*-' $(10\bar{1}0)$ type character and convex planes etch with '***a***-' $(11\bar{2}0)$ type character

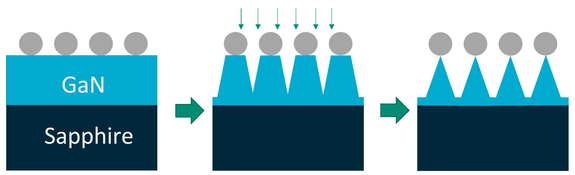


40 min 93-96°C H_3PO_4



5 min 120°C H_3PO_4

Nanowire Etching via Two-Step Top-Top Process



1 μm silica sphere monolayer on 5 μm Si-doped, MOCVD grown GaN

1. Cl_2 based ICP/RIE etch

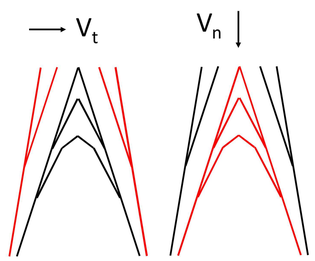
2. Hot H_3PO_4 anisotropic chemical wet etch

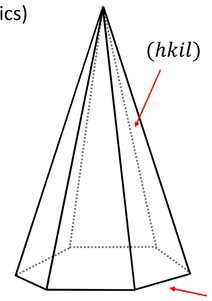
- Silica sphere monolayer serves as semi-periodic lithographic etch mask
- Plasma etch results in NWs with damaged surfaces and large cross sectional areas are unsuitable for further application
- H_3PO_4 improves upon the dry etch by mitigating surface roughness and anisotropically etching semi-polar planes

Q. Li et al., Opt. Express, 19, 25528, 2011

Nanowire Pyramid Etch Evolution

- High-index semi-polar planes are etched
- Semi-polar facets form due to V_n/V_t ratios
- V_t initially dominates → driven by concentration (kinetics)
- V_n driven by surface energy (thermodynamics)





- Semi-polar facet orientation determined to be '*a*-' type
- Measured facets during etching vary from ~73°- 82°: $(hki1) \rightarrow (11\bar{2}1), (22\bar{4}1)$ etc.
- Angles upon over-etching vary from ~60°: $(11\bar{2}2)$ at beginning of over-etch to ~50-45°: $(11\bar{2}3)$ towards later over-etch
- More angle consistency needed for angle dependency, but initial results tentatively show sequential increase in '*l*' index during etching
- Lower index planes are more stable, thus the progressive increase of 'l' index only indicates preferential plane stability

Conclusions

For the first time, a two-step top-down approach was used to etch GaN nanowires in hot H_3PO_4. The resulting nanowires showed an etch progression resulting in sharp, tapered, 6-fold pyramids. The exposed faceting was of $(11\bar{2}l)$ origins and over-etching resulted in a progressive, sequential increase of the '*l*' index, indicating preferential plane stability.

Acknowledgements

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