

Photochemical Functionalization of Gallium Nitride Thin Films with Molecular and Biomolecular Layers

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We demonstrate that photochemical functionalization can be used to functionalize and photopattern the surface of gallium nitride crystalline thin films with well-defined molecular and biomolecular layers. GaN(0001) surfaces exposed to a hydrogen plasma will react with organic molecules bearing an alkene (C=C) group when illuminated with 254 nm light. Using a bifunctional molecule with an alkene group at one end and a protected amine group at the other, this process can be used to link the alkene group to the surface, leaving the protected amine exposed. Using a simple contact mask, we demonstrate the ability to directly pattern the spatial distribution of these protected amine groups on the surface with a lateral resolution of $< 12 \mu\text{m}$. After deprotection of the amines, single-stranded DNA oligonucleotides were linked to the surface using a bifunctional cross-linker. Measurements using fluorescently labeled complementary and noncomplementary sequences show that the DNA-modified GaN surfaces exhibit excellent selectivity, while repeated cycles of hybridization and denaturation in urea show good stability. These results demonstrate that photochemical functionalization can be used as an attractive starting point for interfacing molecular and biomolecular systems with GaN and other compound semiconductors.

Introduction

While semiconductor materials have very well-defined properties under the dry, well-defined conditions typical of conventional microelectronics, there is increased interest in extending semiconductors into aqueous environments for applications such as electronic sensing of chemical and/or biological molecules.¹ A particular challenge to effective integration of biological systems with simple covalent semiconductors such as silicon and diamond, and even common compound semiconductors such as GaAs, is that surface defects usually create electronic states that lie in the middle of the band gap, where they pin the Fermi level and thereby decrease the sensitivity of field-effect sensing devices. Gallium nitride is a particularly intriguing semiconductor for sensing applications because it can be grown as a thin crystalline film^{2,3} as well as quantum dots,¹ and because the high ionic character of GaN causes the intrinsic surface states to be near the respective band edges,^{4,5} where they have less impact on the interfacial electronic properties. While the nature of the surface states is dependent on the chemical state of the surface and on lattice strain, the possibility of semiconductor interfaces that may be more tolerant of defects provides a motivation for understanding how to functionalize the surfaces of GaN and related nitride materials with molecular and/or biomolecular layers.

Although little work has been performed previously on GaN, several approaches have been reported previously for function-

alization of other III–V semiconductors such as GaAs, including the chemical grafting of aryldiazonium salts,⁶ the formation of self-assembled monolayers via reaction with alkanethiols,^{7,8} and adsorption of phosphonic acids onto intentionally oxidized surfaces.⁹ Ultrahigh-vacuum surface-science studies showed that molecules bearing reactive groups such as amines and thiols can link to GaN.^{10–14} Functionalization of GaN under ambient conditions has been achieved using organosilanes^{15,16} and direct noncovalent bonding of guanines to the surface.¹⁷

We have recently shown that hydrogen-terminated surfaces of diamond^{18–20} and other carbon-based materials²¹ can be photochemically functionalized with organic alkenes (olefins) by illumination with ultraviolet (UV) light at 254 nm.¹⁸ A similar procedure also can be used on silicon.^{6,22–28} Photochemical

(6) Stewart, M. P.; Maya, F.; Kosynkin, D. V.; Dirk, S. M.; Stapleton, J. J.; McGuinness, C. M.; Allara, D. L.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 370–378.

(7) Lercel, M. J.; Redinbo, G. F.; Craighead, H. G.; Sheen, C. W.; Allara, D. L. *Appl. Phys. Lett.* **1994**, *65*, 974–976.

(8) Nakagawa, O. S.; Ashok, S.; Sheen, C. W.; Martensson, J.; Allara, D. L. *Jpn. J. Appl. Phys. Part 1* **1991**, *30*, 3759–3762.

(9) Botelho do Rego, A. M.; Ferraria, A. M.; El Beghdadi, J.; Debontridder, F.; Brogueira, P.; Naaman, R.; Rei Vilar, M. *Langmuir* **2005**, *21*, 8765–8773.

(10) Bermudez, V. M. *Chem. Phys. Lett.* **2000**, *317*, 290–295.

(11) Bermudez, V. M. *Surf. Sci.* **2002**, *519*, 173–184.

(12) Bermudez, V. M. *Surf. Sci.* **2002**, *499*, 109–123.

(13) Bermudez, V. M. *Surf. Sci.* **2002**, *499*, 124–134.

(14) Bermudez, V. M. *Langmuir* **2003**, *19*, 6813–6819.

(15) Baur, B.; Steinhoff, G.; Hernando, J.; Purucker, O.; Tanaka, M.; Nickel, B.; Stutzmann, M.; Eickhoff, M. *Appl. Phys. Lett.* **2005**, *87*, 263901–263904.

(16) Kang, B.; Ren, F.; Wang, L.; Lofton, C.; Tan, W.; Pearton, S.; Dabiran, A.; Osinsky, A.; Chow, P. *Appl. Phys. Lett.* **2005**, *87*, 023508–023510.

(17) Neogi, A.; Li, J.; Neogi, P. B.; Sarkar, A.; Morkoc, H. *IEEE Electron. Lett.* **2004**, *40*, 1605–1606.

(18) Strother, T.; Knickerbocker, T.; Russell, J. N., Jr.; Butler, J. E.; Smith, L. M.; Hamers, R. J. *Langmuir* **2002**, *18*, 968–971.

(19) Yang, W. S.; Auciello, O.; Butler, J. E.; Cai, W.; Carlisle, J. A.; Gerbi, J.; Gruen, D. M.; Knickerbocker, T.; Lasseter, T. L.; Russell, J. N., Jr.; Smith, L. M.; Hamers, R. J. *Nat. Mater.* **2002**, *1*, 253–257.

(20) Nichols, B. M.; Butler, J. E.; Russell, J. N., Jr.; Hamers, R. J. *J. Phys. Chem. B* **2005**, *109*, 20938–20947.

(21) Baker, S. E.; Tse, K. Y.; Hindin, E.; Nichols, B. M.; Clare, T. L.; Hamers, R. J. *Chem. Mater.* **2005**, *17*, 4971–4978.

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[†] Department of Chemistry.

[‡] Department of Chemical and Biological Engineering.

(1) Sirbuly, D. J.; Law, M.; Yan, H. Q.; Yang, P. D. *J. Phys. Chem. B* **2005**, *109*, 15190–15213.

(2) Dwikusuma, F.; Kuech, T. F. *J. Appl. Phys.* **2003**, *94*, 5656–5664.

(3) Strite, S.; Morkoc, H. *J. Vac. Sci. Technol., B* **1992**, *10*, 1237–1266.

(4) Levine, J. D.; Mark, P. *Phys. Rev.* **1966**, *144*, 751–763.

(5) Bridger, P. M.; Bandic, Z. Z.; Piquette, E. C.; McGill, T. C. *Appl. Phys. Lett.* **1999**, *74*, 3522–3524.

functionalization processes are attractive because they do not require high temperature or ultrahigh vacuum and should be applicable to a wide variety of surfaces whose intrinsically high reactivity can be passivated by atomic hydrogen. Moreover, photochemical functionalization should provide a means to directly control the spatial distribution of chemical functional groups on the surface. Here, we demonstrate that photochemical functionalization can be used to modify the gallium nitride surface with well-defined molecular monolayers, and that these chemical functional groups can be directly photopatterned with a spatial resolution of $<12\ \mu\text{m}$ using a simple contact mask. Furthermore, we show that photochemical functionalization can be used as a starting point for tethering biomolecules such as DNA to gallium nitride surfaces, yielding DNA-modified GaN surfaces exhibiting excellent selectivity and good stability.

Materials and Methods

Epitaxial GaN(0001) films were grown by both hydride vapor-phase epitaxy (HVPE) and metalloorganic chemical vapor deposition (MOCVD) on *c*-plane sapphire substrates. This orientation exposes Ga atoms at the exposed crystal face. The GaN films were 4–5 or 1–2 μm thick for the respective growth techniques. In both cases, the samples were unintentionally doped n-type, with capacitance–voltage measurements showing a surface carrier concentration of $1.5 \times 10^{18}\ \text{cm}^{-3}$.²⁹ The samples were cleaned in concentrated $\text{H}_2\text{SO}_4/30\% \text{H}_2\text{O}_2$ (3:1 by volume) (*note: exercise caution when handling this solution, since it can be explosive in the presence of organics*) at room temperature for 30 min to remove the carbon contaminants, rinsed with deionized water, and dried under nitrogen.³⁰ The samples were then exposed to ultraviolet light from a low-pressure mercury vapor quartz grid lamp ($\lambda = 254\ \text{nm}$, 0.35 mW/cm²) for 3 h to remove any remaining organic contamination. After these cleaning steps, the samples were exposed to a weak 13.56 MHz inductively coupled hydrogen plasma (20 Torr) for 10 min at room temperature to hydrogen-terminate the surfaces. Previous studies have shown that exposure to atomic H leaves the surface terminated with Ga–H bonds.^{31,32}

Results

Photochemical Functionalization with TFAAD. We first demonstrate the ability to photochemically functionalize H-terminated GaN with an alkene. Here, we present data using the ω -unsaturated amine 10-aminodec-1-ene that has been protected with the trifluoroacetamide functional group.¹⁸ We refer to this molecule as “TFAAD”. The TFAAD molecule was used because it has an alkene group at one end for linking to the surface and a protected amine group at the other end that can be deprotected after surface attachment, yielding primary amine groups that can then be used to link DNA and other molecules to the GaN surface. Furthermore, the CF_3 group provides a good marker for

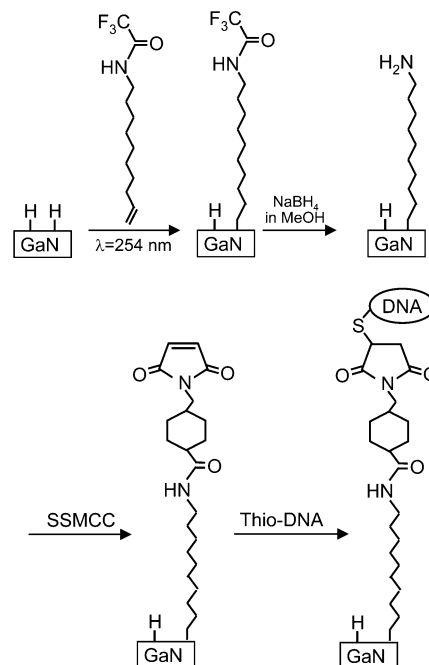


Figure 1. Reaction scheme for attachment of DNA to GaN surfaces.

characterizing the chemistry using X-ray photoelectron spectroscopy (XPS).¹⁸ Figure 1 illustrates the sequence of steps used to covalently link TFAAD to H-terminated GaN surfaces, along with the subsequent steps needed to covalently link single-stranded DNA to the surface. Briefly, the H-terminated samples were photochemically reacted with TFAAD.¹⁸ The protected amine was then deprotected, leaving behind a primary amine that was reacted with a heterofunctional cross-linker, sulfosuccinimidyl 4-(*N*-maleimidomethyl)cyclohexane-1-carboxylate (SSMCC), and finally reacted with thiol-modified DNA to produce a DNA-modified GaN surface.

The first step in this sequence, the photochemical attachment of TFAAD to the H-terminated GaN surface, was accomplished by placing the H–GaN sample in a nitrogen-purged reaction chamber and adding $\sim 5\ \mu\text{L}$ of TFAAD, which wet the surface with a thin, liquid film.^{18–20,33} The sample was covered with a fused quartz window and illuminated with 254 nm light ($\sim 0.35\ \text{mW/cm}^2$) for time periods discussed below. After the samples were ultrasonically rinsed in chloroform (5 min) and methanol (5 min), the functionalized surfaces were characterized using XPS using a monochromatic Al K α source (1486.6 eV photon energy).

Figure 2a shows the XPS spectra for the Ga(3d), C(1s), F(1s), and N(1s) areas before and after modification with TFAAD. The H-terminated GaN surface is characterized by a single Ga(3d) peak at 19.8 eV, with some asymmetry indicating some partial oxidation of the surface. The C(1s) spectrum shows only a small C(1s) peak at 284.9 eV, demonstrating that carbon contamination levels are low. The nitrogen spectrum is complicated, showing a large sharp peak at 397.8 eV and broad peaks near 396 and 392 eV. The peak at 397.8 eV corresponds to bulk nitrogen (N–Ga).³⁰ The broad 396 and 392 eV peaks, however, arise from Auger peaks of Ga. This was confirmed by XPS spectra using a nonmonochromatized Mg source, which showed only one peak at 397.8 eV binding energy. Furthermore, spectra of gallium phosphide using a monochromatized Al K α source showed two peaks near 392 and 396 eV. Thus, despite the apparent

(22) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145–3155.

(23) Stewart, M. P.; Buriak, J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3257–3260.

(24) Cicero, R. L.; Linford, M. R.; Chidsey, C. E. D. *Langmuir* **2000**, *16*, 5688–5695.

(25) Strother, T.; Cai, W.; Zhao, X. S.; Hamers, R. J.; Smith, L. M. *J. Am. Chem. Soc.* **2000**, *122*, 1205–1209.

(26) Strother, T.; Hamers, R. J.; Smith, L. M. *Nucleic Acids Res.* **2000**, *28*, 3535–3541.

(27) Stewart, M. P.; Buriak, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 7821–7830.

(28) Linford, M. R.; Chidsey, C. E. D. *Langmuir* **2002**, *18*, 6217–6221.

(29) Wang, F.; Zhang, R.; Tan, W. S.; Xiu, X. Q.; Lu, D. Q.; Gu, S. L.; Shen, B.; Shi, Y.; Wu, X. S.; Zheng, Y. D.; Jiang, S. S.; Kuech, T. F. *Appl. Phys. Lett.* **2002**, *80*, 4765–4767.

(30) King, S. W.; Barnak, J. P.; Bremser, M. D.; Tracy, K. M.; Ronning, C.; Davis, R. F.; Nemanich, R. J. *J. Appl. Phys.* **1998**, *84*, 5248–5260.

(31) Bellitto, V. J.; Thoms, B. D.; Koleske, D. D.; Wickenden, A. E.; Henry, R. L. *Surf. Sci.* **1999**, *430*, 80–88.

(32) Bellitto, V. J.; Thoms, B. D.; Koleske, D. D.; Wickenden, A. E.; Henry, R. L. *Phys. Rev. B* **1999**, *60*, 4816–4820.

(33) Knickerbocker, T.; Strother, T.; Schwartz, M. P.; Russell, J. N., Jr.; Butler, J. E.; Smith, L. M.; Hamers, R. J. *Langmuir* **2003**, *19*, 1938–1942.

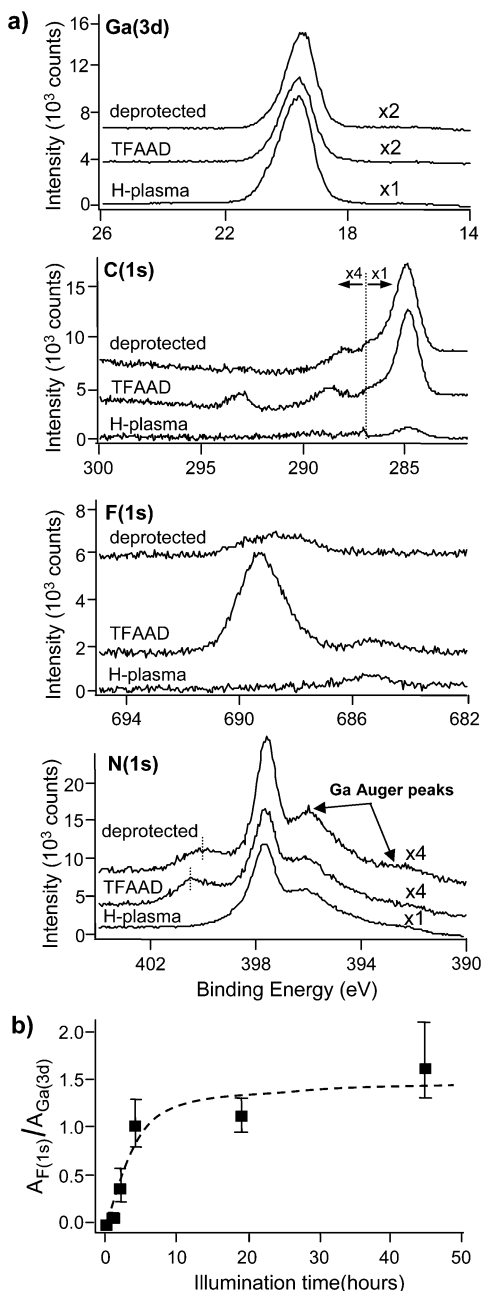


Figure 2. (a) XPS spectra of a GaN sample showing the Ga(3d), C(1s), F(1s), and N(1s) regions. Spectra shown here include the clean, H-plasma-treated surface and the same sample after photochemical attachment of TFAAD and after deprotection to form the primary amine. The Ga, N, and C regions of some spectra have been scaled as indicated in the figure. (b) Functionalization of GaN surfaces with TFAAD as a function of illumination time. The dashed line is only intended to guide the eye.

complexity of the N(1s) spectrum, it appears that the surface is chemically homogeneous except for a small amount of oxidation due to handling in air.

After the photochemical functionalization step, the C(1s) spectrum shows a strong peak at 285.0 eV, a weak shoulder near 286 eV, and two smaller peaks at 288.6 and 293.1 eV. The peak at 285.0 eV comes from the alkyl chain of TFAAD. The peaks at 288.6 and 293.1 eV are attributed to the C atoms of the carbonyl (C=O) group and the $-\text{CF}_3$ group, respectively, while the small shoulder at 286 eV arises from the C atom adjacent to the N atom. The F(1s) spectrum shows a peak at 689.3 eV from the fluorine atoms in the TFA protecting group, while the N(1s) spectrum

shows a new peak at 400.3 eV from the N atom of the amide group. The XPS spectra of the functionalized GaN surface are very similar to those published previously for reaction of TFAAD with diamond.^{19,20}

Figure 2b shows the reaction extent as a function of illumination time for GaN samples exposed to TFAAD, obtained by measuring the ratio of peak areas and correcting for sensitivity factors (F, 1; Ga, 0.40) to give a corrected peak area ratio, $A_{F(1s)}/A_{Ga(3d)}$. The corrected peak area ratio $A_{F(1s)}/A_{Ga(3d)}$ increases linearly for approximately 5 h and then saturates at $A_{F(1s)}/A_{Ga(3d)} = 1.1$. After functionalization the absolute Ga(3d) signal is attenuated to approximately half its original value. This is consistent with a monolayer thickness of ~ 1.5 nm and an inelastic mean free path on the order of 2–3 nm. The fact that the limiting peak area ratio is obtained under conditions where XPS intensity from the underlying bulk GaN is still observed proves that the photochemical surface functionalization self-terminates after one monolayer. Thus, the photochemical functionalization reaction is *self-terminating*: molecules react with the surface until some maximum coverage is reached, and then reaction with the surface stops.

Direct Chemical Photopatterning of Surface Functional Groups. To test whether the photochemical functionalization can be used to directly pattern different chemical groups onto the GaN surface, we created a mask for contact lithography. This mask was fabricated using electron-beam lithography to pattern a photoresist on a UV-transmitting fused quartz substrate, and then depositing chromium on the surface via standard “lift-off” procedures. To test the photopatterning process, a small droplet of TFAAD was placed onto the H-terminated GaN samples. The contact mask was then placed directly on top of the sample, leaving a thin layer of TFAAD trapped between the sample and the mask. The TFAAD liquid layer was measured to be 12–15 μm in thickness using a through-focus series of optical microscope images. When this assembly is illuminated with UV light, the surface regions directly under the chrome regions are not exposed to UV while those under the transparent fused quartz are exposed to UV. Figure 3a shows the mask structure, with light-colored regions representing the chrome regions and the black regions representing the transparent regions.

It is possible to directly image the spatial distribution of surface functional groups via scanning electron microscopy (SEM). Figure 3b shows an SEM image of a GaN surface that was exposed through the contact mask for a period of 18 h. After being rinsed to remove residual physisorbed material, the sample was imaged in the scanning electron microscope using a 2 kV electron energy and an 11 mm working distance, with a small aperture to reduce the primary beam current to approximately 50 pA. The secondary electrons were measured using a conventional Everhart–Thornley secondary electron detector with a +300 V bias. Under these conditions, the regions functionalized with TFAAD give rise to a secondary electron current that is smaller than that observed in the rectangular H-terminated regions. Figure 3b shows the profile of the secondary electron current along the line depicted in Figure 3a. The profile shows that the transition from TFAAD-functionalized to H-terminated regions is sharp, less than 12 μm in width between the two vertical dotted lines. This resolution is likely limited by the 12–15 μm distance from the mask to the sample, which when combined with the use of a diffuse 254 nm light source, leads to a penumbra at the edges of the masked regions.

Functionalization for Biomolecular Interfaces. Surfaces of GaN that have been photochemically functionalized with TFAAD or other appropriate molecules can be used as a starting point

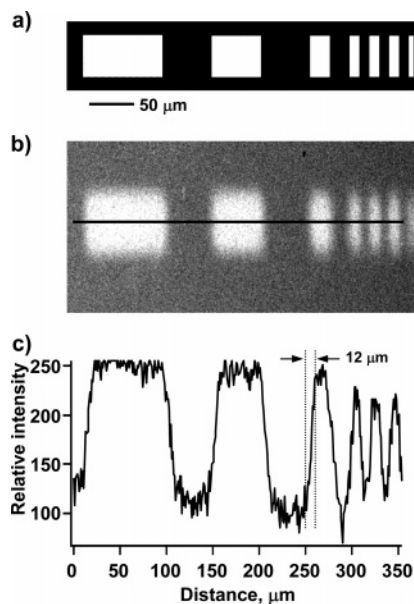


Figure 3. Photochemical patterning of TFAAD onto a H-terminated GaN surface. (a) Top view of the original mask used for patterning. Black represents regions of transparent fused quartz; white represents regions of chromium. (b) SEM image of the patterned surface. Lighter colors represent regions of higher secondary electron yields. (c) Profile showing the variation in the secondary electron yield along the line indicated in (b). Note the abrupt transition, $<12 \mu\text{m}$ in width, between regions of high and low secondary electron yield at the positions of the vertical dotted lines.

for further surface modification. To demonstrate this, we linked TFAAD to the H-terminated GaN surface and then deprotected the amide group by immersion in a solution of 0.3 M NaBH_4 in anhydrous MeOH for 30 min at room temperature and then heating to 65°C for 12 h. This is expected to yield primary amine groups at the free end of each molecule. A comparison of the XPS data shows that deprotection induces $>75\%$ loss of the F(1s) peak at 689.3 eV and nearly complete loss of the C(1s) peak at 293.1 eV. The total N(1s) area does not change significantly, but the peak at 400.3 eV shifts downward to 400.0 eV and broadens slightly as the amide group is converted to a primary amine; similar changes have been observed during deprotection of TFAAD linked to diamond.¹⁹ These changes confirm that the CF_3 group has been removed from the surface, leaving a GaN surface terminated with primary amine groups.

Following the deprotection, the sample was linked to single-stranded DNA as shown in Figure 1. The amine-terminated GaN surface was exposed to a 2 mM solution of SSMCC in 0.1 M triethanolamine buffer solution (pH 7) for 30 min. The *N*-hydroxysuccinimide (NHS) ester group of SSMCC reacts with the primary amine group of the surface to form an amide bond. The maleimide group was then reacted with thiol-modified DNA by applying 0.5 μL of 250 μM thiololigonucleotide and keeping it in the humid chamber overnight at room temperature.^{18,19,33}

To test the specificity of the DNA-modified GaN surfaces, two different oligonucleotides were linked to the surfaces. Each consisted of a thiol group, a short hydrocarbon chain, and a set of 16 bases. The two oligonucleotides had sequences of 5'-HSC₆H₁₂-GC TTA TCG AGC TTT CG-3' (sequences S1) and 5'-HSC₆H₁₂-GC TTA AGG AGC AAT CG-3' (sequence S2); S1 and S2 differ by 4 bases out of 16. We explored the hybridization of these two surface-bound oligonucleotides with two solution-phase oligonucleotides having different sequences that were labeled with fluorescein phosphoramidite (FAM) at the 5' end. The two solution-phase sequences were 5'-FAM-

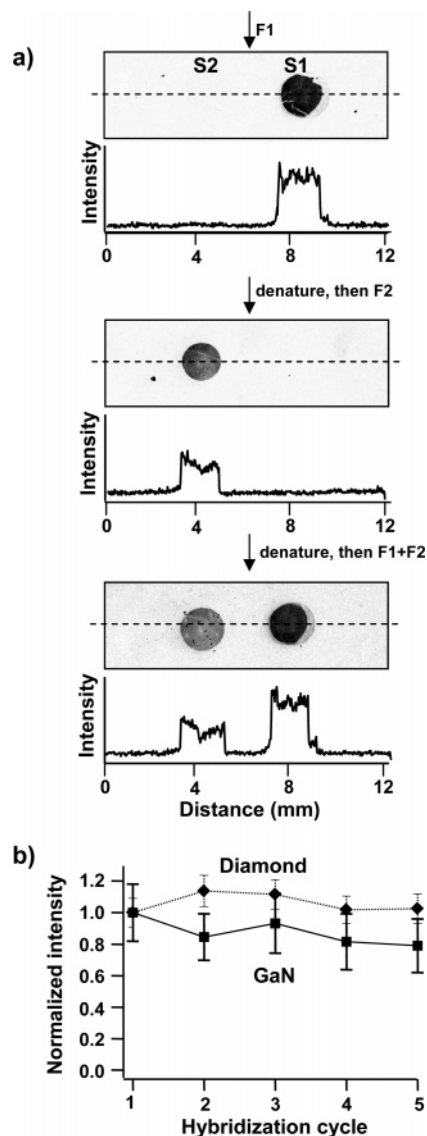


Figure 4. Biomolecular recognition properties of DNA-modified GaN. (a) Images showing fluorescence intensity (black indicates high intensity) on DNA-modified GaN samples functionalized with sequences S1 and S2 and then exposed to F1 (top panels), after denaturation and exposure to F2 (middle panels), and then after denaturation and exposure to a mixture of F1 and F2 (bottom panels). Each measurement includes an intensity map and then a plot showing the fluorescence intensity along the indicated line. (b) Fluorescence intensity of S1-modified GaN after repeated cycles of hybridization (with F1) and denaturation with 8.3 M urea. Also shown is a control sample of DNA-modified polycrystalline diamond.

CGA AAG CTC GAT AAG C-3' (F1, 16 bases complementary to S1 and with a 4-base mismatch to S2) and 5'-FAM-CGA TTG CTC CTT AAG C-3' (F2, 16 bases complementary to S2 and with a 4-base mismatch to S1). All oligonucleotides were purified by high-pressure liquid chromatography before use. In hybridization studies, the 5 μM oligonucleotide (F1, F2, or a mixture of both) in a standard hybridization buffer³⁴ was applied to the DNA-modified GaN surface, allowed to hybridize for 10 min, and then washed twice with the same hybridization buffer to remove any physisorbed material.

Figure 4a shows three fluorescence images of a DNA-modified GaN surface after hybridization with F1, F2, and a mixture.

(34) Hybridization buffer consists of 300 mM NaCl, 20 mM sodium dihydrogen phosphate, 2 mM ethylenediamine tetraacetic acid, and 6.9 mM sodium dodecyl sulfate, adjusted to pH 7.0.

shown are three graphs depicting the variations in fluorescence intensity along the indicated lines. After exposure to F1, a clear single spot appears at the location where S1 is bound to the surface, with no detectable increase in intensity at the location where S2 is bound. This demonstrates that F1 selectively hybridizes to S1. After this image was obtained, the sample was denatured in 8.3 M urea solution for 5 min at room temperature and rinsed with deionized water, and the fluorescence intensity was measured again (not shown here) to ensure complete removal of F1. The surface was then exposed to F2 for 10 min and imaged again. The appearance of the spot at the location of S2 shows that hybridization occurred as expected. The third image was taken after denaturation in urea solution and exposure to a mixture of F1 and F2. As expected, the fluorescence image shows hybridization at both locations. Some spatial variation in intensity is observed within each spot, with the edges showing higher intensity than the central region; we attribute this to variation in the density of oligonucleotides S1 and S2 covalently linked to the surface, analogous to the well-known "coffee-ring effect".³⁵ The fluorescence intensity associated with S2 is always lower than that of S1; this has been observed previously with these same two sequences²¹ and is attributed to the fact that oligonucleotide S2 can form hairpin-type structures that lower its overall hybridization efficiency compared with S1.

One of the most important qualities of DNA-modified surfaces is their selectivity in binding to complementary vs noncomplementary sequences. The data in Figure 4 show that, after exposure to either S1 alone (Figure 4a, top panel) or to S2 alone (Figure 4a, middle panel), there is no detectable intensity at the position on the surface where the noncomplementary oligonucleotide is located. This indicates that the DNA-modified surfaces have excellent selectivity, binding only to the molecules in solution having the complementary sequence and not to the molecules with noncomplementary sequences.

To be an effective substrate for applications such as biosensing, it is advantageous for the functionalized GaN surfaces to be stable when exposed to harsh chemical environments. The stability of DNA-functionalized GaN surfaces was tested using repeated cycles of hybridization and denaturation. In each cycle, the surface-bound DNA (S1) was hybridized with its fluorescently labeled complement (F1) for 10 min, and the average intensity of the fluorescent spot was measured. The sample was then denatured in an 8.3 M urea solution for 5 min at room temperature and rinsed with deionized water, and the fluorescence intensity was measured again to verify that complete denaturation occurred. This hybridization/denaturation process was performed five times. A polycrystalline diamond thin film modified with DNA via the same chemistry was also tested as a control in this stability experiment because previous studies of diamond have shown it to be extremely stable to repeated cycles of hybridization and denaturation.^{18,19,33}

Figure 4b shows the fluorescence intensities of DNA-modified GaN and DNA-modified diamond surfaces after exposure to F1 (oligonucleotide complementary to S1) over the five cycles. The error bars reflect the standard deviation within the experimentally measured sample area for individual samples. The amount of DNA hybridizing to DNA-modified GaN shows a small cumulative loss of ~20% after five hybridization–denaturation cycles; however, this is within the experimental error associated with the measurements, such that it is not statistically significant. The DNA-modified diamond sample also shows excellent stability, in agreement with previous results.¹⁹ The overall stability

is also similar to that reported previously on DNA-modified surfaces of gold and silicon.¹⁹ While the experiments shown here on GaN indicate that there is little or no significant degradation of the sample after five hybridization–denaturation cycles, in studies using different samples we have sometimes observed an increase in the lateral variations in fluorescence intensity with repeated cycling, and even in Figure 4 the standard deviation within the measured sample area is greater for GaN than for diamond. The increase in lateral variations may be due to scratches or other imperfections generated by the repeated physical handling needed to conduct the multiple hybridization–denaturation measurements, or it may be a sign of some chemical degradation of the sample after repeated exposure to harsh 8.3 M urea solution used in this test. Nevertheless, the ability to functionalize five times in succession with no significant loss of intensity clearly demonstrates that the DNA-modified surface is covalently linked to the surface and can exhibit very good selectivity and stability.

Discussion

Our present studies show that the photochemical reaction of H-terminated GaN surfaces with organic alkenes can be a useful starting point for providing GaN with new types of functionality by linking molecular and/or biomolecular groups to its surfaces.

The starting point for this work is hydrogen-terminated GaN. Previous studies of H termination of GaN using atomic hydrogen concluded that this procedure produces surfaces terminated with Ga–H bonds.^{31,32} While this study used H atoms generated by dissociation from a hot filament instead of a weak plasma, we also expect our surfaces to be terminated similarly. The photochemical functionalization of H-terminated surfaces of silicon^{23–27} and of diamond^{18–20} in direct contact with organic alkenes using light at 254 nm has been reported previously.^{23,27} In both cases reaction is believed to occur by abstraction of surface H atoms to produce surface "dangling bonds", which can in turn react with alkenes in solution. In the case of H-terminated diamond we showed that illumination with 254 nm light ejects electrons into the adjacent reactive fluid, and we hypothesized that these electrons produce reactive species in the liquid that, in turn, abstract H atoms from the H-terminated diamond surface to initiate the reaction with the alkenes.²⁰ The mechanism of initiation on silicon remains controversial, but is generally believed to occur through some type of electron–hole pair mechanism.^{23,27,36} In the case of GaN, a previous study³⁷ showed significant photoemission using photon energies as low as 4.1 eV from degenerately doped GaN samples. Those experiments used samples with carrier concentrations of $2 \times 10^{18} \text{ cm}^{-3}$, which is very close to the surface carrier concentration of $1.5 \times 10^{18} \text{ cm}^{-3}$ we measured on our samples from capacitance–voltage measurements.³⁷ A more recent theoretical investigation estimates the work function of bare Ga-terminated GaN(0001) at ~4.5 eV.³⁸ While much more needs to be done to identify the exact mechanism of the functionalization on GaN, these results suggest that a photoelectron emission process similar to that observed on diamond may be responsible. More importantly, the results presented here show that GaN surfaces can be functionalized with molecular monolayers (TFAAD) using photochemistry and then further modified with molecules such as DNA. The resulting surfaces exhibit high selectivity, along with stability that is comparable to that of functionalized surfaces of diamond, silicon,

(36) Langner, A.; Panarello, A.; Rivillon, S.; Vassilyev, O.; Khinast, J. G.; Chabal, Y. J. *J. Am. Chem. Soc.* **2005**, *127*, 12798–12799.

(37) Pankove, J. I.; Schade, H. *Appl. Phys. Lett.* **1974**, *25*, 53–55.

(38) Tsai, M.-H.; Sankey, O. F.; Schmidt, K. E.; Tsong, I. S. T. *Mater. Sci. Eng., B* **2002**, *88*, 40–46.

(35) Deegan, R. D.; Bakajin, O.; Dupont, R. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature* **1997**, *389*, 827–829.

and gold¹⁹ when exposed to repeated cycles of hybridization and denaturation.

Conclusions

The results presented here demonstrate that H-terminated GaN surfaces can be functionalized via photochemical reaction with organic alkenes (olefins) when illuminated with 254 nm light. The resulting surfaces can be used as a starting point for functionalization with biomolecular layers exhibiting excellent selectivity and good stability. Combined with the unusual electronic properties of GaN, these results provide a pathway for more complete integration of GaN with organic and biological

species for a range of applications including hybrid organic–inorganic electronic devices and electronic biosensors. It is likely that this method can be used for other H-passivated compound semiconductors, thereby providing a more general method for functionalizing and photopatterning chemical groups on compound semiconductor surfaces.

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