

Supporting Information

In-situ chemical functionalization of gallium nitride with phosphonic acid derivatives during etching

*Stewart J. Wilkins,[†] Michelle Greenough,[□] Consuelo Arellano,[§] Tania Paskova,^{†,‡} Alben
Ivanisevic^{†,§§,*}*

[†]Department of Materials Science and Engineering, North Carolina State University, Raleigh,
North Carolina, 27606, USA

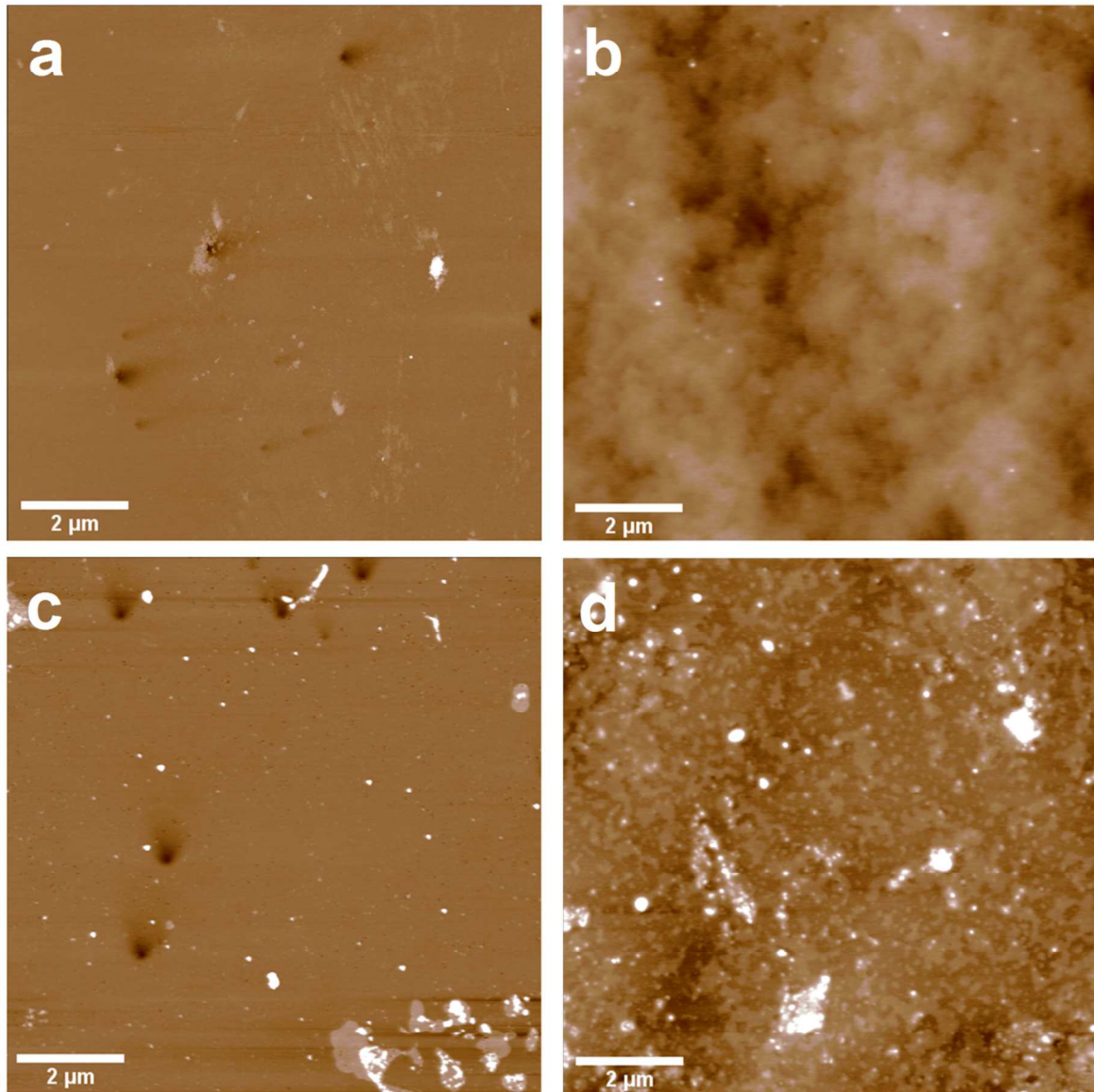
[□]Department of Chemistry, Wagner College, Staten Island, New York, 10301, USA

[§]Department of Statistics, North Carolina State University, Raleigh, North Carolina 27695, USA

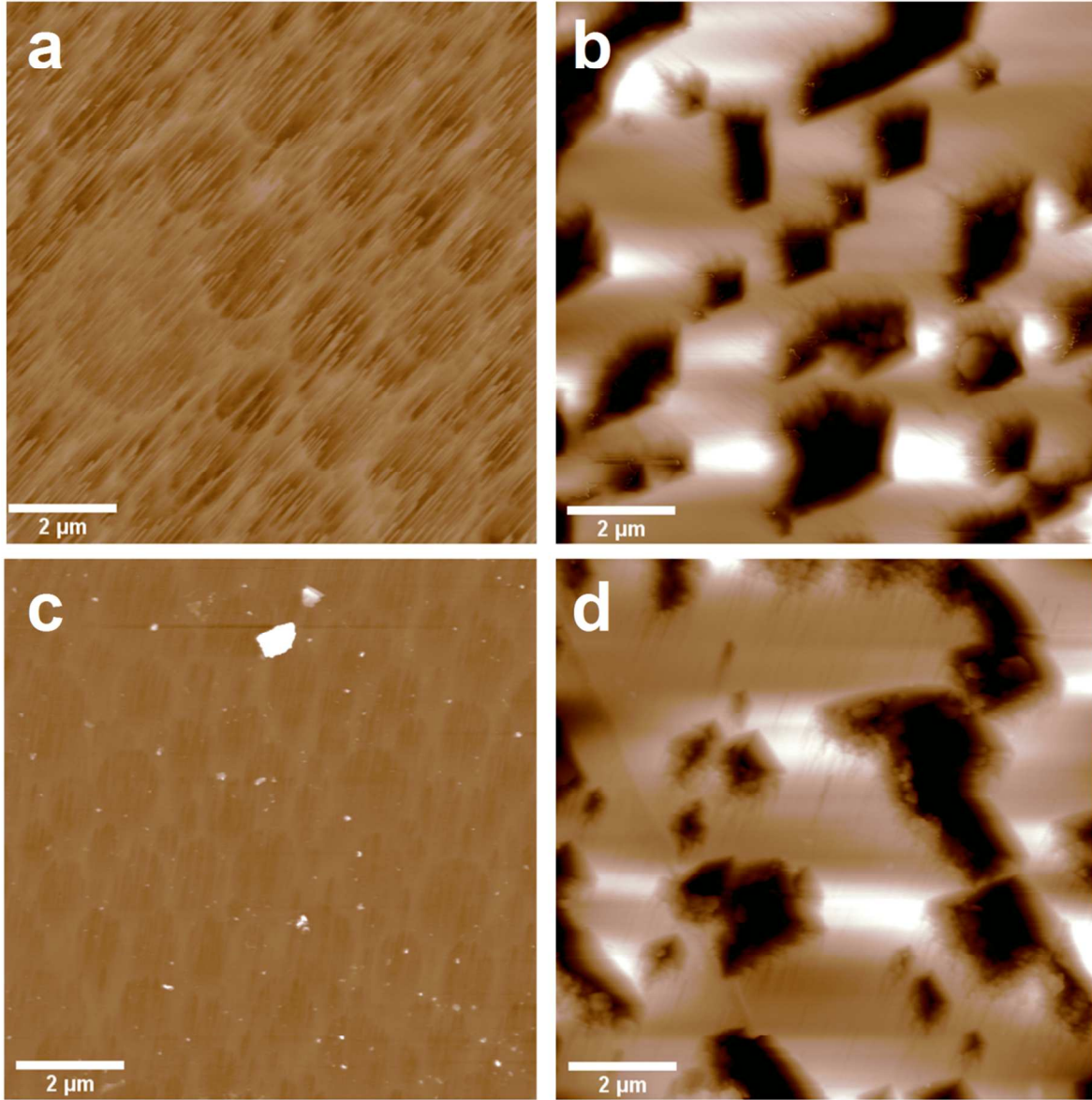
[‡]Department of Electrical and Computer Engineering, North Carolina State University, Raleigh,
North Carolina, 27606, USA

^{§§}NCSU /UNC-CH Joint Department of Biomedical Engineering, North Carolina State
University, Raleigh, North Carolina, 27606, US

AFM



AFM images of polar c-plane free-standing bulk (a, c) and thin heteroepitaxial c-plane layer GaN residing on a c-plane sapphire substrate (b, d) prior to etching (a, b) and after etching with 40°C propyl phosphonic acid and phosphoric acid (c, d). The height scales are 13 nm (a), 16 nm (b), 15 nm (c), and 31 nm (d) with 2 μm scale bars.



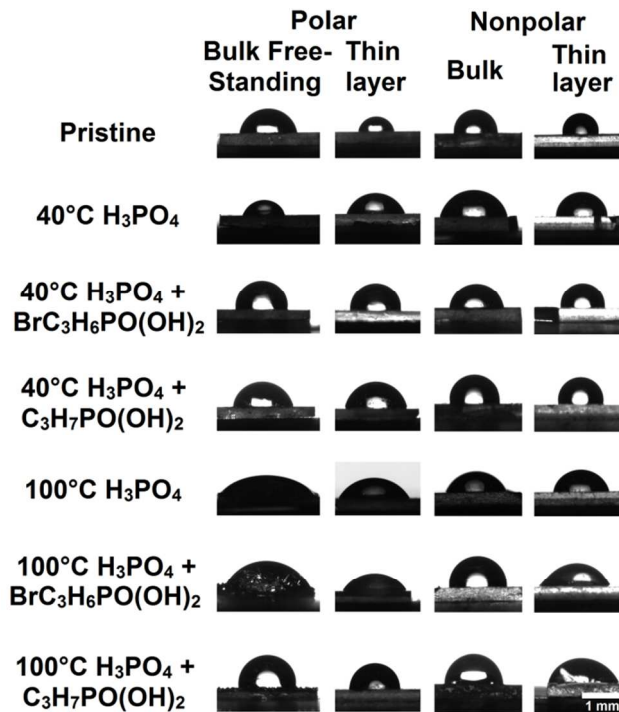
AFM images of nonpolar a-plane bulk GaN sample (a, c) and thin heteroepitaxial a-plane layer GaN residing on r-plane sapphire substrate (b, d) before etching (a, b) and after etching with 40°C (3-bromopropyl) phosphonic acid and phosphoric acid (c, d). The height scales are 26 nm (a), 380 nm (b), 77 nm (c), and 420 nm (d) with 2 μm scale bars.

Nonpolar

Polar

Treatment	Thin Layer	Bulk	Free-standing Bulk	Thin Layer
Pristine	93.0 ± 12.0 nm	3.0 ± 1.2 nm	3.4 ± 1.2 nm	4.9 ± 4.7 nm
40°C H ₃ PO ₄	103.3 ± 82.3 nm	2.7 ± 0.1 nm	9.1 ± 6.5 nm	2.2 ± 0.5 nm
40°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	117.4 ± 15.1 nm	4.8 ± 2.7 nm	8.1 ± 8.3 nm	16.6 ± 12.2 nm
40°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	11.8 ± 12.4 nm	31.9 ± 27.1 nm	1.5 ± 0.5 nm	5.1 ± 1.6 nm
100°C H ₃ PO ₄	18.6 ± 6.2 nm	23.2 ± 10.9 nm	13.3 ± 6.9 nm	90.0 ± 25.0 nm
100°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	63.0 ± 10.9 nm	16.0 ± 10.2 nm	238.6 ± 114.4 nm	111.4 ± 83.6 nm
100°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	86.3 ± 30.2 nm	14.1 ± 1.0 nm	156.4 ± 213.8 nm	7.4 ± 10.1 nm

Water Contact Angle



Water droplet images from contact angle measurements on polar c-plane free-standing bulk GaN and heteroepitaxial thin layer GaN on c-plane sapphire as well as nonpolar a-plane

bulk GaN and thin heteroepitaxial a-plane layer GaN residing on r-plane sapphire at different stages of treatment. Scale bar is 1 mm.

Treatment	Nonpolar		Polar	
	Thin Layer	Bulk	Free-standing Bulk	Thin Layer
Pristine	$92.9^\circ \pm 3.0^\circ$	$90.0^\circ \pm 5.1^\circ$	$80.6^\circ \pm 4.6^\circ$	$72.1^\circ \pm 2.7^\circ$
40°C H ₃ PO ₄	$84.3^\circ \pm 6.1^\circ$	$78.2^\circ \pm 4.7^\circ$	$72.9^\circ \pm 6.1^\circ$	$67.9^\circ \pm 1.0^\circ$
40°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	$102.8^\circ \pm 7.8^\circ$	$84.7^\circ \pm 9.0^\circ$	$99.9^\circ \pm 2.4^\circ$	$99.1^\circ \pm 4.7^\circ$
40°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	$99.8^\circ \pm 4.3^\circ$	$103.1^\circ \pm 5.7^\circ$	$77.7^\circ \pm 3.8^\circ$	$81.4^\circ \pm 5.6^\circ$
100°C H ₃ PO ₄	$71.8^\circ \pm 4.0^\circ$	$67.8^\circ \pm 4.6^\circ$	$36.3^\circ \pm 9.1^\circ$	$52.7^\circ \pm 6.6^\circ$
100°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	$59.8^\circ \pm 8.0^\circ$	$92.9^\circ \pm 7.1^\circ$	$63.9^\circ \pm 20.1^\circ$	$52.7 \pm 6.0^\circ$
100°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	$75.6^\circ \pm 6.7^\circ$	$73.5^\circ \pm 6.6^\circ$	$97.2^\circ \pm 15.1^\circ$	$89.4^\circ \pm 5.3^\circ$

XPS

Bulk free-standing polar GaN	Br	C	Ga	N	O	P
Pristine	0.00%	40.79%	28.01%	14.10%	17.10%	0.00%
40°C H ₃ PO ₄	0.00%	36.90%	8.9%	5.10%	46.80%	2.40%
40°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.00%	58.36%	14.84%	6.72%	19.28%	0.80%
40°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.00%	65.06%	12.58%	4.02%	18.09%	0.25%
100°C H ₃ PO ₄	0.00%	10.40%	4.60%	2.60%	66.10%	16.30%
100°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.00%	34.00%	15.53%	7.96%	31.10%	11.42%
100°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.00%	40.01%	18.25%	10.19%	24.67%	6.88%
Thin Layer Polar	Br	C	Ga	N	O	P

GaN						
Pristine	0.00%	41.83%	32.96%	9.75%	15.47%	0.00%
40°C H ₃ PO ₄	0.00%	60.10%	8.3%	4.00%	27.60%	0.00%
40°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.00%	70.74%	8.04%	2.12%	18.23%	0.87%
40°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.00%	68.84%	11.24%	2.72%	16.26%	0.94%
100°C H ₃ PO ₄	0.00%	61.40%	5.70%	3.40%	18.50%	1.10%
100°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.00%	26.96%	46.68%	8.54%	14.78%	3.03%
100°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.00%	67.36%	14.61%	3.52%	13.36%	1.16%

Bulk Nonpolar GaN	Br	C	Ga	N	O	P
Pristine	0.00%	63.72%	16.73%	4.80%	14.75%	0.00%
40°C H ₃ PO ₄	0.00%	44.70%	6.20%	4.30%	44.00%	0.80%
40°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.00%	73.28%	9.64%	2.32%	14.57%	0.18%
40°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.00%	78.09%	4.51%	1.08%	16.12%	0.19%
100°C H ₃ PO ₄	0.00%	48.20%	4.90%	3.00%	39.90%	3.90%
100°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.00%	72.42%	8.80%	2.56%	15.74%	0.49%
100°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.00%	51.00%	20.69%	6.62%	19.32%	2.36%

Thin Layer Nonpolar GaN	Br	C	Ga	N	O	P
Pristine	0.00%	77.45%	4.57%	1.21%	16.77%	0.00%
40°C H ₃ PO ₄	0.00%	49.70%	12.50%	7.90%	26.90%	3.10%
40°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.00%	80.38%	2.55%	0.49%	16.59%	0.00%
40°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.00%	80.49%	1.91%	0.56%	17.05%	0.00%
100°C H ₃ PO ₄	0.00%	65.10%	9.40%	4.80%	17.90%	2.80%
100°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.00%	68.93%	11.78%	3.63%	14.63%	1.04%
100°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.00%	74.35%	9.33%	2.73%	13.09%	0.51%

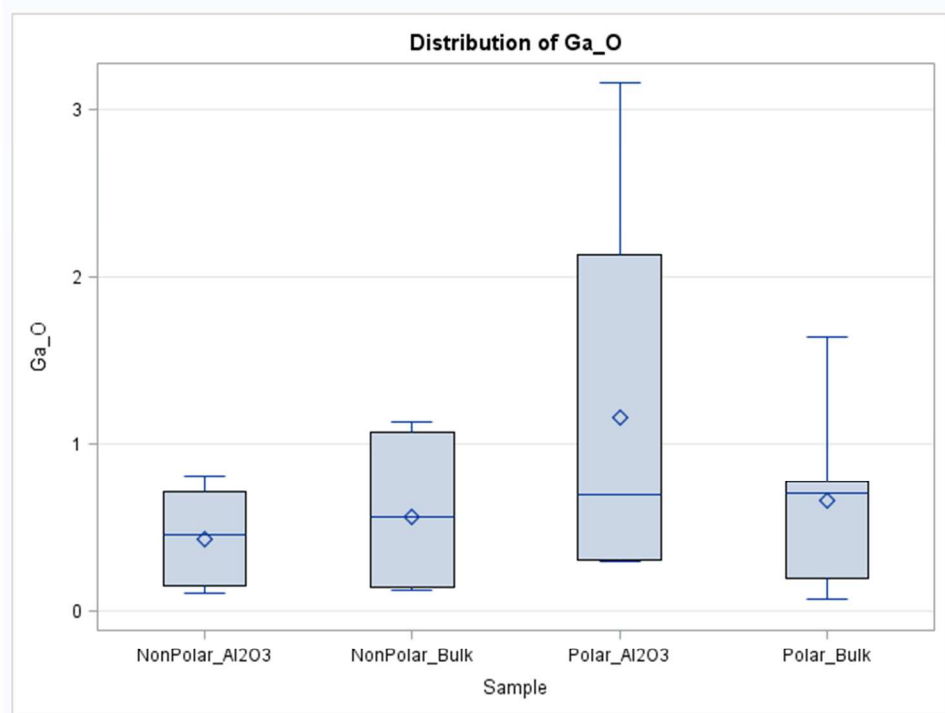
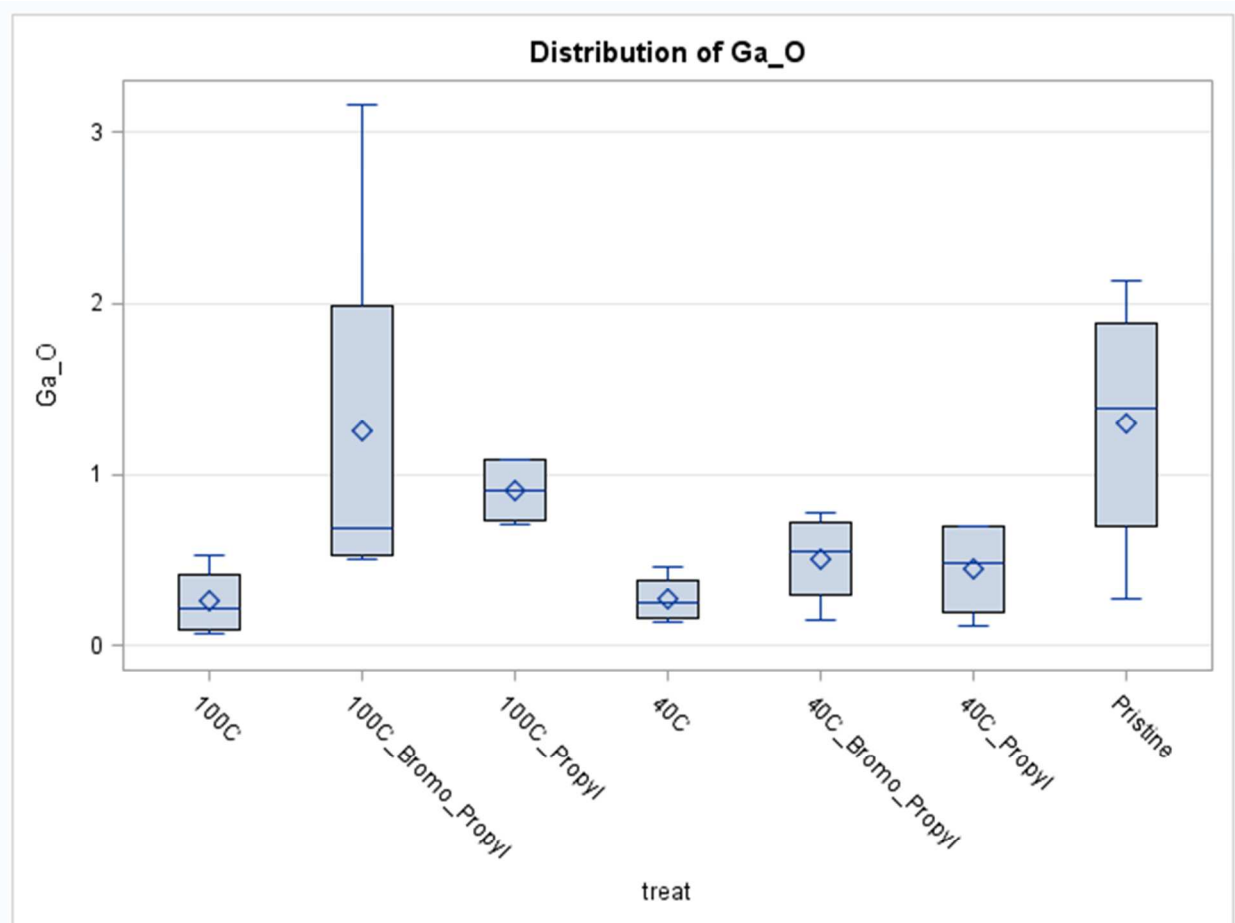
Polar			Nonpolar	
Free-standing Bulk	Thin Layer		Bulk	Thin Layer

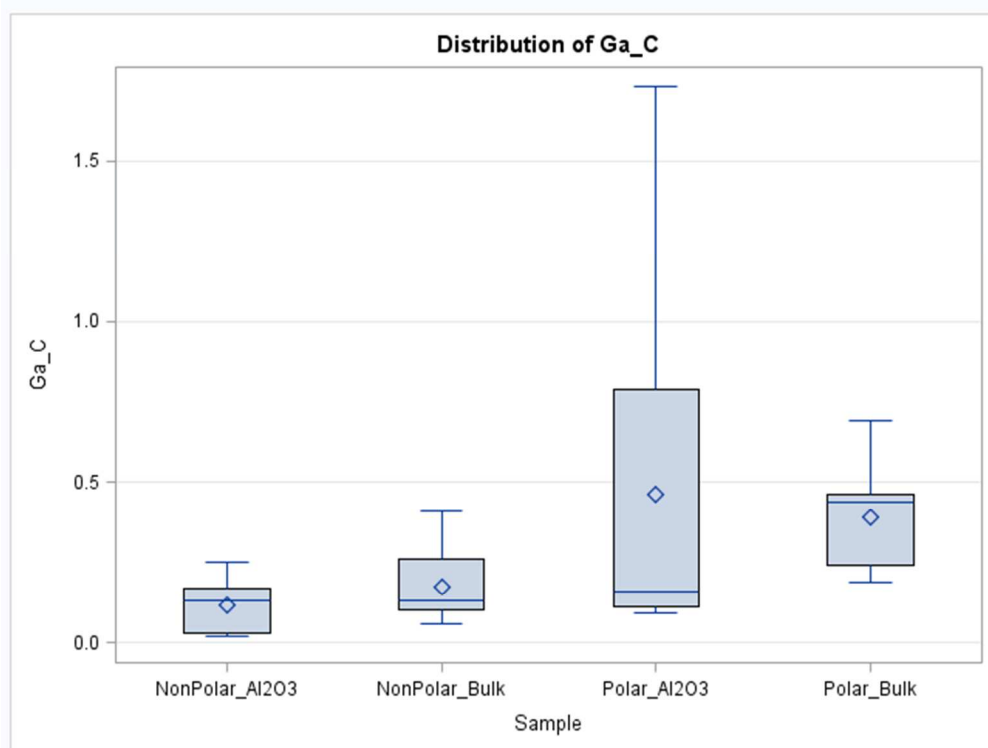
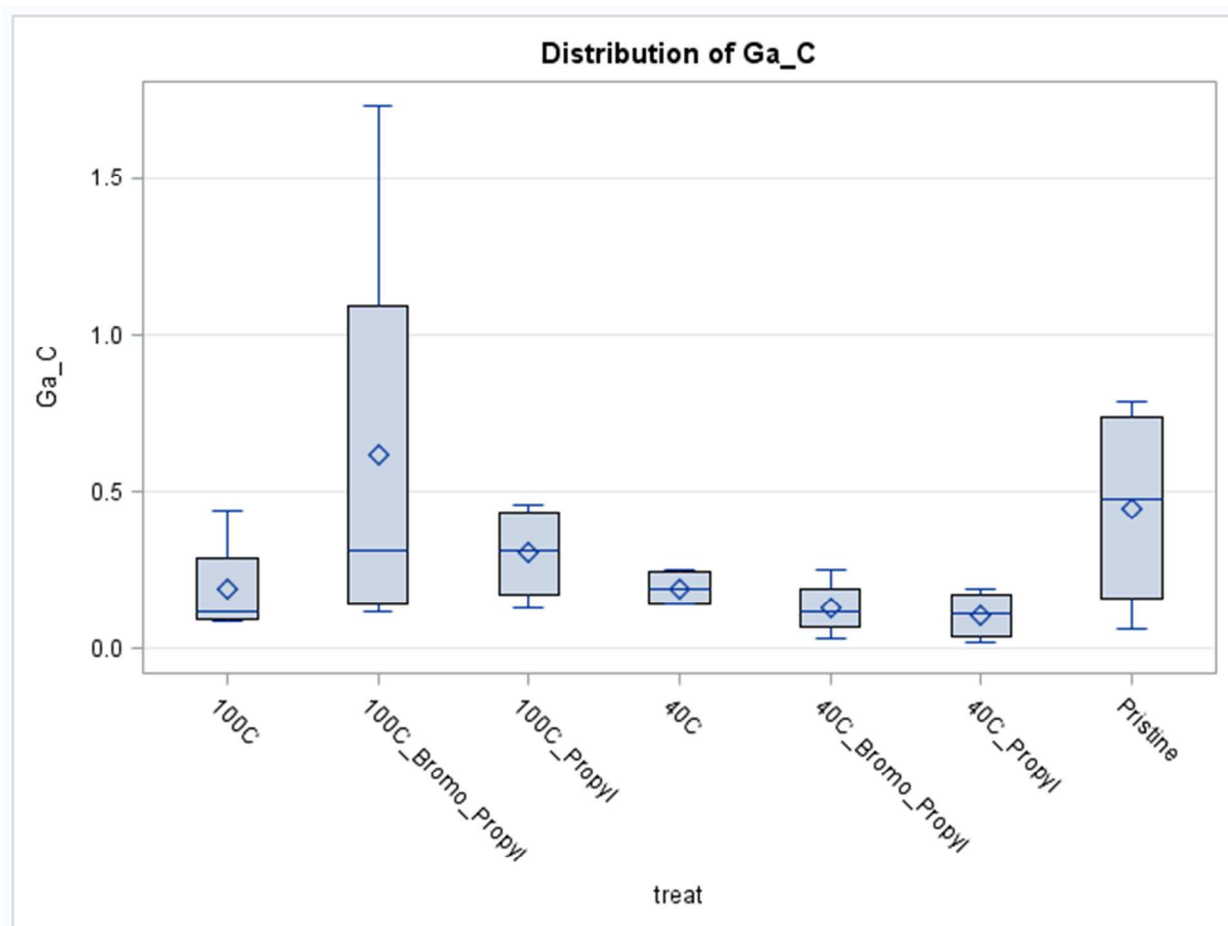
Pristine	8.9	14.0	19.8	-
40°C H ₃ PO ₄	0.3	19.0	1.1	4.4
40°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	8.4	14.1	18.4	-
40°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	8.7	11.0	18.4	-
100°C H ₃ PO ₄	0.5	12.8	1.1	7.1
100°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	11.2	14.1	29.0	14.4
100°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	5.4	5.0	19.9	15.1

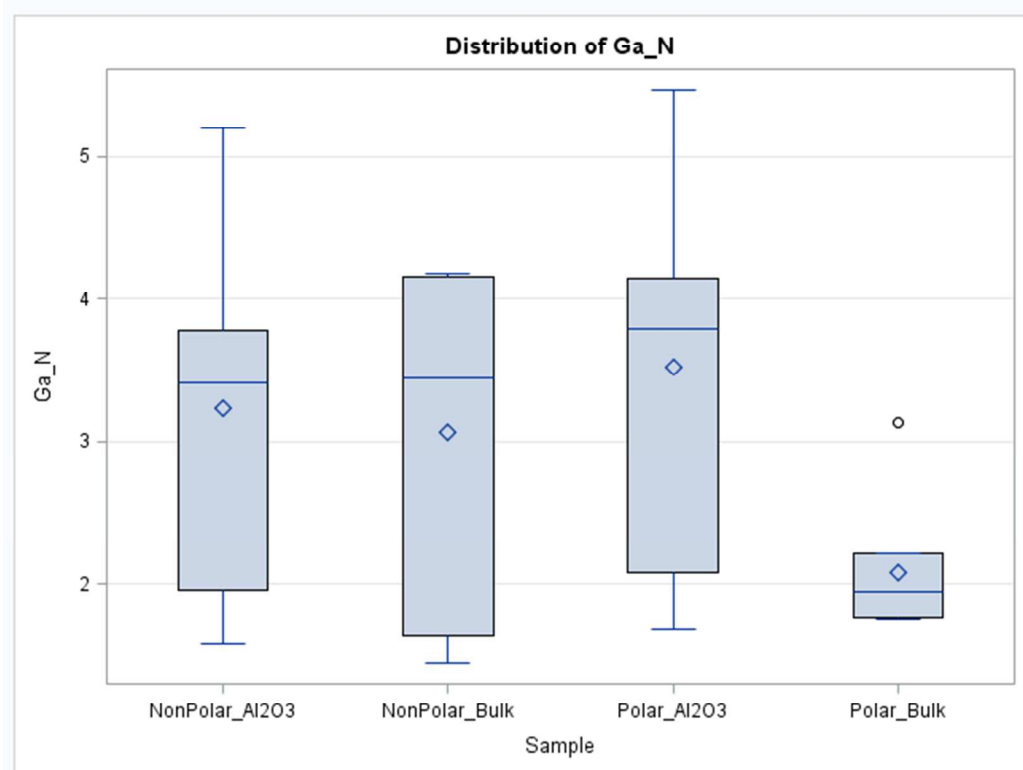
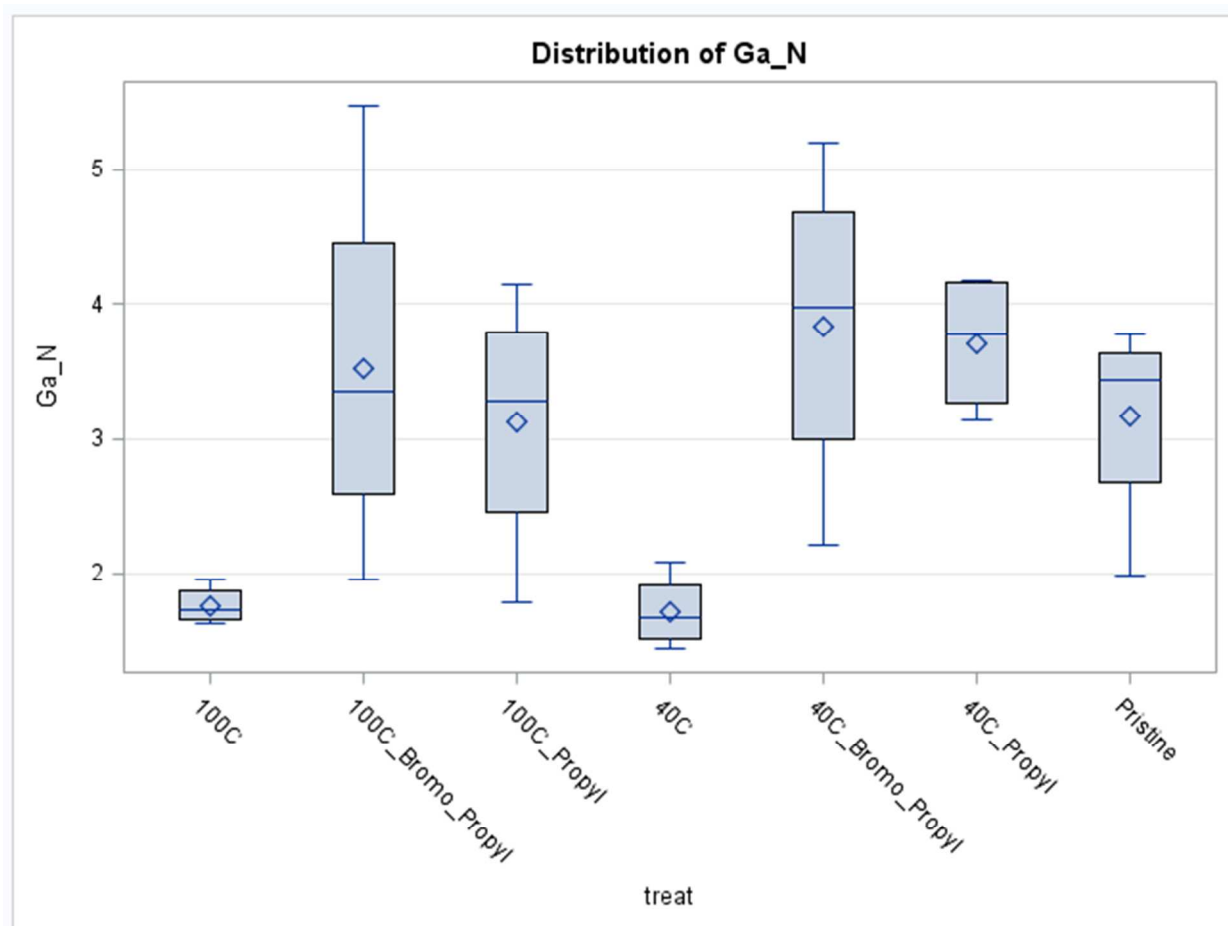
Ga/O	Nonpolar		Polar	
Treatment	Thin Layer	Bulk	Free-standing Bulk	Thin Layer
Pristine	0.27	1.13	1.64	2.13
40°C H ₃ PO ₄	0.46	0.14	0.19	0.30
40°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.15	0.66	0.77	0.44
40°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.11	0.28	0.70	0.69
100°C H ₃ PO ₄	0.53	0.12	0.07	0.31
100°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	0.81	0.56	0.50	3.16
100°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	0.71	1.07	0.74	1.09

Ga/C	Nonpolar		Polar	
Treatment	Thin Layer	Bulk	Free-standing Bulk	Thin Layer
Pristine	0.06	0.26	0.69	0.79
40°C H ₃ PO ₄	0.25	0.14	0.24	0.14
40°C H ₃ PO ₄ +	0.03	0.13	0.25	0.11

40°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	1.400	1.310	1.275	1.269
40°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	1.557	1.375	1.370	1.263
100°C H ₃ PO ₄	1.301	1.389	1.611	1.235
100°C H ₃ PO ₄ + BrC ₃ H ₆ PO(OH) ₂	1.351	1.312	1.439	1.265
100°C H ₃ PO ₄ + C ₃ H ₇ PO(OH) ₂	1.302	1.287	1.488	1.288
Max	1.557	1.389	1.611	1.288
Min	1.284	1.258	1.275	1.235
Difference	0.273	0.131	0.336	0.053

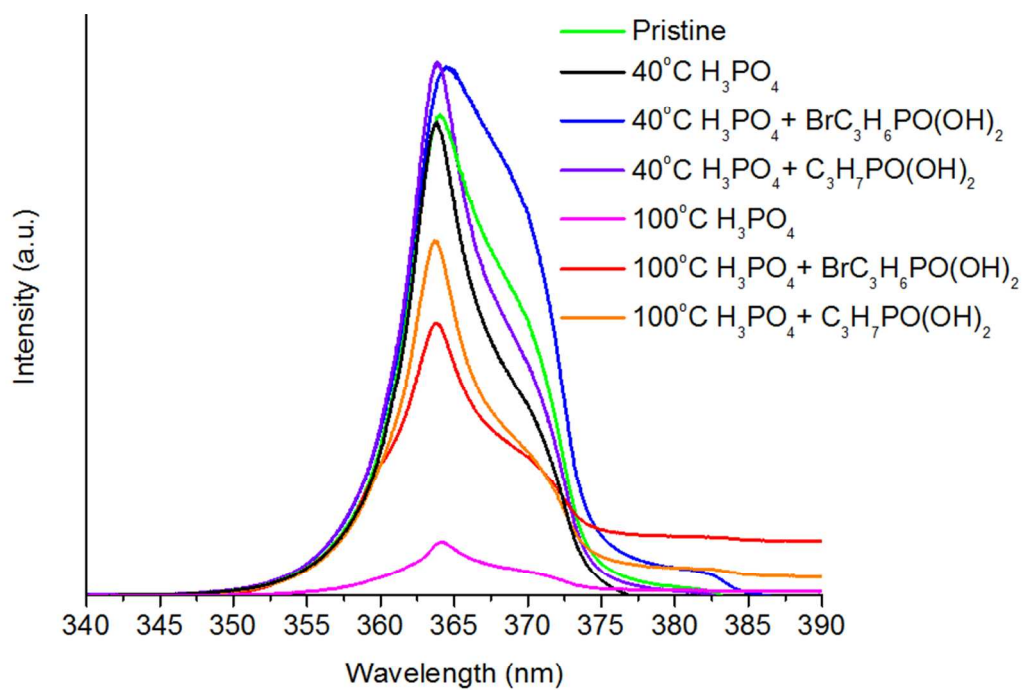




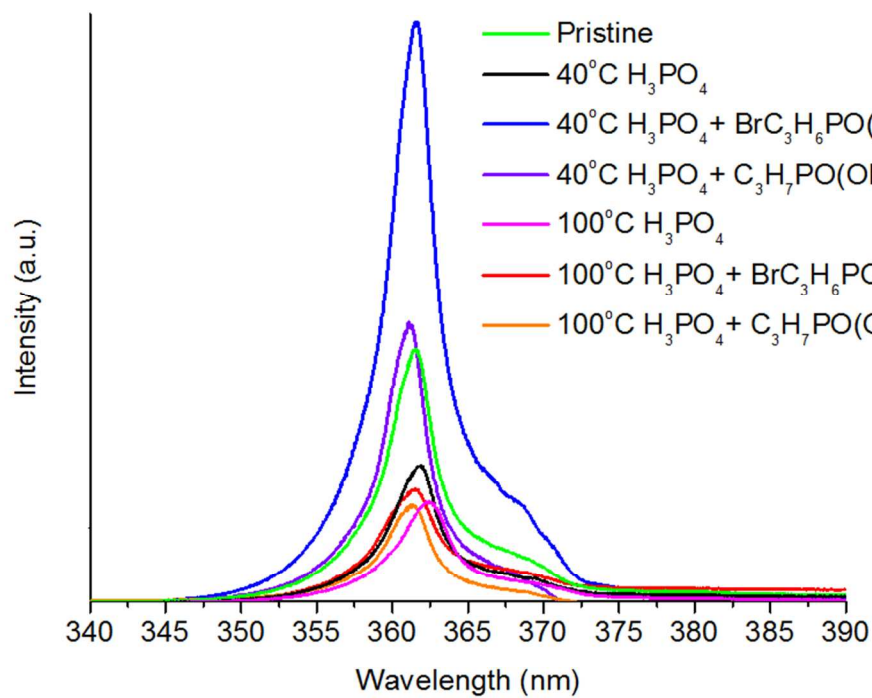


Photolumuminescence

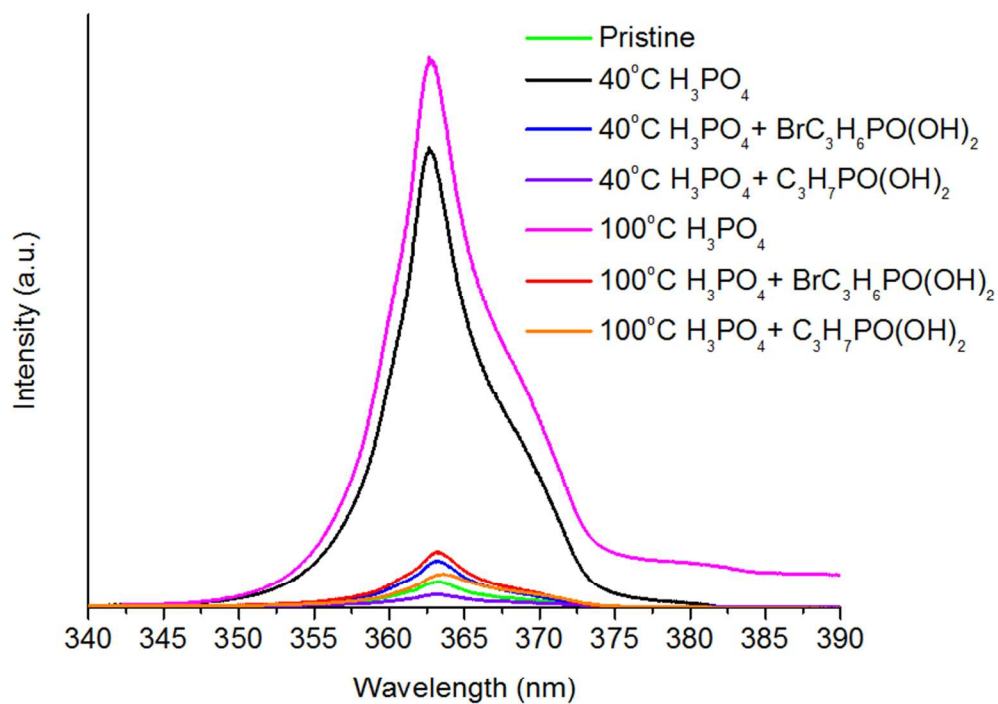
Polar Free Standing Bulk GaN



Polar Thin Layer GaN on Al₂O₃



Nonpolar Bulk GaN



Nonpolar Thin Layer GaN on Al_2O_3

