Modification of the Surface Properties of Al$_x$Ga$_{1-x}$N Substrates with Gradient Aluminum Composition Using Wet Chemical Treatments

Sara Gleco,‡ Oleksandr Romanyuk,†,‡ Ivan Gordeev,‡ Karla Kuldová,‡ Tania Paskova,‡,§ and Albena Ivanisevic*,†,‡

†Department of Materials Science and Engineering and §Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States
‡Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, Prague 6 162 00, Czech Republic

Supporting Information

ABSTRACT: The surface properties of biomolecular gradients are widely known to be important for controlling cell dynamics, but there is a lack of platforms for studying them in vitro using inorganic materials. The changes in various surface properties of an Al$_x$Ga$_{1-x}$N film (0.173 ≤ x ≤ 0.220) with gradient aluminum content were quantified to demonstrate the ability to modify interfacial characteristics. Four wet chemical treatments were used to modify the surface of the film: (i) oxide passivation by hydrogen peroxide, (ii) two-step functionalization with a carboxylic acid following hydrogen peroxide pretreatment, (iii) phosphoric acid etch, and (iv) in situ functionalization with a phosphonic acid in phosphoric acid. The characterization confirmed changes in the topography, nanostructures, and hydrophobicity after chemical treatment. Additionally, X-ray photoelectron spectroscopy was used to confirm that the chemical composition of the surface, in particular, Ga$_2$O$_3$ and Al$_2$O$_3$ content, was dependent on both the chemical treatment and the Al content of the gradient. Spectroscopic evaluation showed red shifts in strain-sensitive Raman peaks as the Al content gradually increased, but the same peaks blue-shifted after chemical treatment. Kelvin probe force microscopy measurements demonstrated that one can modify the surface charge using the chemical treatments. There were no predictable or controllable surface charge trends because of the spontaneous oxide-based nanostructured formations of the bulk material that varied based on treatment and were defect-dependent. The reported methodology and characterization can be utilized in future interfacial studies that rely on water-based wet chemical functionalization of inorganic materials.

1. INTRODUCTION

Surface gradients often utilized in interface studies are designed and fabricated with specific characteristics in mind such as chemistry, shape, topography, density, curvatures, and stiffness. The inspiration behind surface gradients is derived from nature where a number of processes are facilitated by gradients. For example, cell dynamics such as growth, differentiation, and migration are mediated by signaling pathways generated by chemical gradients. The prevalence of chemical gradients in biological systems has been widely studied but often details regarding specific chemical concentrations and gradient slopes are unclear because of a lack of platforms for in vitro studies. A quantitative understanding of chemical gradients is important to develop biomedical applications that require control over cell dynamics, such as tissue regeneration and axon guidance.

Efforts have been made to mimic gradients by immobilizing biomolecules on different surfaces. Hydrogels and nanofibers are commonly used materials for in vitro biomolecular gradient studies. In comparison to organic materials, relatively fewer reports are available on immobilizing biomolecular gradients on inorganic substrates. III-nitride semiconductors provide a versatile platform for studying biological gradients because they are biocompatible and have tunable surface properties for controlling the immobilization of biomolecules. Organic interfaces can be formed on inorganic surfaces using chemical surface treatments that modify the nanostructure and surface chemistry of inorganic materials such as III-nitrides. The surface properties of III-nitrides, such as hydrophobicity, topography, and surface charge, can be modulated through these modifications. Additionally, compositional monotonic gradients that can be introduced during III-nitride growth allow for gradient surface modification by in situ selective chemical etching without the need for complex approaches such as photolithography, microfluidics, or bioprinting.

In this study, Al$_x$Ga$_{1-x}$N (0.173 ≤ x ≤ 0.220) films were modified using four different wet beaker chemistries to alter
surface properties. The modified surfaces were characterized using a variety of techniques to measure altered surface properties along the Al/Ga composition gradient after chemical treatment. The topography, roughness, and surface charge were evaluated via tapping mode atomic force microscopy (AFM), scanning electron microscopy (SEM), and Kelvin probe force microscopy (KPFM), respectively. Additionally, X-ray photoelectron spectroscopy (XPS) was utilized to measure the changes in the chemical composition of the surface caused upon chemical treatment along the Al gradient. Raman spectroscopy was employed to detect changes in the chemical composition of the film on the Al content of the wafer. This work demonstrates that simple wet chemical treatments can be used to modify the surface properties of an Al\textsubscript{x}Ga\textsubscript{1-x}N film and that a compositional Al/Ga gradient can be used to form a surface chemistry gradient. The findings are expected to serve as guiding principles and design rules for engineering the surface properties of inorganic substrates for biological interfaces.

2. RESULTS AND DISCUSSION

2.1. Gradient Characterization and Surface Preparation. The Al content, \(x\), of Al\textsubscript{x}Ga\textsubscript{1-x}N films has a strong influence on the properties of the material. Many reports are available on the dependence of the electrical and optical properties of Al\textsubscript{x}Ga\textsubscript{1-x}N on the Al content of the film.\textsuperscript{21–24} The Al content is also known to affect the dislocation density of Al\textsubscript{x}Ga\textsubscript{1-x}N films grown heteroepitaxially on various substrates because of different levels of strain induced by lattice and thermal expansion coefficient mismatch.\textsuperscript{25–27} Surface defect type and density also vary for variable Al content, which affects the roughness, electron affinity, and morphology of the surface.\textsuperscript{18,25,28} We aimed to use these varying surface properties to selectively modify the surface of an Al\textsubscript{x}Ga\textsubscript{1-x}N gradient film with composition \(x\) varying between 0.173 and 0.220 by using wet etching and chemical functionalization approaches to form chemical gradients.

As illustrated in Figure 1a, the Al content of the film changed continuously, but we defined three regions, B–D (Figure 1b), for simplicity of comparison. The wafer was diced as shown in Figure 1 so that each region of the gradient was treated with all of the four treatment types, as indicated in Table 1. The Al content of the gradient Al\textsubscript{x}Ga\textsubscript{1-x}N wafer at the regions B–D was determined by using standard XRD measurements. The details are provided in the Supporting Information, and it was summarized that the value of \(x\) was 0.173 in region B, 0.204 in region C, and 0.220 in region D.

As shown in Table 1, we compared four different treatments and a clean sample for each region of the gradient. The chemical treatments we used in this investigation were aqueous and low-temperature benchtop techniques, so they can be done safely and for low cost in a typical chemistry laboratory. Before the treatments, each piece of the diced wafer was etched with HCl to remove the native oxide from the surface.\textsuperscript{16} One set of samples did not receive any further treatment and are referred to as clean set of samples. A second and third set of samples were treated with H\textsubscript{2}O\textsubscript{2} after HCl etching to passivate the surface with oxidoxydride.\textsuperscript{29,30} It has been reported that the amount of oxygen on the surface of Al\textsubscript{x}Ga\textsubscript{1-x}N films increases with increasing mole fraction of Al.\textsuperscript{18} By passivating the surface with oxidoxydride, we aimed to control oxide formation on the sample surface of the second set. After H\textsubscript{2}O\textsubscript{2} passivation, the third set of the samples was capped with a hydrocarbon using 4-chlorobutyric acid (C\textsubscript{4}H\textsubscript{7}ClO\textsubscript{2}) to inhibit oxide formation after chemical treatment. It is well documented in the literature that the etch rate of H\textsubscript{3}PO\textsubscript{4} at surface pits resulting from dislocations in III-nitrides is faster than defect-free areas by the removal of Ga atoms at the surface through oxidoxydride.\textsuperscript{17,25,31,32} Preferential etching by H\textsubscript{3}PO\textsubscript{4} forms etch pits with hexagonal morphology where dislocations are located at the surface of polar GaN films.\textsuperscript{17,33,34} We used H\textsubscript{3}PO\textsubscript{4} to modify the sample nanostructure and chemistry of the Al\textsubscript{x}Ga\textsubscript{1-x}N film in the fourth set of samples to cause a change in surface properties. We added (3-bromopropyl)phosphonic acid (C\textsubscript{3}H\textsubscript{7}BrO\textsubscript{3}P) to H\textsubscript{3}PO\textsubscript{4} for the treatment of the fifth set of samples to functionalize the surface with a phosphonic acid to prevent oxide formation, which we have previously reported on GaN.\textsuperscript{35}

2.2. Surface Characterization. Surface pits with a mean diameter of 0.5 ± 0.2 \(\mu\)m related to dislocations were observed on the surface of the clean sample. There were oxide nanopillar

![Figure 1. Diagram showing (a) diced Al\textsubscript{x}Ga\textsubscript{1-x}N wafer where rows 1–5 received different chemical treatments and columns B–D had different Al contents and (b) value of \(x\) at regions B–D of the wafer.](image)

Table 1. Treatments That Rows 1–5 of the Al\textsubscript{x}Ga\textsubscript{1-x}N Wafer Illustrated in Figure 1 Received

| row | treatment |
|-----|-----------|
| 1   | H\textsubscript{2}O\textsubscript{2} |
| 2   | H\textsubscript{2}O\textsubscript{2}/4-chlorobutyric acid (C\textsubscript{4}H\textsubscript{7}ClO\textsubscript{2}) |
| 3   | H\textsubscript{3}PO\textsubscript{4} |
| 4   | H\textsubscript{3}PO\textsubscript{4}/(3-bromopropyl)phosphonic acid (C\textsubscript{3}H\textsubscript{7}BrO\textsubscript{3}P) |
| 5   | clean |
clusters, shown in Figure 2a, across the clean surface and the H$_2$O$_2$- and H$_2$O$_2$/C$_4$H$_7$ClO$_2$-treated surfaces. The shape of the pillars varied from rectangular to hexagonal. Because the pillar clusters were observed on the clean surface, it suggests that they were not formed during chemical treatment. The H$_2$O$_2$- and H$_2$O$_2$/C$_4$H$_7$ClO$_2$-treated surfaces had clusters of truncated rectangular nanostructures with striations along the length, as shown in Figure 2b,c, with the morphology of GaOOH particles. The lengths were distributed into two groups: 1.1 ± 0.2 and 0.4 ± 0.02 μm. These were also seen on the clean surface but with much lower frequency, indicating that H$_2$O$_2$ promotes the formation of these nanostructures. Hexagonal etch pits were observed after treating with H$_3$PO$_4$ and H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P (Figure 2d), with primarily two sizes. The larger etch pits had a mean width of 23.4 ± 1.0 μm, whereas the smaller etch pits had a 5.4 ± 0.2 μm mean width. Smaller pits were observed on the clean surface but were not seen on the H$_3$PO$_4$-etched surfaces because they were enlarged through etching. Another unique feature observed on the H$_3$PO$_4$- and H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P-treated surfaces was needle-like oxide nanostructures with a mean length of 4.1 ± 1.2 μm protruding from the surface, as shown in Figure 2e.

Figure 3 shows that there were no statistical differences or trends in the roughness with respect to the Al content (see the Supporting Information for summary of all statistical analysis). However, we observed that there were statistically significant differences in the roughness between C and D regions of the H$_3$PO$_4$-treated surfaces and various gradient regions of the other treatments. Although there was not a trend in the roughness results, the combined results of AFM and SEM characterization indicated that we were able to modify the topography of the surface through chemical treatments. The lack of a trend in the AFM data could be explained by the relatively small 2 μm × 2 μm scans obtained at arbitrary locations on each surface (representative AFM images can be found in the Supporting Information). The various nanostructures in Figure 2 that we observed via SEM should affect the roughness. However, they were formed at random locations on the surface and were similar in size to the scan size, so there was no guarantee that such a feature was included in the AFM scans. Because we observed statistical differences in the roughness and nanostructure formation, we conclude that the topography of Al$_{x}$Ga$_{1-x}$N can be modified through chemical treatment.

Figure 4 summarizes water contact angle measurements, which showed that the H$_3$PO$_4$- and H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P-treated surfaces were the most hydrophilic. The H$_2$O$_2$ and H$_2$O$_2$/C$_4$H$_7$ClO$_2$-treated surfaces did not affect contact angle compared to the clean surface. There was no observed trend in wetting with respect to the Al content variation. This could be explained by a relatively small increase in x from region B to region D, which may not be a large enough difference to greatly influence the etch behavior of the material.

2.3. Chemical Composition Changes. The atomic percentages of O, C, N, Al, Ga, and P were measured by XPS survey scans to detect changes in surface composition with respect to the treatments and Al content. This is summarized in Figure 5. There was no observed trend in the data from the survey scans corresponding to the Al gradient. The XRD measurements showed that there was an increase in the Al content of the film from region B to region D of the film. However, we did not observe a difference in the Al/Ga composition of the film as measured by XPS, which we
attribute to the presence of large oxide structures on the surfaces. However, there were differences between treatments. The Ga 3s, Ga 2p, Ga 3p, Ga 3d, and Ga 3p3/2 peaks were summed to obtain the total Ga content, which was found to be the element present in the highest amount for the clean, H2O2, and H2O2/C4H7ClO2 treatments for the B−D regions of the gradient. The H2O2 and H2O2/C4H7ClO2 treatments had approximately the same Ga content, 39.24−40.71%, as the clean sample, 37.67−39.66%. However, the Ga 3p peak was absent and the 3p3/2 was present for the H2O2 and H2O2/C4H7ClO2 surfaces, while the opposite was true for the clean surfaces, which indicated that there was a change in the Ga species after H2O2 passivation. We observed a decrease in the Ga content between 14.97 and 28.07% for the H3PO4-etched surface treatments because Ga was etched from the surface by this treatment. The percentages of the Ga 3s and Ga 2p peaks were roughly the same as those of the clean treatment, while the Ga 3p and Ga 3d peaks showed a decrease. Unlike the clean and H2O2-passivated surfaces, Ga was not present in the highest quantity for H3PO4 region B and H3PO4/C3H8BrO3P region C, which contained more O than Ga as measured by the sum of the O 1s and O 2s peaks. The O content was in the range of 13.42−36.21% for the H3PO4 treatments, while the clean and H2O2 treatments had less O, ranging from 5.76 to 7.01%. There was also a shift in the O species present on the surface for the H3PO4 treatments as indicated by an increase in the O 2s peak, which was absent in the clean and H2O2 spectra. There was no P present on the clean samples, as determined by the sum of the P 2p and P 2s peaks. Although we did not intend to alter the P species on the surface through H2O2 passivation, the results showed between 10.49 and 11.17% P after treatment, most likely because of impurities in H2O2 used during the treatment. We found that the P content was present in the highest percentage on the H3PO4-treated surfaces with no difference between the capped and uncapped treatment. We also observed a P 2s peak for the H3PO4 treatments, indicating that there was a difference in the P species on the surface compared to the H2O2-treated surfaces. The amount of N measured by the N 1s peak was present in the second highest quantity for the clean and H2O2-containing treatments, ranging between 29.38 and 33.24%. There was less N for the H3PO4 treatments and, except for H3PO4-B and H3PO4/C3H8BrO3P-C, O was present in the second highest quantity on the surfaces in the range of 9.18−23.73%. The carbon content, measured by the C 1s peak, was relatively similar for all treatments. The largest difference in C content was observed for the H3PO4 treated surfaces, which was between 8.27 and 16.19% compared to 5.22−8.8% for the clean and H2O2-treated surfaces.

High-resolution regional XPS scans of the Al 2p, Ga 3d, O 1s, and C 1s peaks were analyzed to assess changes in the species present with respect to treatment and gradient position. These data are summarized in Figure 6a−d. There were trends in these results corresponding to both the Al content gradient and the treatment. The Al 2p peak was deconvoluted to the Al−N and Al2O3 species, and the data are summarized in Figure 6a. The Al−N species was found to decrease from region B to region D for the clean samples. There was a corresponding increase of Al2O3 on the surface from region B to region D, which indicated that oxide formation was favored as the Al content increased, which agrees with the literature.18 We also observed an increase in Al−N and a decrease in Al2O3.

Figure 4. Mean water contact angle for treatments with respect to the gradient. Asterisks indicate statistical difference between groups (ANOVA p < 0.05).

Figure 5. Total atomic percentages of regions B−D for each treatment: (a) clean, (b) H2O2, (c) H2O2/C4H7ClO2, (d) H3PO4, and (e) H3PO4/C3H8BrO3P as determined by XPS survey scan.
from B to D for the H₂O₂ and H₂O₂/C₄H₇ClO₂ treatments. There was a greater percentage of Al₂O₃ on the H₂O₂-treated surface compared to that on the clean surface. However, when capped by C₄H₇ClO₂, there was a lower percentage of Al₂O₃ than the uncapped surface, but there was still a greater percentage than the clean surface. We note that the total relative amount of Al₂O₃ for the clean and H₂O₂-passivated surfaces was relatively the same (see the Supporting Information). The surfaces that were treated only with H₃PO₄ showed a decrease in Al−N percentage between B and D, but region C did not lie between these two values, so there was no clear trend. Similarly, the percentage of Al₂O₃ was lower at region B than at region D, but region C was not between these values. For regions B−D, the percentage of Al₂O₃ was greater after H₃PO₄ etching. The H₃PO₄/C₃H₈BrO₃P treatment caused a significant increase in the percentage of Al−N and a decrease in the percentage of Al₂O₃ from B to D. The magnitude of this change was also much greater than the changes observed for the other treatments, as shown in Figure 6a. The significant decrease in Al₂O₃ with increasing Al content compared to the other treatments suggested that Al₂O₃ formation was inhibited by capping the surface with a phosphonic acid derivative.

The Ga 3d peak, shown in Figure 6b, was deconvoluted to Ga−N, Ga₂O₃, and Auger Ga−N. The Auger Ga−N data were relatively the same for all treatments and gradient regions, ranging from 3.31 to 11.47%, with no trend in the data. The clean surfaces showed an increase from 50.84 to 75.61% Ga−N and a decrease in Ga₂O₃ from 37.69 to 12.98% from region B to region D of the gradient. The decrease in Ga−N correlated to the results of the Al 2p peak, which showed that the Al−N species decreased from B to D. Furthermore, there was a decrease in Ga₂O₃ as Al₂O₃ increased from B to D. We found no clear trend in Ga−N and Ga₂O₃ with respect to the gradient for H₂O₂ or H₂O₂/C₄H₇ClO₂. There were slight changes in the values after these treatments were compared to clean treatment, but they remained roughly the same. The lowest value for Ga−N was 51.65% and the largest was 70.62%. For Ga₂O₃, the smallest and largest values were 21.22 and 29.96%, respectively. The percentage of Ga₂O₃ was not affected by the gradient in the same way Al₂O₃ formation was for the H₂O₂ treatment, which decreased as the Al content increased. For the capped surface, we observed similar results, suggesting that capping inhibits both Al₂O₃ and Ga₂O₃ formation. The trend for H₃PO₄ and H₃PO₄/C₃H₈BrO₃P treatments for Ga−N and Ga₂O₃ was the same as that for the clean treatment, although the magnitude of the change was greater for the H₃PO₄-containing treatments. From region B to D, Ga−N increased from 24.84 to 75.86% and Ga₂O₃ decreased from 69.56 to 18.55% after H₃PO₄ treatment. The addition of C₃H₈BrO₃P during etching caused an increase in Ga−N from 19.64 to 75.73% and a decrease in Ga₂O₃ from 74.37 to 16.4% from regions B to D. The increased Ga₂O₃ percentage after H₃PO₄ etching compared to the clean surfaces suggested that Ga₂O₃ was more readily formed after etching. However, the magnitude of difference in Ga₂O₃ percentage between the H₃PO₄-etched surfaces and clean surfaces decreased as the Al content increased. This was also confirmed by comparing the overall relative Ga₂O₃ content on the surfaces (see the Supporting Information). The greatest relative Ga₂O₃ content was 13.68% on region B surface after H₃PO₄ etching, while the clean surface had 10.53% at region B. However, at region D, there was a smaller magnitude of difference between the surfaces that were H₃PO₄-etched,
9.48%, versus clean surfaces, 7.058%. Because there was less Al in region B than in region D, more etching was likely to occur because H$_3$PO$_4$ preferentially etched Ga–N. Thus, more Ga–N was removed from the surface to promote Ga$_2$O$_3$ formation by etching. The relative total amount of Al$_2$O$_3$ did not show a trend, but it was the highest after H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P treatment at 4.52% and lowest after H$_2$O$_2$/C$_4$H$_7$ClO$_2$ at 0.73%. This can be explained by relatively low Al content compared to Ga, which meant fewer Al atoms were available to form Al$_2$O$_3$, so more Ga$_2$O$_3$ was formed. Unlike Al$_2$O$_3$, capping the surface with a phosphonic acid derivative did not appear to affect Ga$_2$O$_3$ formation because similar results were observed for the uncapped H$_3$PO$_4$-treated surface.

The O 1s peak was deconvoluted into Ga$_2$O$_3$, O−C, and O−H species, and the results are summarized in Figure 6c. There was no trend in Ga$_2$O$_3$, O= C, or O=H for the clean surface with respect to the gradient. The range of the O 1s species was 75.61−82.84% Ga$_2$O$_3$, 13.78−21.81% O=C, and 2.58−4.98% O−H. Similarly, the H$_2$O$_2$- and H$_2$O$_2$/C$_4$H$_7$ClO$_2$-treated surfaces showed no trend with respect to the gradient and the percentages of the species were approximately the same as the clean surfaces, 64.45−80.94% Ga$_2$O$_3$, 11.62−20.22% O=C, and 1.15−23.92% O−H. The biggest differences in the O 1s species were observed after treated with H$_3$PO$_4$ and H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P. The O=C species was not observed on the surface after H$_3$PO$_4$ etching. The percentage of Ga$_2$O$_3$ decreased to 38.21−45.32% and O=H increased to 54.68−61.79% after the uncapped H$_3$PO$_4$ treatment, but no trend with respect to the gradient was observed. However, when capped with C$_3$H$_8$BrO$_3$P, the percentage of Ga$_2$O$_3$ decreased from 53.64 to 26.44% from regions B to D and the percentage of O=H content increased from 46.36 to 73.56% from regions B to D. This agreed with the Ga$_3$O$_3$ species of the Ga 3d peak. Furthermore, because the total percentage of O was not found to change with respect to the gradient after H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P treatment, as shown in Figure 5, capping the surface with C$_3$H$_8$BrO$_3$P seems to inhibit the formation of Ga$_2$O$_3$ in favor of O−H formation.

The C 1s peak, shown in Figure 6d, was deconvoluted to C=C, C=O−C, and O−C=O species. A decrease in C=C from 68.55 to 60.1% and an increase in O=C=O from 13.34 to 21.58% were observed from regions B to D on the clean surface. No trend was observed for the C−O=C species on the clean surfaces, which ranged from 18.11 to 18.34%. After H$_2$O$_2$ treatment, there was a small decrease in C=C from 59.1 to 51.59% and an increase from 26.63 to 32.18% C=O−C from regions B to D, while there was no trend in O−C=O content. The overall decrease in C=C and increase in C−O=C compared to the clean surfaces, which ranged from 18.11 to 18.34%. After H$_2$O$_2$ treatment, there was a small decrease in C=C from 59.1 to 51.59% and an increase from 26.63 to 32.18% C=O−C from regions B to D, while there was no trend in O−C=O content. The overall decrease in C=C and increase in C−O=C compared to the clean surfaces, which ranged from 18.11 to 18.34%. After H$_2$O$_2$ treatment, there was a small decrease in C=C from 59.1 to 51.59% and an increase from 26.63 to 32.18% C=O−C from regions B to D, while there was no trend in O−C=O content. The overall decrease in C=C and increase in C−O=C compared to the clean surfaces, which ranged from 18.11 to 18.34%.

The C species detected on the H$_3$PO$_4$- and H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P-treated surfaces did not have a trend with respect to the gradient. The two treatments had approximately the same percentage of each species, which ranged from 67.46 to 75.68% C−C, 18.1 to 21.23% C−O−C.
and 5.28 to 11.31% O−C≡O. There was a slight increase in the overall C−C percentage after both H$_3$PO$_4$ treatments and a decrease in the O−C≡O percentage compared to the clean surfaces for each region of the gradient. However, because there was no trend with respect to the gradient, it was likely related to contamination of the surface from the environment.

2.4. Spectroscopic Changes. We recorded Raman spectra (Figure 7a–c) in the spectral range from 100 to 1000 cm$^{-1}$ to evaluate the structural characteristics of the Al$_x$Ga$_{1−x}$N film with respect to the Al content and chemical treatment. The A$_1$(TO) mode of GaN, found between 316.54 and 543.82 cm$^{-1}$ for each treatment and region of the gradient, shifts to higher wavenumbers as the Al content of the Al$_x$Ga$_{1−x}$N film increases. This peak has been reported at 32 cm$^{-1}$ for unstrained GaN and the sensitivity of this peak to Al content in Al$_x$Ga$_{1−x}$N alloys has been documented. The increased Al content red-shifts the phonon frequency because of strain present in the lattice of GaN as the material becomes more AlN-like. We observed a shift to the lower wavenumber of the A$_1$(TO) peak after treatment, indicating that this peak is sensitive to chemical treatment. The shape of the A$_1$(TO) peak for the clean samples changed as the Al content increased because the GaN E$_2$(high) peak, located at 587 cm$^{-1}$ for region D, red shifts as the Al content increased and separates from the A$_1$(TO) peak. The E$_2$(high) peak has been reported at 567 cm$^{-1}$ for unstrained GaN and shifted to higher phonon frequencies at a faster rate than the A$_1$(TO) peak as the Al content increased, which agrees with our results. We observed a red shift of the E$_2$(low) peak as Al composition increased from regions B to D and a blue shift after surface treatment. This peak was reported at 144 cm$^{-1}$ for unstrained GaN. We observed the highest frequency of the E$_2$(low) peak at 153.68 cm$^{-1}$ for region D (Figure 7c) of the clean surface and the lowest frequency at 147.97 cm$^{-1}$ for H$_2$O$_2$-treated region B (Figure 7a). A shoulder at roughly 145 cm$^{-1}$ was observed for the clean, H$_3$PO$_4$-, and H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P-treated surfaces for all regions of the gradient. However, the shoulder coalesced with the E$_2$(low) peak for the H$_2$O$_2$ and H$_2$O$_2$/C$_3$H$_8$ClO$_2$ treatments. A peak was observed at roughly 894 cm$^{-1}$ corresponding to the A$_1$(LO) AlN phonon mode. It was difficult to differentiate this peak from the noise because of a low signal. However, it was at roughly the same frequency for each of the treated samples and region of the gradient. After H$_3$PO$_4$ etching, a peak at roughly 930 cm$^{-1}$ became noticeable for all regions of the gradient.

2.5. Surface Charge Changes. Figure 8 shows a summary of the surface potential measured by KPFM corresponding to the Al content and surface treatment. We did not observe a trend with respect to the Al gradient or treatment. However, there was statistically significant difference in the results, indicating that we were able to change the surface potential through surface treatment. This is seen in Figure 8 where the red Greek letters marked by an asterisk indicate a significant difference in the root-mean-squared (rms) potential of the surface compared to the surfaces marked with a corresponding black Greek letter. For example, region B of the H$_2$O$_2$/C$_3$H$_8$ClO$_2$-treated surface was statistically different from regions B and D of the H$_2$O$_2$ surface and all regions of the gradient of the clean, H$_3$PO$_4$-, and H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P-treated surfaces. The only significant difference for the H$_3$PO$_4$- and H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P-treated surfaces from the other treatments was from region C of H$_3$PO$_4$. The lack of differences indicated that H$_3$PO$_4$ etching did not tend to significantly impact the surface potential.

We evaluated through a variety of characterization techniques changes in the surface properties of an Al$_x$Ga$_{1−x}$N film (0.173 ≤ x ≤ 0.220) after surface treatment with H$_2$O$_2$, H$_2$O$_2$/C$_3$H$_8$ClO$_2$, H$_3$PO$_4$, and H$_3$PO$_4$/C$_3$H$_8$BrO$_3$P. We observed that all chemical treatments affected the morphology of the nanostructures on the sample surface in a different way. Compared to the clean surfaces, which had few nanostructures consisting mostly of clusters of oxide nanopillars, the H$_2$O$_2$ and H$_2$O$_2$/C$_3$H$_8$ClO$_2$ treatments caused the formation of clusters of striated rectangular oxide nanostructures. The H$_3$PO$_4$ and

![Figure 8](image-url)
H₃PO₄/C₃H₈BrO₃P treatments led to unique surfaces with hexagonal etch pits and needle-like oxide nanostructures. The roughness of the surface was modified through surface treatment, however, because the nanostructures formed at uncontrollable positions on the surface and changes in roughness were not observed across the entire surface. We demonstrated that the hydrophobicity of the surface can be modified through H₃PO₄ and H₃PO₄/C₃H₈BrO₃P treatments, leading to a more hydrophilic surface. We did not observe changes in the morphology, roughness, or hydrophobicity corresponding to the Al gradient, but we confirmed through XPS that there were changes in the surface chemistry that depend on the Al content. Most notably, we observed an increase in the percent of Al₂O₃ content formed on the surface with an increase of the Al content on the clean surfaces, while there was a reversal in this trend after all surface treatments. The strain-related Raman peaks were observed to shift to higher frequencies with increasing Al content on the clean surfaces. After surface treatment, the strain-related peaks shifted to lower frequencies, indicating that strain was manipulated by the treatments. We also observed that the surface charge could be modulated by surface chemistry, but like the roughness, it is not controllably changed because of the unpredictable formation of surface nanostructures. In conclusion, we have demonstrated that the interfacial properties of an AlₓGa₁−ₓN film can be modulated through simple wet beaker chemistry treatments. The chemical treatments we used modified the surface chemistry of the AlₓGa₁−ₓN film corresponding to the Al/Ga compositional gradient without the need for more complex patterning approaches. These findings are useful for applications such as bioelectronics because they can be used as guiding principles toward the engineering of interfaces with specific characteristics.

4. EXPERIMENTAL SECTION

4.1. Semiconductor Growth. The AlGaN layer was grown by Kyma Technology using hydride vapor phase epitaxy. The nonuniformity in the composition is due to lack of uniformity of the absolute Al and Ga flux ratio reaching the sample surface across a 2 in. wafer, leading to a nonuniform Al and Ga incorporation in the solid phase. The lack of uniformity in the Al and Ga atom distributions across the wafer is related to the nonsymmetric disposition of the Ga and Al channel exits with respect to the wafer center, which was further intentionally enhanced by not using wafer rotation during the film growth. By stopping the wafer rotation during growth, an intentional composition gradient was achieved.

4.2. Chemical Modification. The thin-film wafer was diced into similarly sized pieces of approximately 1 cm × 1 cm. The periphery of the wafer at the high and low Al content was not evaluated because of poor quality of the film near the edges. The samples were split into five groups as shown in Figure 1, allowing for each part of the gradient to receive four different chemical treatments as described in Table 1. All individual samples were cleaned by sonication prior to chemical functionalization with (i) acetone for 20 min, (ii) methanol for 20 min, and (iii) deionized (DI) water for 10 min and dried with N₂ gas after each step. The samples were then etched in a solution of equal parts by volume 12 M HCl and DI water at 80 °C. One group of clean samples were not treated further. The remaining four groups received one of the treatments as indicated in Table 1. The technical details of chemical functionalization can be found in our previous work.35,44

4.3. Contact Angle Measurements. Static contact angle measurements were performed using a ramé-hart automated dispensing system and a ramé-hart model 200 F4 series standard goniometer to collect the images. DI water drops were dispensed by 2 μL onto the surface. Three measurements were taken for each sample. DropImage Standard (version 2.4) was utilized for image analysis.

4.4. AFM and KPFM. Roughness and surface potential measurements were performed using an Asylum Research MFP-3D Origin AFM. Roughness measurements were done by scanning three random positions on each piece of the diced wafer to obtain height, amplitude, phase, and z-sensor data in air at room temperature by tapping mode. Images of 2 μm × 2 μm were obtained at a scanning frequency of 1 Hz using Si probes (f = 150 kHz, k = 8 N/m) from Asylum Research. The rms roughness was obtained from the images using Igor Pro (version 6.2.2.2).

Surface potential measurements were performed using the KPFM mode in air at room temperature with Ti/Ir (5/20)-coated Si probes from Asylum Research (f = 285 kHz, k = 42 N/m). Images of 500 nm × 500 nm were obtained with a scanning frequency of 1 Hz at three random positions on each piece of the wafer along the gradient. The samples were grounded by soldering a copper wire to the wafer surface with In solder to minimize surface potential drift during the scans, which was found to be a source of large standard deviations in our previous work.45 The rms surface potential values were obtained from the images using Igor Pro (version 6.2.2.2).

4.5. SEM. The nanostructures of the samples were analyzed using the Tescan MAIA 3 field-emission scanning electron microscope equipped with an in-beam secondary electron detector and a back-scattered electron detector. Secondary electron imaging was done to observe the topography of the samples, and backscattered electrons were captured to observe elemental differences of the surfaces. Image processing was performed with ImageJ (version 1.52n).

4.6. XPS. An AXIS Supra X-ray photoelectron spectrometer (Kratos Analytical Ltd, UK) was used to acquire XPS data by Al Kα radiation (1486.6 eV, probe area is 0.7 × 0.3 mm², resolution is 0.45 eV, measured on the Ag 3d₅/₂ line width). A survey scan was obtained for each sample. High-resolution scans of the C 1s, O 1s, N 1s, Ga 3d, Al 2p, and P 2p regions were performed for each sample. The data were calibrated to the C 1s peak at 284.8 eV and analyzed using CasaXPS (version 2.3.19PR1.0) to determine atomic percentages and fit peaks to determine the percentage of specific chemical species.

4.7. Raman Spectroscopy. A LabRam HR Evolution 0.8 m focal length single-stage spectrometer with diffraction grating 1800/mm was used to perform Raman spectroscopy measurements. The excitation power of a 532 nm laser was ~200 W cm⁻², an objective with magnification 100× collected signals from approximately a 1 μm circular spot. Three survey scans at random positions in the region 100−1000 cm⁻¹ were obtained per sample with an acquisition time of 10 s and 30 accumulations. The three scans obtained for each sample were averaged, normalized, and analyzed using Origin 2018b (version b9.5.5.409).

4.8. Statistical Analysis. Origin 2018b (version b9.5.5.409) was utilized to perform all statistical analyses using two-way ANOVA tests with a significance level of 0.05.
Biomaterials for Axon Guidance Studies: Moving beyond Proof of Concept.

Substrates for Axon Guidance Studies: Moving beyond Proof of Concept.

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank NSF under OISE 1458427 and the Ministry of Education, Youth and Sports of the Czech Republic (projects LM2015088, NPU LO1603—ASTRANIT and project no. SOLID21—CZ.02.1.01/0.0/0.0/16_019/0000760) for financial support.

REFERENCES

1. Keenan, T. M.; Folch, A. Biomolecular Gradients in Cell Culture Systems. Lab Chip 2008, 8, 34–57.

2. Roy, J.; Kennedy, T. E.; Costantino, S. Engineered Cell Culture Substrates for Axon Guidance Studies: Moving beyond Proof of Concept. Lab Chip 2013, 13, 498–508.

3. Lu, H. H.; Subramony, S. D.; Boushell, M. K.; Zhang, X. Tissue Engineering Strategies for the Regeneration of Orthopedic Interfaces. Ann. Biomed. Eng. 2010, 38, 2142–2154.

4. Guarnieri, D.; Borzacchiello, A.; De Capua, A.; Ruvo, M.; Netti, P. A. Engineering of Covalently Immobilized Gradients of RGD Peptides on Hydrogel Scaffolds: Effect on Cell Behaviour. Macromol. Symp. 2008, 266, 36–40.

5. Tayalia, P.; Mooney, D. J. Controlled Growth Factor Delivery for Tissue Engineering. Adv. Mater. 2009, 21, 3269–3285.

6. Charron, F.; Tessier-Lavigne, M. Novel Brain Wiring Functions of Morphogen-Mediated Axon Guidance. BioEssays 2009, 31, 1013–1025.

7. Sánchez-Camacho, C.; Bovolenta, P. Emerging Mechanisms in Morphogen-Mediated Axon Guidance. Adv. Mater. 2017, 19, 8787–8801.

8. Keenan, T. M.; Folch, A. Biomolecular Gradients in Cell Culture Systems. Lab Chip 2008, 8, 34–57.

9. Roy, J.; Kennedy, T. E.; Costantino, S. Engineered Cell Culture Substrates for Axon Guidance Studies: Moving beyond Proof of Concept. Lab Chip 2013, 13, 498–508.

10. Lu, H. H.; Subramony, S. D.; Boushell, M. K.; Zhang, X. Tissue Engineering Strategies for the Regeneration of Orthopedic Interfaces. Ann. Biomed. Eng. 2010, 38, 2142–2154.

11. Tayalia, P.; Mooney, D. J. Controlled Growth Factor Delivery for Tissue Engineering. Adv. Mater. 2009, 21, 3269–3285.

12. Charron, F.; Tessier-Lavigne, M. Novel Brain Wiring Functions of Morphogen-Mediated Axon Guidance. BioEssays 2009, 31, 1013–1025.

13. Sánchez-Camacho, C.; Bovolenta, P. Emerging Mechanisms in Morphogen-Mediated Axon Guidance. Adv. Mater. 2017, 19, 8787–8801.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01467.

Additional experimental details, statistical analysis, and characterization data (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: ivanisevic@ncsu.edu.

ORCID

Oleksandr Romyanyuk: 0000-0003-0430-3706

Albena Ivanisevic: 0000-0003-0336-1170

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

ACS Omega 2015, 4, 11760–11769

DOI: 10.1021/acsomega.9b01467
(33) Jung, Y.; Ahn, J.; Baik, K. H.; Kim, D.; Pearton, S. J.; Ren, F.; Kim, J. Chemical Etch Characteristics of N-Face and Ga-Face GaN by Phosphoric Acid and Potassium Hydroxide Solutions. *J. Electrochem. Soc.* 2011, 159, H117–H120.

(34) Jung, Y.; Baik, K. H.; Mastro, M. A.; Hite, J. K.; Eddy, C. R.; Kim, J. Chemical Etching Behaviors of Semipolar (112) and Nonpolar (110) Gallium Nitride Films. *Phys. Chem. Chem. Phys.* 2014, 16, 15780–15783.

(35) Wilkins, S. J.; Greenough, M.; Arellano, C.; Paskova, T.; Ivanisevic, A. In Situ Chemical Functionalization of Gallium Nitride with Phosphonic Acid Derivatives during Etching. *Langmuir* 2014, 30, 2038–2046.

(36) Leem, J. W.; Lee, H. K.; Jun, D.-H.; Heo, J.; Park, W.-K.; Park, J.-H.; Yu, J. S. Electrochemically Synthesized Broadband Antireflective and Hydrophobic GaOOH Nanopillars for III-V InGaP/GaAs/Ge Triple-Junction Solar Cell Applications. *Opt. Express* 2014, 22, A328–A334.

(37) Adams, W. T.; Vinupez, N. R.; Romanyuk, O.; Gordeev, I.; Paskova, T.; Ivanisevic, A. Nanostructured GaOOH Modified with Reactive Yellow, Red and Blue Water-Soluble Dyes. *AIP Adv.* 2019, 9, 025005.

(38) Reddy, L. S.; Ko, Y. H.; Yu, J. S. Hydrothermal Synthesis and Photocatalytic Property of β-Ga2O3 Nanorods. *Nanoscale Res. Lett.* 2015, 10, 364.

(39) Bae, H.; Yoo, T.; Yoon, Y.; Lee, I.; Kim, J.; Cho, B.; Hwang, W. High-Aspect Ratio β-Ga2O3 Nanorods via Hydrothermal Synthesis. *Nanomaterials* 2018, 8, 594.

(40) Li, J.; An, L.; Lu, C.; Liu, J. Conversion between Hexagonal GaN and β-Ga2O3 Nanowires and Their Electrical Transport Properties. *Nano Lett.* 2006, 6, 148–152.

(41) Cros, A.; Angerer, H.; Ambacher, O.; Stutzmann, M.; Höpler, R.; Metzger, T. Raman Study of the Optical Phonons in AlxGa1−xN Alloys. *Solid State Commun.* 1997, 104, 35–39.

(42) Kuball, M. Raman Spectroscopy of GaN, AlGaN and AlN for Process and Growth Monitoring/Control. *Surf. Interface Anal.* 2001, 31, 987–999.

(43) Haboeck, U.; Siegle, H.; Hoffmann, A.; Thomesen, C. Lattice Dynamics in GaN and AlN Probed with First- and Second-Order Raman Spectroscopy. *Phys. Status Solidi C* 2003, 0, 1710–1731.

(44) Snyder, P. J.; Davis, H.; Berg, N. G.; Pearce, B.; Romanyuk, O.; Jiricek, P.; Paskova, T.; Ivanisevic, A. Passivation of Semipolar (10-1-1) GaN with Different Organic Adsorbates. *Mater. Lett.* 2019, 236, 201–204.

(45) Snyder, P. J.; Reddy, P.; Kister, R.; LaJeunesse, D. R.; Collazo, R.; Ivanisevic, A. Noninvasive Stimulation of Neurotypic Cells Using Persistent Photoconductivity of Gallium Nitride. *ACS Omega* 2018, 3, 615–621.