



# Modified surface chemistry, potential, and optical properties of polar gallium nitride via long chained phosphonic acids



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## ABSTRACT

Surface potential, chemistry, topography, and optical properties were modulated utilizing the attachment of phosphonic acids (11-mercaptopundecylphosphonic acid, 1H,1H,2H,2H-perfluorooctanephosphonic acid, and 1,8-octanediphosphonic acid) with phosphoric acid to polar (c-plane) GaN. These changes were identified using X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) with kelvin probe force microscopy (KPFM), photoluminescence (PL), and water contact angle. The results indicated that the attachment of phosphonic groups to gallium nitride strongly depends on the formation of a native oxide layer and subsequent passivation. It was seen that a fluorine terminated phosphonic acid increased the overall surface oxide versus other groups, as well as reduced the surface potential and improved the photoluminescence relative to other treatments. Sulfur terminated phosphonic acid demonstrated a similar reduction in surface potential and oxide formation to fluorine based phosphonic acid; however, improvements of optical luminescence on the same scale were not achieved.

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## 1. Introduction

Surface functionalization of gallium nitride (GaN), a III–V semiconductor, provides unique properties such as increased water hydrophobicity [1–3], extra binding sites [4], and modified optical properties [5]. GaN has gained significant attention due to its electrical and optical properties that are dependent on crystallographic orientations [6], but also improved chemical stability [7] and biocompatibility [8] over other semiconducting platforms such as GaAs [9] or GaP [10]. This has enabled new applications for GaN such as chemical and biological sensors [11]. To date, surface functionalization of GaN has been performed using carboxylic [2], thiol [1], and phosphonic groups [12]. In terms of surface stability, phosphonic acids produce the strongest surface bonding and improve performance with increased oxide coverage. Thiols and carboxylic groups require pristine surfaces for adhesion, which in turn requires the use of highly controlled environments. The exposure to aqueous environments replaces thiol groups with hydroxyl and oxide groups, thus limiting the effectiveness of thiol treatments on GaN [2,3]. Short and long chained alkanephosphonic acid

functionalization of GaN have been explored previously [2,3,12,13]; however, the use of phosphonic acids with terminal groups of high electronegativity has not been reported. The use of benzyl phosphonic acids and terminated alkanephosphonates has been shown for materials such as TiO<sub>2</sub> [14], indium tin oxide (ITO) [15–20], and ZnO [21–23]. Phosphonic acids provide not only a change in surface chemistry, but also in electrical characteristics such as improved charge injection for TiO<sub>2</sub> [14] and removal of midgap surface states through band bending for ZnO [22]. In the case of organic dye sensitized solar cells and organic light emitting diodes (OLEDs), matching the electrical structure across interfaces is crucial for improved device efficiency.

In situ functionalization of polar (c-plane) free-standing bulk GaN via phosphonic acids altered surface electrical and chemical signatures as well as produced quantifiable changes to optical properties. This was performed by altering the concentration of phosphoric acid and adding 11-mercaptopundecylphosphonic acid (MUDPA), 1H,1H,2H,2H-perfluorooctanephosphonic acid (PFOPA), and 1,8-octanediphosphonic acid (ODPA) to various treatments. Phosphoric acid is known to catalyze with regions of high energy within GaN, such as defects, with water to form gallium oxide and ammonia [24]. The formation of gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) alters the surface optical properties as the band gap shifts from 3.4 eV (GaN) to approximately 5.0 eV [25,26]. In addition to producing gallium oxide, aqueous solutions increase the amount of surface

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hydroxyl groups, with subsequent attachment of additives via condensation reactions. By attaching groups to the thin oxide layer, additional chemical attacks are lessened by stabilizing this oxide layer, which additionally provides unique surface properties and additional secondary reaction platforms [13]. X-ray photoelectron spectroscopy (XPS) was utilized to identify changes to the surface chemistry, while atomic force microscopy (AFM) and kelvin probe force microscopy (KPFM) identified alterations to the surface topography and potential. Optical properties and water hydrophobicity were observed via photoluminescence (PL) and water contact angle.

## 2. Materials and methods

### 2.1. Sample preparation

Polar (0001) free-standing GaN with a dislocation density in the range of  $5 \times 10^5$  to  $1 \times 10^6$  cm<sup>-2</sup> was manufactured by hydride-vapor phase epitaxy (HVPE) [27]. The sample was approximately 1.2 mm thick prior to being separated from a sapphire substrate and chemical-mechanically polished on the gallium terminated side. 3 mm × 2 mm rectangles were formed from dicing and were pre-treated with solvent baths of acetone and methanol before being washed with deionized (DI) water (18.2 MΩ cm). Nitrogen was used to dry the samples before being placed in a 100 °C 50/50 vol.% hydrochloric acid (Fisher Scientific 35–38% vol.)/water solution for 10 min. The samples were rinsed with DI water for 2 s, immediately dried with nitrogen and were held in a desiccator under vacuum for storage.

### 2.2. Sample treatment

A total of five samples were treated with various solutions of phosphoric acid (Fisher Scientific, 95%) and phosphonic acid additives: (i) 95% phosphoric acid; (ii) 50/50 vol.% water/phosphoric acid; (iii) 50/50 vol.% 3 mM 11-mercaptoundecylphosphonic acid (Sigma–Aldrich, 97%)/phosphoric acid; (iv) 50/50 vol.% 3 mM 1H,1H,2H,2H-perfluorooctanephosphonic acid (Sigma–Aldrich, 95%)/phosphoric acid; and (v) 50/50 vol.% 3 mM 1,8-octanediphosphonic acid (Sigma–Aldrich, 97%)/phosphoric acid. All the samples were treated for 150 min at 40 °C, rinsed with DI water for 2 s, dried with nitrogen, and characterized.

### 2.3. Characterization

The samples were examined with a Kratos Axis Ultra XPS within 2 h from treatment to safeguard purity. The surface chemistry was analyzed with a monochromated Al Kα ( $h\nu = 1486.7$  eV) source with charge neutralizer (2.0 A filament current). Copper tape was used to mount samples to an aluminum sample holder. Three random spots were taken on each specimen at 0°, 45°, and 60° photoemission angles per spot. Five sweeps of 20 eV pass energies were averaged to produce high resolution region scans of C1s, Ga2p, Ga3d, N1s, P2p, S2p, F1s, and O1s. Survey scans were formed with 160 eV pass energies and were only scanned once. All scans were recorded at pressures at or below  $3 \times 10^{-8}$  Torr. Casa XPS (Ver. 2.3.16 PR) software was used for peak deconvolution following charge correction using C1s (284.8 eV) [28]. The XPS is calibrated to Ag (368.21 eV) according to ISO TC/201 [29]. The full-width at half-maximum (FWHM) of deconvoluted peaks was limited to the primary peak according to a Lorentzian fit after removing the background with a Shirley approximation. Kratos provided atomic sensitivity factors were utilized for surface quantification. Ga3d region was used to calculate atomic percentages rather than Ga2p due to its greater depth profiling [30]. Ga Auger peaks from the N1s spectra were not

included in the surface quantification. The Ga2p region scans were normalized for presentation.

Room temperature photoluminescence was recorded with a Horiba Jobin Yvon LabRam ARAMIS Raman/PL setup utilizing a 325 nm HeCd laser excitation source. The microscope was aligned to Teflon (middle Raman peak of 1295 cm<sup>-1</sup>) with a 40× UV objective at a 2400 grating/min resolution. The objective height was locked following a calibration to capture spectra from 330 to 400 nm across all samples. The real-time display (RTD) exposure time, accumulated exposure time, and number of accumulations were 1 s, 1 s, and 5 s, respectively, with a 60% signal filter. Each sample was evaluated in five random locations to account for surface variances.

Surface roughness and potential were taken using an Asylum Research Ciper AFM following the PL measurements. Three random  $5 \mu\text{m} \times 5 \mu\text{m}$  locations were imaged on each sample using a 1 Hz scan rate under the Surface Kelvin Probe Microscopy (SKPM) setup within the Igor Pro (Ver. 10.0) software. This utilizes a tapping mode protocol that produces both topographic and surface potential images simultaneously. No stage bias was used in this setup. Asylum Research AC240TM tips were used for all samples, with Asylum Research ASYELEC-01 tips used for data verification. All images were flattened within Igor Pro and averaged to calculate root mean square (RMS) roughness and surface potential values. Statistical significance for both PL and AFM/KPFM was performed utilizing a *t*-test within SAS (Ver. 9.4 TS) software.

Water contact angle was studied with a Ramé-hart Model 200-F4 goniometer equipped with a 28 ga. (AWG) needle using DI water. Water droplets were formed by placing one drop on the surface and slowly retracting the needle. Once retracted, water drops were captured at 2 frames per second for 5 s. The half-angle was averaged to produce an average contact angle for each test, which was performed four more times to produce a total sample average. Following each drop, nitrogen was blasted on the surface to ensure a dry surface. The water contact angles were captured with DROPImage (Ver. 2.4.07) software. Optical microscopy images were captured with a Zeiss Axiovert 40 MAT microscopy with a Zeiss Epiplan 10× objective lens.

## 3. Results and discussion

Material interfaces play a crucial role in the electrical properties of organic based devices. For example, in the case of dye sensitized solar cells, the ability to match the work function of the electrode and sensitizer enables improved efficiency as the mid gap band bending between materials is decreased. This provides a greater customizability for materials selection for organic electronics. Alkanephosphonic acids have demonstrated the ability to alter physical properties such as surface roughness and water hydrophobicity, but only by adding additional side/terminal groups do the phosphonates provide beneficial electrical properties. Among the available phosphonic acids, MUDPA, PFOPA, and ODPa (Fig. 1) were selected due to their unique terminal groups that promote unexplored packing and properties on GaN.

### 3.1. Surface homogeneity

Different scanning probe modes were utilized to assess the changes on the GaN interface after in situ-functionalization with the three different phosphonic acid molecules. The surface topography images (Fig. A.1) of GaN display a wavy structure that has been previously observed on other thick c-plane GaN substrates [31]. Though the surface does not display the traditional pit formation [32] associated with polar GaN or hillock structure seen on HVPE grown substrates [33], crack and finger-like formations can

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