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Enhanced Material Removal Rate For III/V Semiconductors

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Introduction

- GaN is the next important semiconductor material after silicon that can be operated at high temperatures.
- It is the key material for the next generation of high frequency and high power transistors.
- Gallium nitride (GaN) based semiconductors are utilized in;
  - blue lasers diodes (LDs)
  - light-emitting diodes (LEDs)
  - high-power, high-frequency field effect transistor (FET) devices
- GaN provides direct and wide band-gap energy and high electron mobility[1]
- In order to make LEDs from GaN, it is required to planarize the wafer surface and hence chemical mechanical planarization (CMP) is needed
- GaN is a very hard film and removal rates tend to be very low when CMP is applied[2]

1. Hideo A., Hidetoshi T., Koji K., Haruji K., Kazuhiko S.,and Toshiro D., Chemical Mechanical Polishing of Gallium Nitride with Colloidal Silica, Journal of The Electrochemical Society, 158 (12) H1206-H1212 (2011).
2. Tavernier P. R., Margalith T., Coldren L.A.,DenBaars S.P., and Clarke D.R., Chemical Mechanical Polishing of Gallium Nitride, Electrochemical and Solid-State Letters, 5 (8) G61-G64 (2002).

Introduction

Properties of GaN as compared to other semiconductor materials

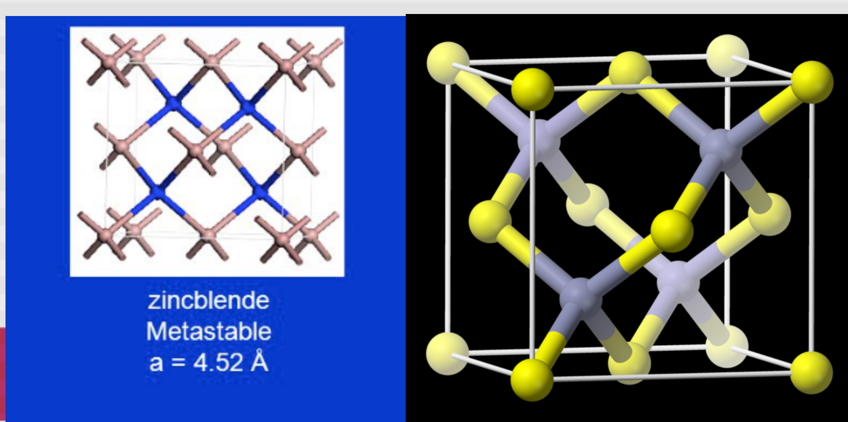
Material	Bandgap (eV)	Electron Mobility (cm2/Vs)	Hole Mobility (cm2/Vs)	Critical Field *Ec* (V/cm)	Thermal Conductivity σT (W/m•K)	Coefficient of Thermal Expansion (ppm/K)
InSb	0.17, D	77,000	850	1,000	18	5.37
InAs	0.354, D	44,000	500	40,000	27	4.52
GaSb	0.726, D	3,000	1,000	50,000	32	7.75
InP	1.344, D	5,400	200	500,000	68	4.6
GaAs	1.424, D	8500	400	400,000	55	5.73
GaN	3.44, D	900	10	3,000,000	110 (200 Film)	5.4-7.2
Ge	0.661, I	3,900	1,900	100,000	58	5.9
Si	1.12, I	1,400	450	300,000	130	2.6
GaP	2.26, I	250	150	1,000,000	110	4.65
SiC (3C, b)	2.36, I	300-900	10-30	1,300,000	700	2.77
SiC (6H, a)	2.86, I	330 - 400	75	2,400,000	700	5.12
SiC (4H, a)	3.25, I	700		3,180,000	700	5.12
C (diamond)	5.46-5.6, I	2,200	1,800	6,000,000	1,300	0.8

Introduction

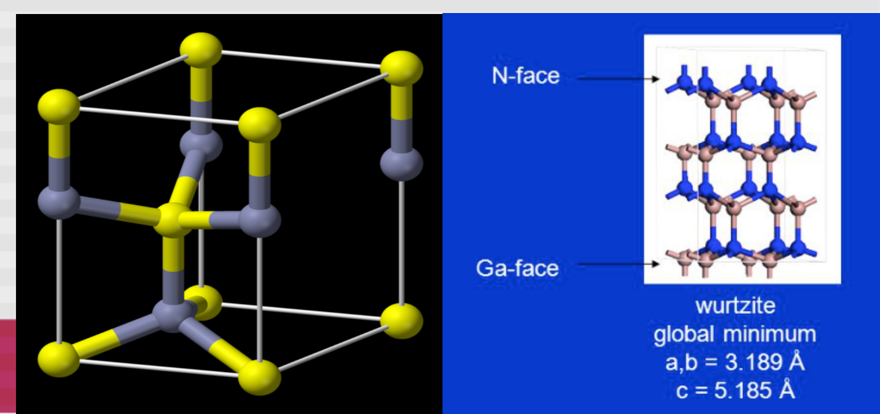
Crystallographic properties of GaN

PROPERTY / MATERIAL	Cubic (Beta) GaN	Hexagonal (Alpha) GaN
Structure	Zinc Blende	Wurzite
Stability	Meta-stable	Stable
Lattice Parameter(s) at 300K	0.450 nm	a_0 = 0.3189 nm c_0 = 0.5185 nm
Density at 300K	6.10 g.cm^{-3}	6.095 g.cm^{-3}
Nature of Energy Gap E_g	Direct	Direct
Energy Gap E_g	3.2 eV	3.4 eV

Cubic (Beta) GaN



Hexagonal (Alpha) GaN



Background

Common approaches to increase material removal rate;

- Increase applied downforce [1]
- Pre-polish the GaN surface by using a diamond based abrasive slurry that enhances the mechanical abrasions [surface finish was very rough][1-2].
- Use colloidal silica based slurries to improve surface quality by enabling polishing on the gallium reach face of GaN (β-Face) yet the nitride reach face (α-Face) showed extremely low polishing rate due to chemical inertness [*important evidence that softer silica particle were able to remove the hard GaN material without inducing sub-surface damage*] [2].
- A damage-free surface was achieved with chemical mechanical polishing with KOH solution with soft polishing pad, while it required application of relatively high pressures (2–6 kg/cm^2) and a long time of polishing (~40hrs) finally achieving a surface roughness of 0.57 nm[3].

1. Hideo A., Hidetoshi T., Koji K., Haruji K., Kazuhiko S.,and Toshiro D., Chemical Mechanical Polishing of Gallium Nitride with Colloidal Silica, Journal of The Electrochemical Society, 158 (12) H1206-H1212 (2011).
2. Tavernier P. R., Margalith T., Coldren L.A.,DenBaars S.P., and Clarke D.R., Chemical Mechanical Polishing of Gallium Nitride, Electrochemical and Solid-State Letters, 5,(8),G61-G64 (2002).
3. S.A.Ghosh. Structural and Electrical Characterization of GaN Thin Films on Si(100). *American Journal of Analytical Chemistry*, 2011, 2, 984-988.

Literature Review

Journal of The Electrochemical Society, **158** (12) H1206-H1212 (2011)
0013-4651/2011/158(12)/H1206/7/$28.00 © The Electrochemical Society

Chemical Mechanical Polishing of Gallium Nitride with Colloidal Silica

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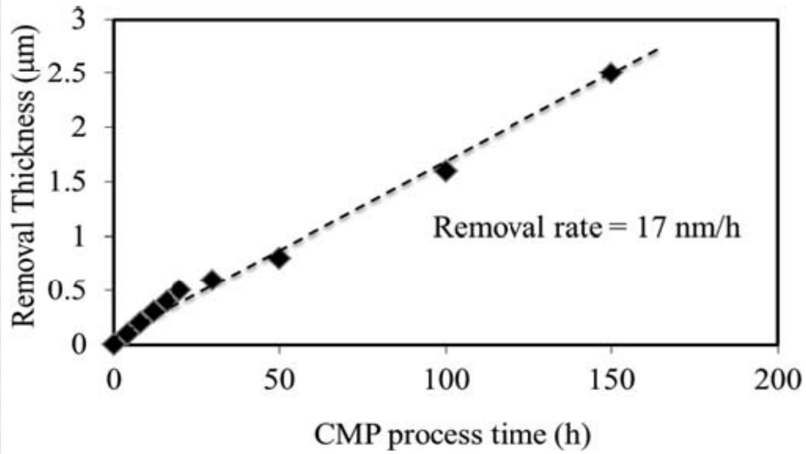
[b]*Department of Mechanical Engineering, Kyushu University, Fukuoka 819-0395, Japan*

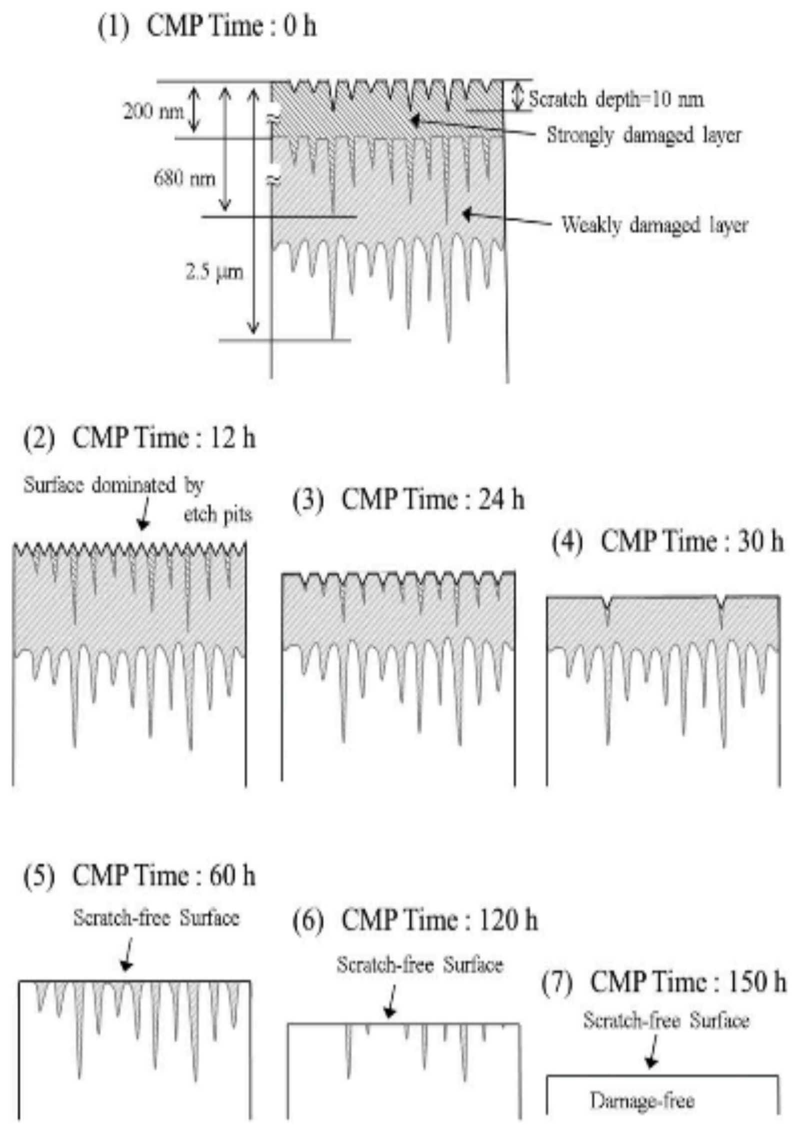
Table I. Polishing conditions.

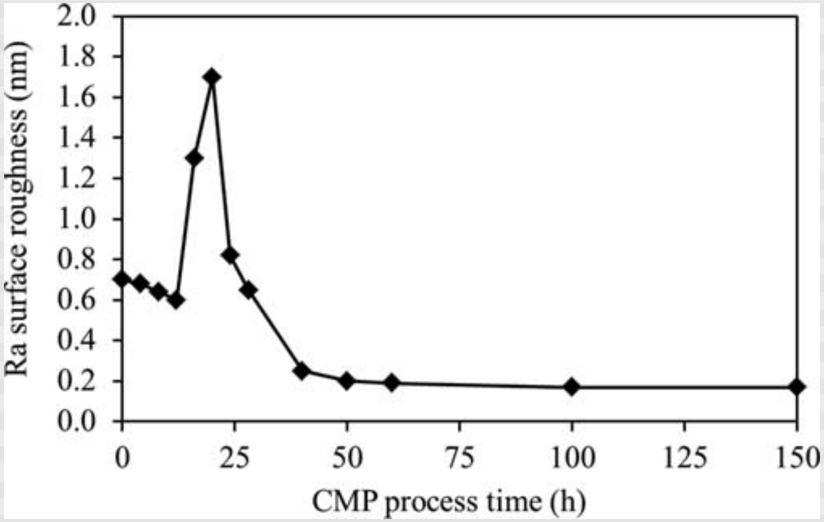
Platen rotation speed	rpm	50
Carrier rotation speed	rpm	40
Applied pressure	kg/cm^2	0.4
Diameter of platen	mm	300
Polishing pad type		Suede type
Slurry type		Colloidal silica
Slurry pH		10.5
Abrasive particle size	nm	40
Abrasive concentration	%	40



- Colloidal silica based slurry can be used for CMP of GaN which gave a removal rate of 17 nm/h at 0.4 kg/cm^2 (5.7 PSI) downforce.
- An atomically flat surface of Ra = 0.1 nm level finish was achieved after 40 hrs of CMP.

Surface morphologies of GaN substrate during the CMP process





- Ra surface roughness measured in 5 × 5 μm^2 plotted as a function of CMP process time.

Objective

- Promote material removal rate of GaN CMP
  - Compare surface nature and correlating CMP responses of α−face and β−face GaN coupons
  - Evaluate the impact of;
    - pH
    - Slurry flow rate
    - Slurry solids loading
    - Downforce

    on MRR response.
  - Evaluate the impact of;
    - Alternative process chemistries &
    - Temperature

    on MRR response.
  - Design a tool configuration to adopt the new process conditions
- Implement the findings to alternative hard to polish materials and III/V semiconductors.

Materials and Methods

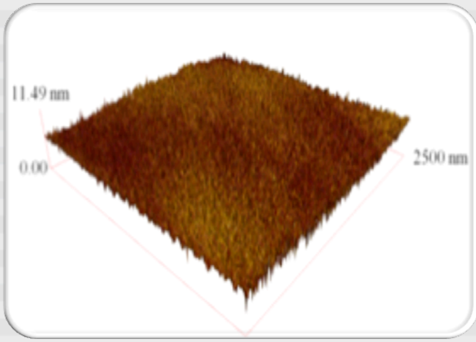
Materials

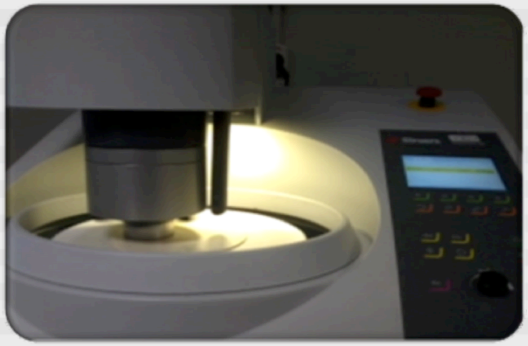
- **GaN Wafers:**
  - 1.0 x 1.0 mm^2 GaN coupons (High-Quality Free-Standing GaN substrates)

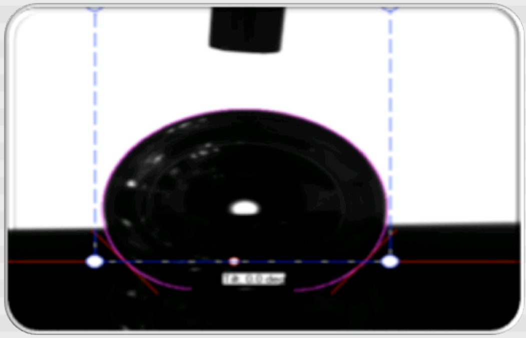
	Desktop Tegrapol-31 Polisher at Ozyegin University
Substrate	1.0 x 1.0 mm^2 GaN coupons
Abrassive Particles	Silica slurry
Rotational Speed (rpm)	150
Pad	SUBAIV-IC1000 stacked polishing pad
Applied Pressure (psi)	~ 9- 44
Slurry Flow Rate (ml/min)	20-200
Conditioning	In-situ
Conditioner	3M

Materials and Methods

Methods







Surface Roughness Analyses

Nanomagnetics AFM

CMP Analysis

Tegrapol-31 polisher by using SubaIV-IC1000 stacked polishing pad

Contact Angle and Surface Energy Analyses

KSV ATTENSION Theta Lite Optic Contact Angle Goniometer

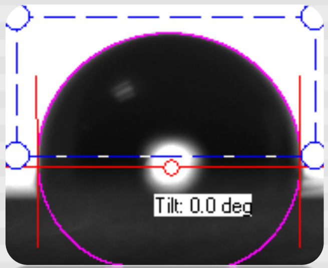
Outline

Compare surface nature and correlating CMP responses of $\alpha-$face and $\beta-$face GaN coupons

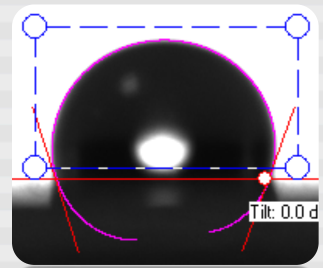
- Contact angle
- Surface energy
- Work of adhesion
- FTIR spectrum
- CMP

Wettability, surface energy and Wa Measurements on GaN

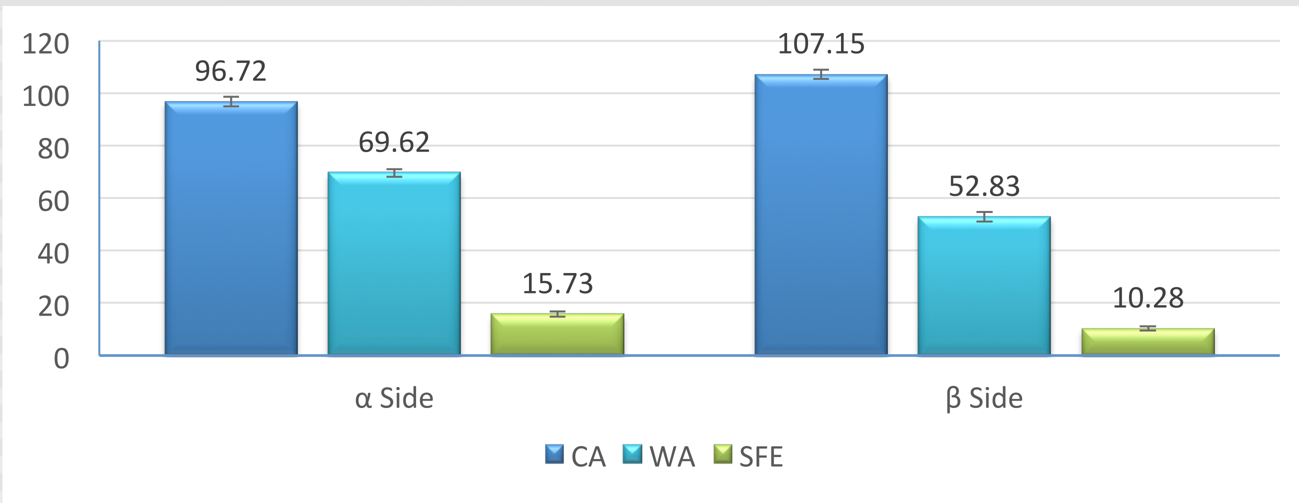
Contact angle measured with DI water droplet



α face 97°

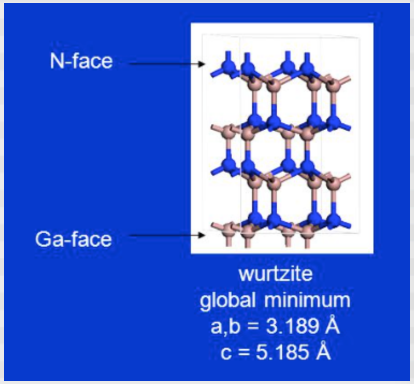


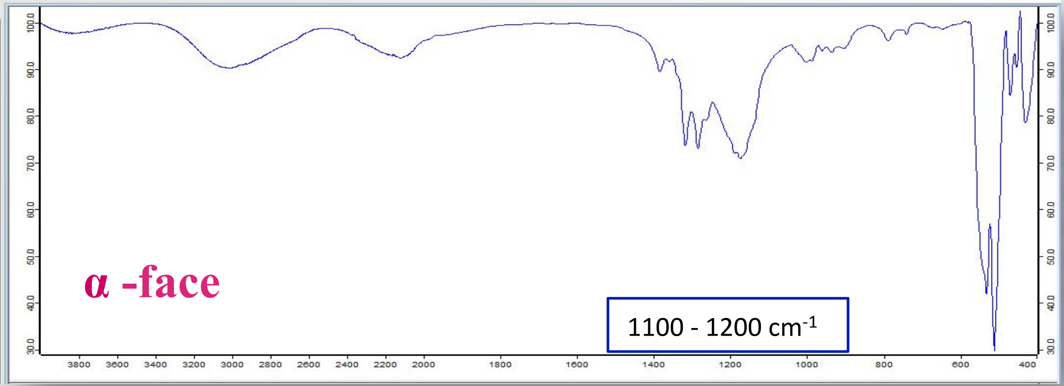
β face 107°

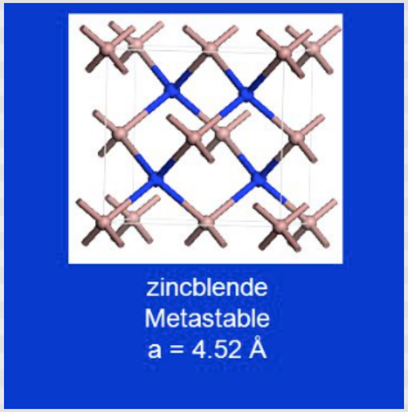


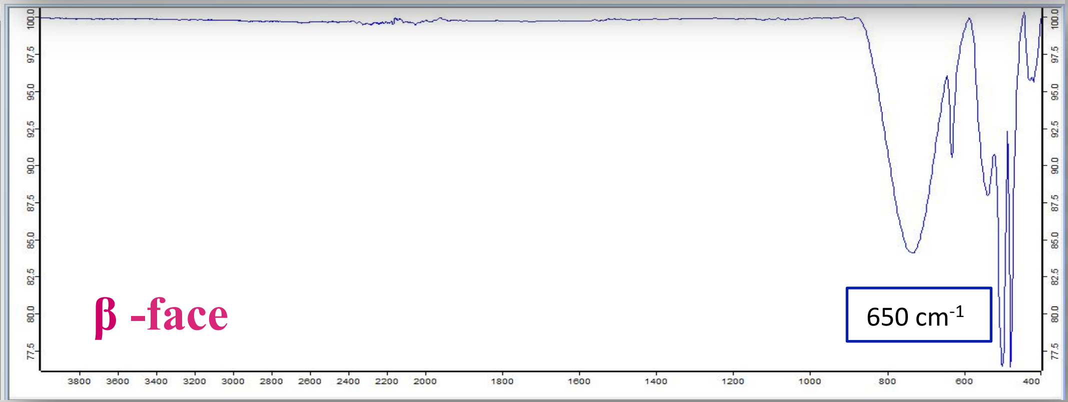
- The wettability response of the GaN coupons change based on the crystallographic orientation. β face has higher contact angle indicating higher hydrophobicity yet the α face is higher in energy due to closer atomic packing.

Surface FTIR analyses based on crystallographic orientation









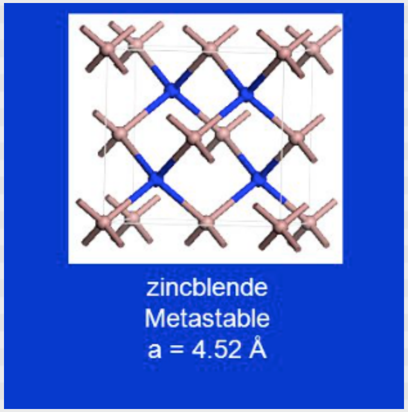
- An absorption peak at 650 cm^{-1} due to GaN bond stretch.
- GaN absorbs infrared light at near 1100 cm^{-1} with shoulder at 1200 cm^{-1} due to Si-O bond stretching vibration and at 816 and 446 cm^{-1} due to ring structure.

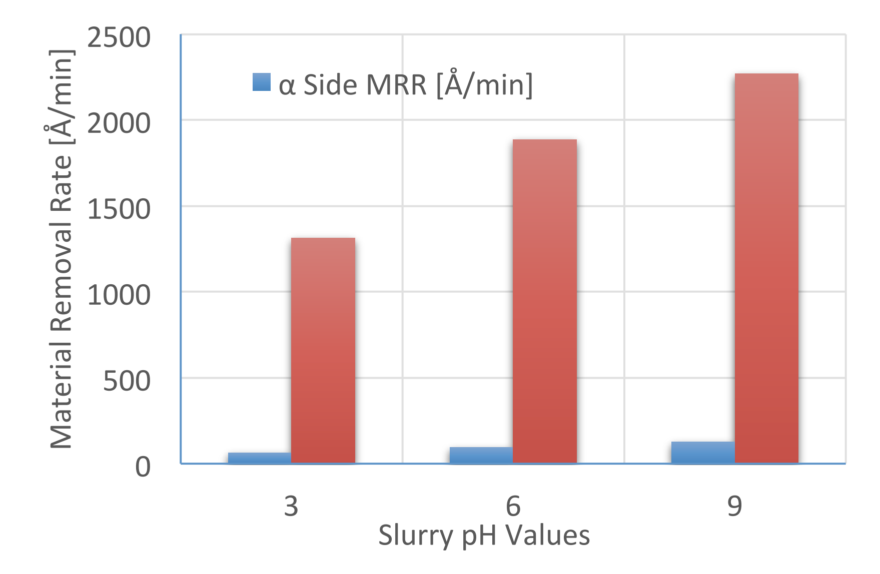
CMP Evaluation on GaN

Material Removal Rate Evaluation as a Function of pH

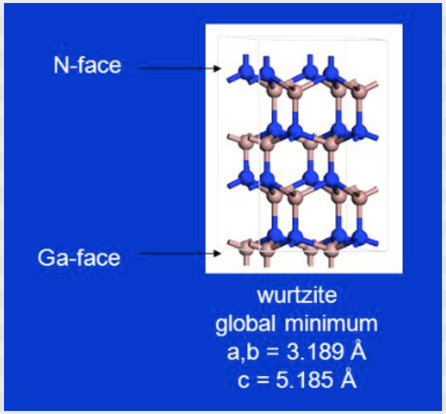
Slurry pH Value	α Side MRR [Å/min]	β Side MRR [Å/min]
3	62.9	1313.9
6	94.3	1887.6
9	125.8	2269.6

Cubic (Beta) GaN





Hexagonal (Alpha) GaN



- Material removal rate is increasing as a function of pH.
- The maximum MRR is determined at pH 9.

Material removal mechanism on GaN surface

Basic chemical interaction mechanism explaining the reaction on the α-face of GaN in the colloidal silica slurry;

Along the [1 1 2 0] direction for N-polar GaN selective etching takes place through

(i) formation of a nitrogen terminated layer with one negatively charged dangling bond on each nitrogen atom,

(ii) adsorption of hydroxide ions,

(iii) formation of oxides and

(iv) dissolution of the oxides.

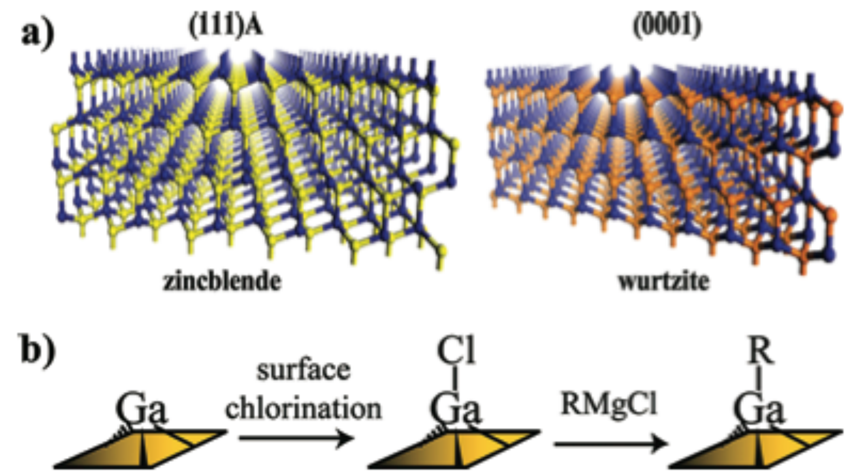


Figure 1. (a) Graphical representation of (left) zincblende GaAs and (right) wurtzite GaN crystal slabs. The (111)A and (0001) faces are at the top of each slab, respectively, and feature an atop Ga atom with one bonding orbital not participating in lattice bonding. (b)Wet chemical functionalization of atop Ga atoms at GaAs(111)A and GaN(0001) surfaces through surface Ga−C bonds produced through sequential chlorination and reaction with a Grignard reagent.

* Tavernier P. R., Margalith T., Coldren L.A.,DenBaars S.P., and Clarke D.R., Chemical Mechanical Polishing of Gallium Nitride, Electrochemical and Solid-State Letters, 5,(8),G61-G64 (2002).

* Sabrina L. Peczonczyk,† Jhindan Mukherjee,† Azhar I. Carim,† and Stephen Maldonado, Wet Chemical Functionalization of III−V Semiconductor Surfaces: Alkylation of Gallium Arsenide and Gallium Nitride by a Grignard Reaction Sequence, Langmuir, 28, 4672−4682 (2012).

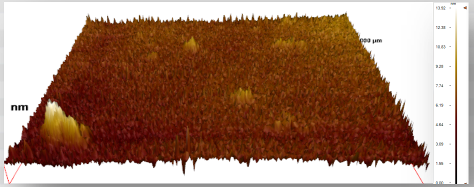
Outline

Evaluate CMP performance as a function of;

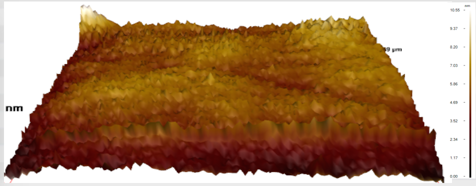
- pH
- Slurry solids loading
- Slurry flow rate
- Downforce

CMP performance evaluation as a function of pH

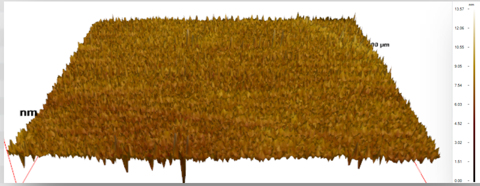
Gallium Nitride MRR and surface roughness response as a function of pH



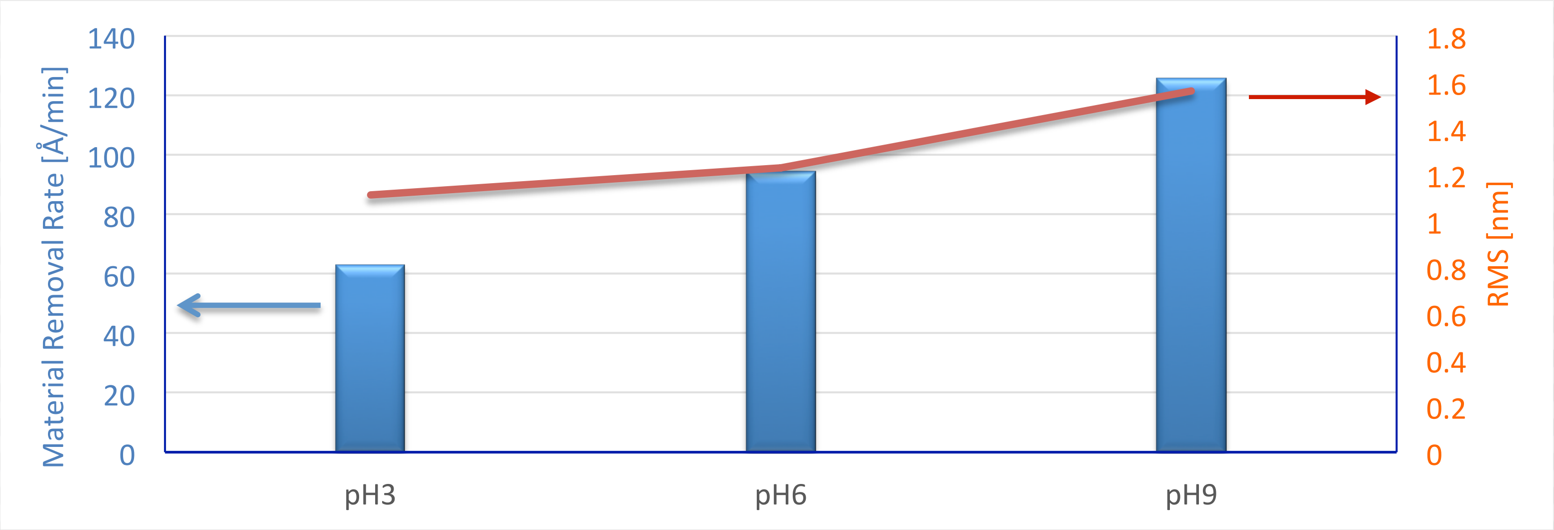
RMS: 1.11 ± 0.11



RMS: 1.23 ± 0.11



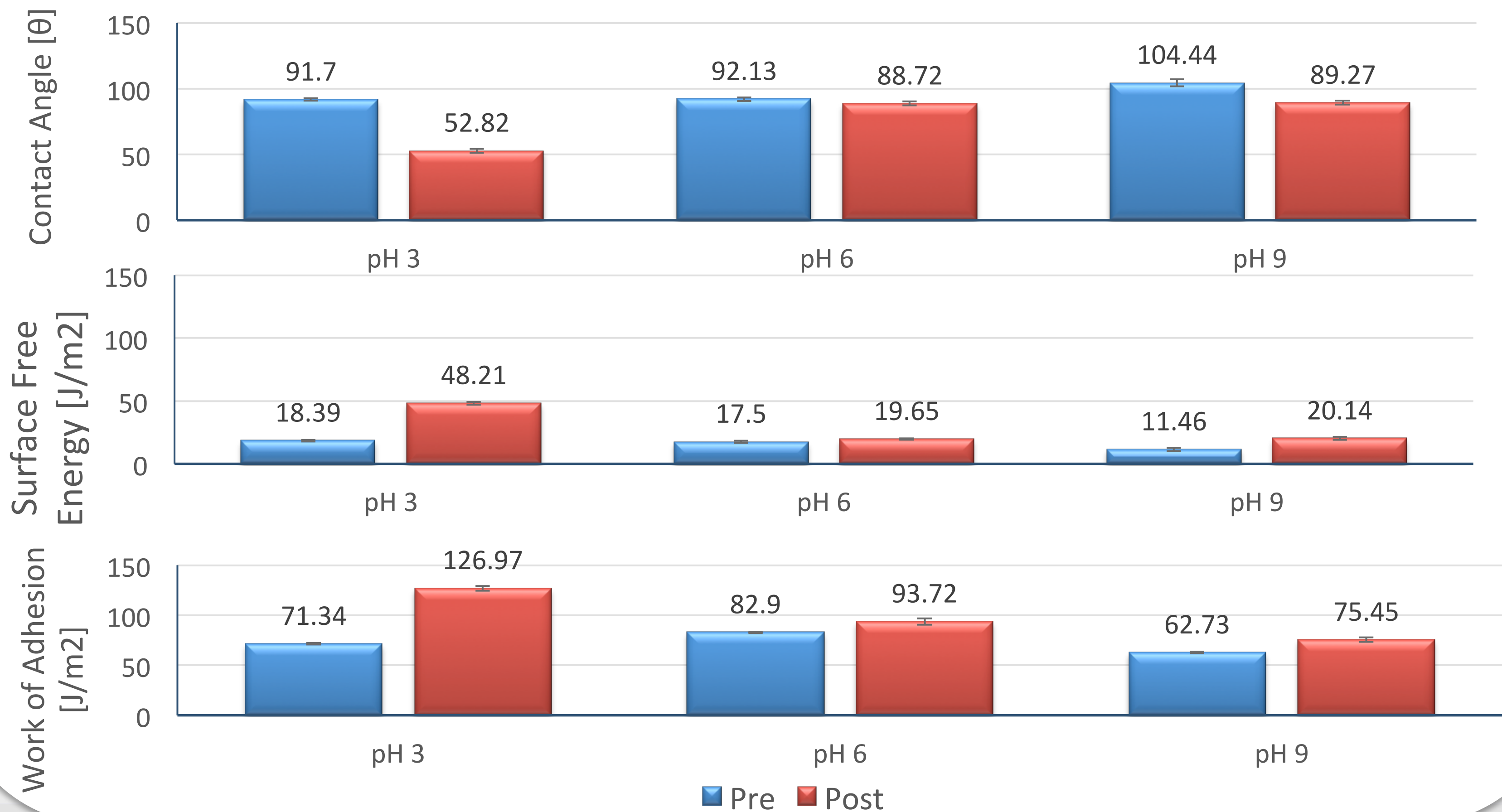
RMS: 1.56 ± 1.04



- Material removal rate increases with increasing pH value of the slurry reaching ~125 Å/min (750nm/hr) at pH 9 verifying Tevernier's removal mechanism.

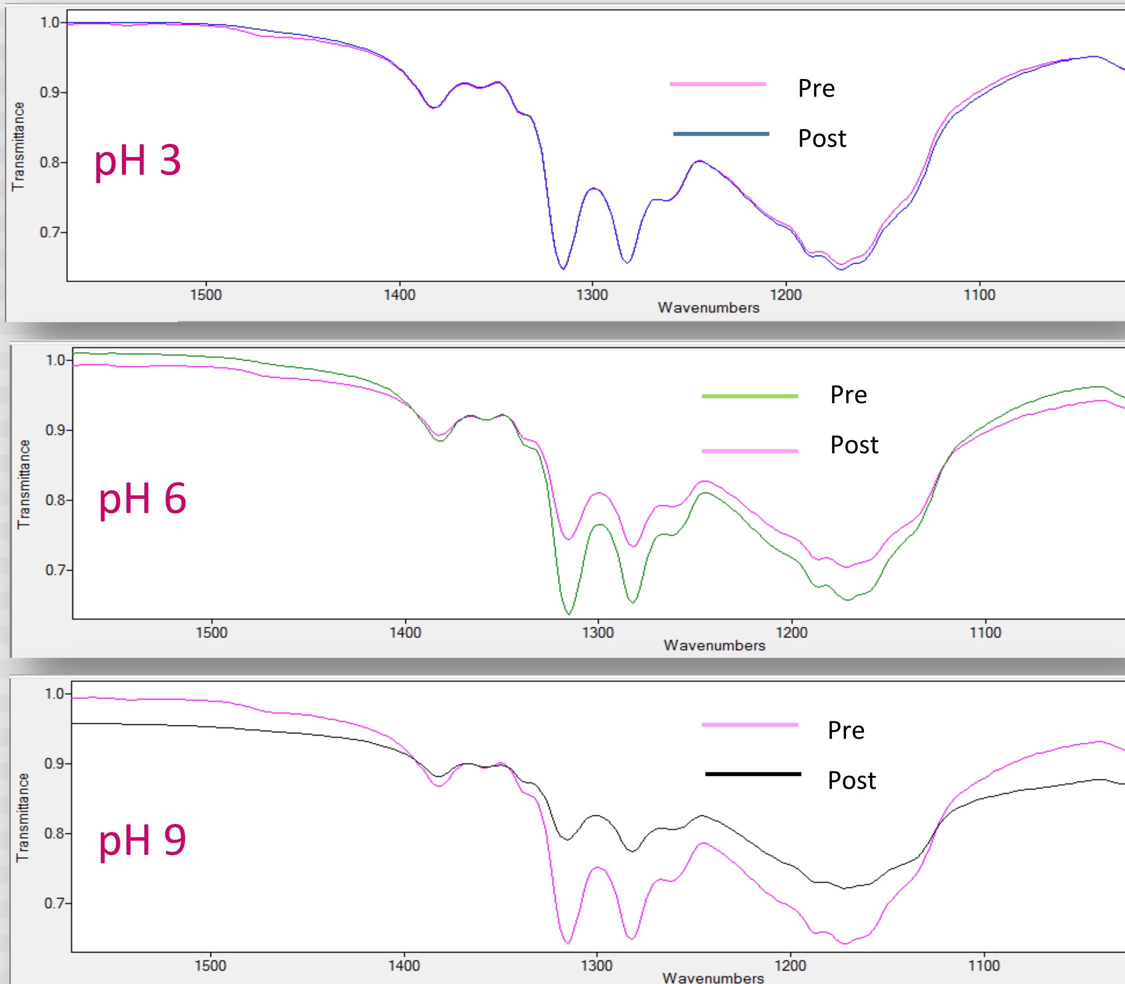
Surface nature characterization as a function of pH

CA, surface energy and Wa analyses pre and post CMP application



- CMP activates the surface at pH6 & pH 9 which can be attributed to the activated OH groups

Surface nature characterization as a function of pH

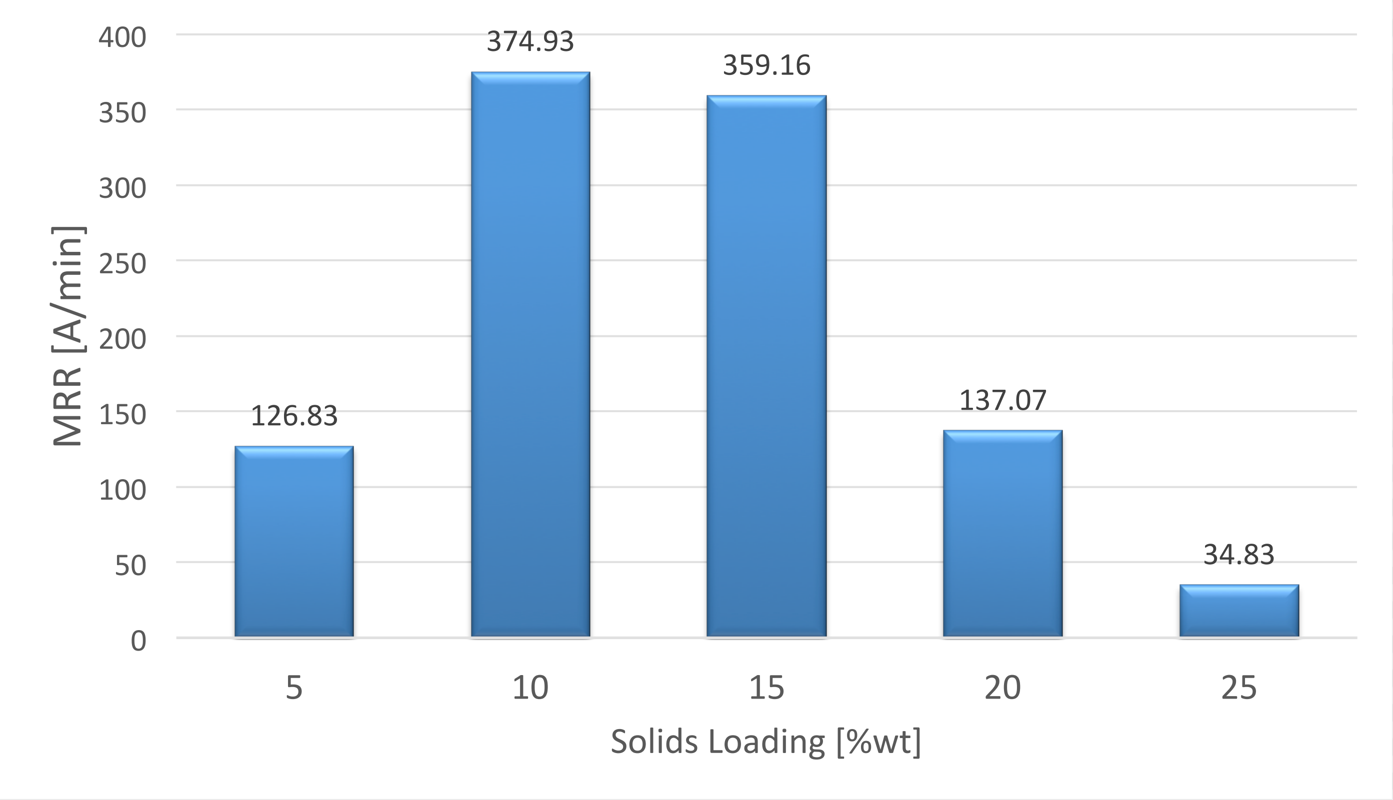


- GaN peaks at near 1100 cm^{-1} with shoulder at 1200 cm^{-1} due to Si-O bond stretching vibration are reduced post CMP at pH 6 & 9.

CMP Evaluation on GaN

Material Removal Rate Evaluation as a Function of Slurry Solids Loading

(Oxide Slurry, pH 9, Downforce 30N, Slurry Flow Rate 20 ml/min)

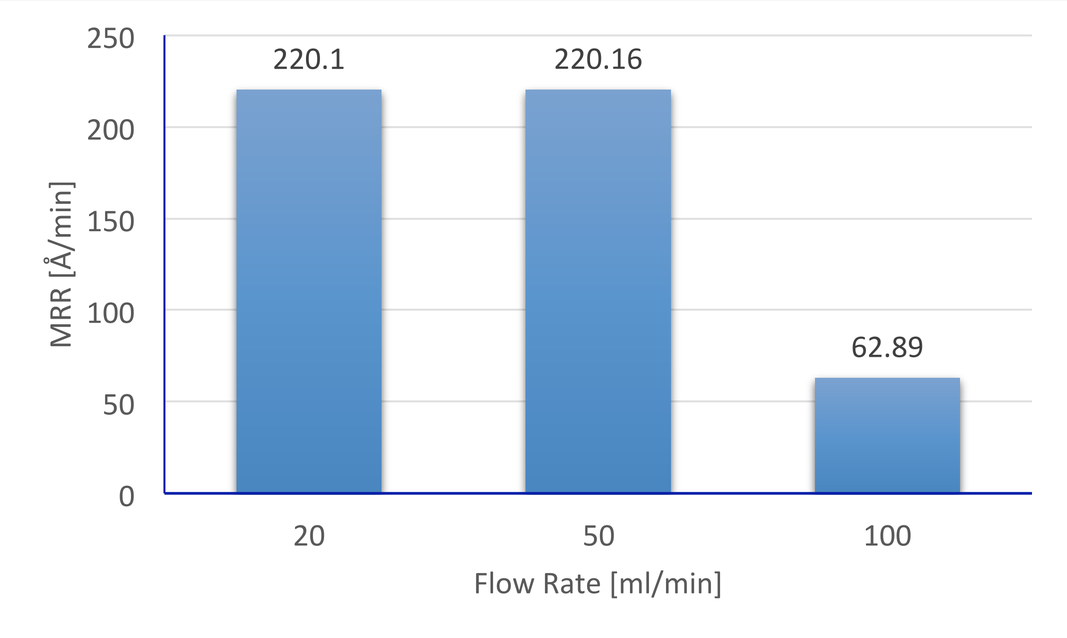


- Material removal rate is maximum at 10 wt% solids loading.

CMP Evaluation on GaN

Material Removal Rate Evaluation as a Function of Slurry Flow Rate

(Oxide Slurry, pH 9, Downforce 30N, Slurry Solids Loading 10%wt)

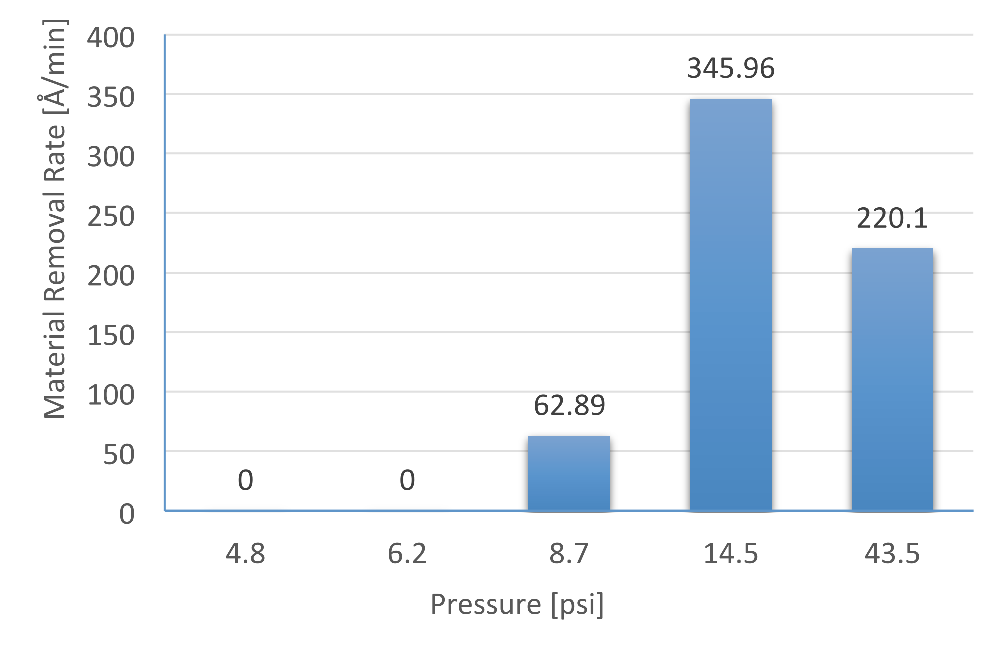


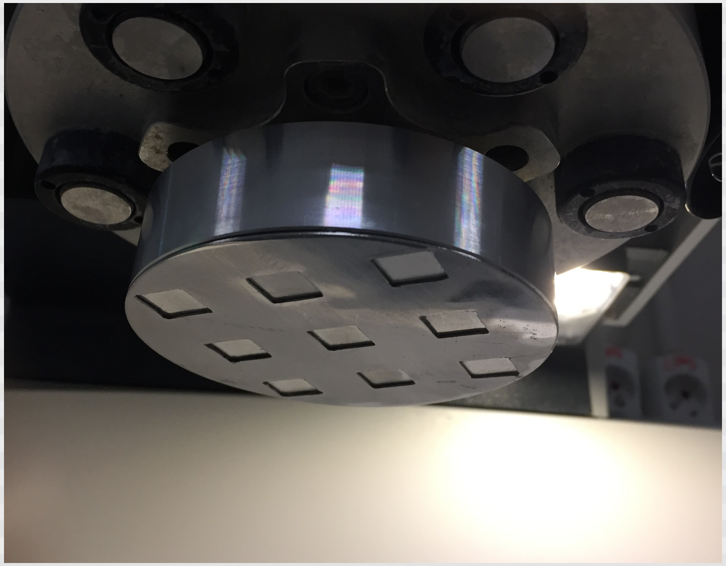
- Material removal rate increases with increasing slurry flow rate stabilizing after 20-25 ml/min.
- 20ml/min is set as the optimal slurry flow rate.

CMP Evaluation on GaN

Material Removal Rate Evaluation as a Function of Downforce

(Oxide Slurry, pH 9, Slurry Flow Rate 20 ml/min, Slurry Solids Loading 10%wt)





Holder design for downforce studies

- Material removal rate increases with increasing downforce until the slurry flow rate is blocked at very high pressures.
- 14.5 psi is set as the optimal pressure.

Summary

- GaN has very limited material removal rate (MRR) in CMP.
- Type of surface crystalline structure affects the MRR responses.
- Contact angle measurements were shown to correlate to the removal rate responses as a function of the surface crystalline structure.
- In order to increase the MRR while minimizing surface defect formation slurry pH, operations chemistry and temperature were evaluated.
- The MRR increased with increasing pH, decreasing slurry temperature and using soft polishing pads or inducing long pad break-in with harder pads delineating the chemical nature of the GaN polishing process.
- MRR values of ~880 Å/min (5280nm/hr) were achieved as compared to 17nm/hr reported in the literature.
- A new process chemistry adjustment and tool design was proposed for the GaN CMP.

Questions / Comments?

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