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Photopolymerization of Self-Assembled Monolayers of Diacetylenic Alkylphosphonic Acids on Group-III Nitride Substrates

Feng Li,[†] Evgeniy Shishkin,[†] Michael A. Mastro,[‡] Jennifer K. Hite,[‡]
Charles R. Eddy, Jr.,[‡] J. H. Edgar,[§] and Takashi Ito*,[†]

[†]*Department of Chemistry, Kansas State University, 213 CBC Building, Manhattan, Kansas 66506-0401,*
[‡]*Code 6880, U.S. Naval Research Laboratory, 4555 Overlook Avenue, SW, Washington, D.C. 20375, and*
[§]*Department of Chemical Engineering, Kansas State University, Durland Hall, Manhattan, Kansas 66506-5102*

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This paper describes the fabrication and characterization of photopolymerizable alkylphosphonate self-assembled monolayers (SAMs) on group-III nitride substrates including GaN and $Al_xGa_{1-x}N$ (AlGaN; $x = 0.2$ and 0.25). Contact angle goniometry, visible absorption spectroscopy, and atomic force microscopy were used to assess the formation, desorption, and photopolymerization of SAMs of diacetylenic alkylphosphonic acids ($CH_3(CH_2)_n{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_mPO(OH)_2$; $(m, n) = (3, 11), (6, 8)$, and $(9, 5)$). As with GaN substrates (Ito, T.; Forman, S. M.; Cao, C.; Li, F.; Eddy, C. R., Jr.; Mastro, M. A.; Holm, R. T.; Henry, R. L.; Hohn, K.; Edgar, J. H. *Langmuir* **2008**, *24*, 6630−6635), alkylphosphonic acids formed SAMs on UV/O_3-treated AlGaN substrates from their toluene solutions in contrast to other primary substituted hydrocarbons with a terminal −COOH, $-NH_2$, −OH, or −SH group. Diacetylenic alkylphosphonate SAMs on group-III nitrides could be polymerized by UV irradiation (254 nm), as indicated by the appearance of a visible absorption band around 640 nm and also by their significantly reduced desorption from the surface in a 0.1 M aqueous NaOH solution. A longer UV irradiation time was required to maximize the photopolymerization of a SAM having a diacetylene group close to the terminal phosphonate moiety, probably because of the hindrance of the topochemical polymerization due to the limited flexibility of the cross-linking moieties on an atomically rough substrate surface.

Introduction

This paper reports the properties of diacetylenic alkylphosphonate self-assembled monolayers (SAMs) on UV/O_3-treated, metal-polar group-III nitride substrates. These SAMs were characterized using contact angle goniometry, transmission visible absorption spectroscopy, and atomic force microscopy (AFM). Alkylphosphonate SAMs were formed on an $Al_xGa_{1-x}N$ (AlGaN) substrate, as with GaN, upon immersion in a toluene solution of an alkylphosphonic acid. A series of diacetylenic alkylphosphonic acids were synthesized to study the effects of cross-linking positions within the SAMs on their photopolymerization efficiency. Visible absorption spectra suggested that UV irradiation initially led to the photopolymerization of adjacent conjugated diacetylene groups in a SAM and then to the degradation of the cross-linked moieties, which was correlated to the stability of the SAM in 0.1 M NaOH.

Because of their unique electrical properties, low toxicity, and excellent chemical/physical stability, group-III nitride semiconductors, such as GaN and AlGaN, are employed in chemical and biological sensors.[1−3] These sensors measure changes in their electrical properties induced by the adsorption of analytes onto nitride's surface. Oxide-coated GaN and AlGaN could be used for fabricating a pH sensor because of the high affinity of its surface to OH^- and/or H^+.[1,4−7] In addition, the selectivity and sensitivity of a nitrides-based sensor can be tailored by modifying the nitride's surface with a thin layer that selectively recognizes chemical species of interest.[3] For example, organosilane SAMs with terminal binding moieties were immobilized directly onto the AlGaN surface in the gate region to control the detection selectivity of AlGaN-based transistor-type sensors.[8−11] However, formation of thick polymer layers due to the high reactivity of organosilanes with water and also the hydrolysis of organosilane SAMs at basic pH[12,13] can deteriorate the reproducibility of the sensor performance. Thiolate SAMs[14] were more commonly used to develop AlGaN-based chemical and biological sensors for various chemical and biological analytes.[3,15,16] These SAMs could

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*To whom correspondence should be addressed. E-mail: ito@ksu.edu. Telephone: 785-532-1451. Fax: 785-532-6666.

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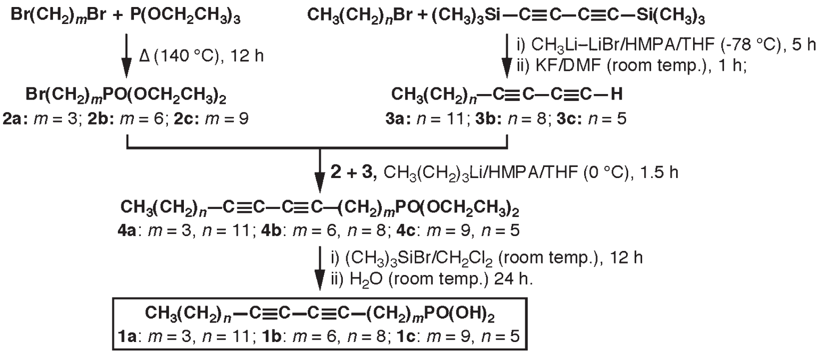
Scheme 1. Synthesis of Diacetylenic Alkylphosphonic Acids (1a−c)



be immobilized on the gold-coated gate of an AlGaN-based transistor by simpler procedures without multilayer formation. However, the thin gold layer deposited on an AlGaN gate reduced the detection sensitivity of the transistor-type sensors.

It was previously reported by us[17,18] and other researchers[19] that oxide-coated GaN substrates could be directly modified with SAMs of *n*-octadecylphosphonic acid (ODPA). The SAM formation was shown by their large water contact angle (103−109°),[17,18] ellipsometric thickness (ca. 2.4 nm),[18] XPS spectra,[18−20] and FTIR spectra.[19] In our previous reports,[18] ODPA SAMs were formed by soaking a UV/O_3-treated GaN in its organic solution regardless of the GaN polarity or dopant concentration. In contrast, primary substituted hydrocarbons with terminal −OH, −SH, $-NH_2$, and −COOH groups did not strongly adsorb onto GaN substrates.[18] The weak adsorption of $-NH_2$ and −COOH groups will allow us to modify GaN surface with organophosphonate SAMs having these terminal functional groups that can be used as linkers of other functional moieties such as antibodies. However, ODPA SAMs desorbed from GaN substrates upon immersion in aqueous solution, especially in basic solution, probably reflecting the high solubility of deprotonated ODPA in the solution,[18] electrostatic repulsion between the negatively charged ODPA and substrate surface,[18] and/or the dissolution of the gallium oxide layer.[19] The stability of a SAM in aqueous solution, which is required for its future applications to chemical and biological sensors, may be improved by cross-linking molecules in the SAM.[12]

In this study, we prepared SAMs of diacetylenic alkylphosphonic acids ($CH_3(CH_2)_n{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_mPO(OH)_2$; **1a**−**1c** in Scheme 1) on GaN and AlGaN substrates and investigated their UV-initiated polymerization behavior and their stability in basic solution. These molecules have the same chain length (i.e., $m + n =$ constant) and a conjugated diacetylene moiety at different positions. A conjugated diacetylene was chosen as a polymerization moiety, because its photopolymerization was widely investigated to improve the physical and chemical stability of nanoscale molecular assemblies,[21,22] Langmuir−Blodgett (LB) films,[12,22−27] and SAMs.[28,29] The polymerization of diacetylenic moieties occurs by simply irradiating with 254 nm UV light, although it requires well-ordered molecular packing, which is known as topochemical polymerization.[12,21,22,27] The high chemical stability of polydiacetylenes, in addition to the selective photopolymerization at the UV-irradiated area, made it possible to apply diacetylenic SAMs as ultrathin photoresists in photolithography.[30] Diacetylenic SAMs with terminal functionalities were prepared to fabricate controlled multilayers[31,32] and also to covalently immobilize chemical and biological recognition moieties.[33] In addition, polydiacetylenes have unique optical properties, leading to their applications for optical electronic devices and chemical/biological sensors.[22,33,34] The combination of the unique optical and electric properties of GaN/AlGaN and diacetylenic SAMs may thus provide a means for developing unique chemical and biological sensing devices.

Experimental Section

Chemicals and Materials. 1,3-Dibromopropane ($C_3H_6Br_2$; Alfa Aesar), 1,6-dibromohexane ($C_6H_{12}Br_2$; Aldrich), 1,9-dibromononane ($C_9H_{18}Br_2$; Aldrich), 1,4-bis(trimethylsilyl)-1,3-butadiyne ($C_{10}H_{18}Si_2$; Aldrich), 1-bromohexane ($C_6H_{13}Br$; Aldrich), 1-bromononane ($C_9H_{19}Br$; Aldrich), 1-bromododecane ($C_{12}H_{25}Br$; Acros Organics), hexamethylphosphoric triamide (HMPA; MP Biomedicals), methyllithium−lithium bromide complex (Acros Organics), *n*-butyllithium (Acros Organics), trimethylsilylbromide (C_3H_9SiBr; Aldrich), potassium fluoride dihydrate (Allied Chemical), triethyl phosphite ($(C_2H_5O)_3P$; Aldrich), *n*-octadecanol ($C_{18}H_{37}OH$; Alfa Aesar), *n*-hexadecyl mercaptan ($C_{16}H_{33}SH$; Acros Organics), *n*-octadecylamine ($C_{18}H_{37}NH_2$; Alfa Aesar), *n*-octadecanoic acid ($C_{17}H_{35}COOH$; Aldrich), *n*-octadecylphosphonic acid ($C_{18}H_{37}PO(OH)_2$, ODPA; Alfa Aesar), *N*,*N*-dimethylformamide (DMF; Fisher), and sodium hydroxide (Fisher) were used as received. Tetrahydrofuran (THF; Fisher) was dried by distillation from Na. CH_2Cl_2 was dried by distillation from CaH_2. All aqueous solutions were prepared with water having a resistance of 18 MΩ cm or higher (Barnstead Nanopure Systems). GaN epiwafers (GaN layer thickness ∼ 3 μm; on single-side polished sapphire wafers), $Al_{0.2}Ga_{0.8}N$ epiwafers (AlGaN layer thickness ∼ 1 μm; on double-side polished sapphire wafers), and $Al_{0.25}Ga_{0.75}N$

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epiwafers (AlGaN layer thickness ~ 1 μm; on double-side polished sapphire wafers) were prepared via metalorganic chemical vapor deposition (MOCVD) using thin (ca. 25−35 nm thick) aluminum nitride nucleation layers on commercial *a*-plane sapphire substrates. All GaN and AlGaN samples were *c*-plane, that is, (0001), oriented, metal- (i.e., Ga- or AlGa-) polar, and unintentionally doped. Details of the growth method are described elsewhere.[35]

Synthesis of Diacetylenic Alkylphosphonic Acids (1a−1c; Scheme 1). ^{1}H and ^{13}C NMR spectra were measured on a Varian INOVA 400 Fourier transform NMR spectrometer, and chemical shifts were reported in δ values in ppm downfield of tetramethylsilane. IR spectra were measured on a Nicolet Protege 640 spectrophotometer. Exact MS data were measured at the Mass Spectroscopy Laboratory, University of Kansas.

(*a*) *Synthesis of Diethyl* (ω-*Bromoalkyl*)*phosphonates* (**2a−2c** *in Scheme 1*).[36] The mixture of triethyl phosphite (10 mmol) with alkyl dibromide (10 mmol) was heated at 140 °C overnight. After cooling to room temperature, the reaction mixture was purified by silica gel column chromatography (elution with pure CH_2Cl_2 and then 1:15 petroleum ether/ethyl acetate) to give colorless oil. Diethyl (3-bromopropyl) phosphonate (**2a**): Yield 87%. ^{1}H NMR ($CDCl_3$) *d* 4.10 (q, J = 6.0 Hz, 4H, OCH_2), 3.48 (t, J = 6.4 Hz, 2H, $BrCH_2$), 2.15 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 1.36 (t, J = 6.8 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) *d* 61.89 (d, J = 6 Hz), 33.87 (d, J = 19 Hz), 26.15 (d, J = 4 Hz), 24.59 (d, J = 142 Hz), 16.67 (d, J = 6 Hz). IR (cm^{-1}): 2979, 2929, 2855, 1464, 1458, 1441, 1391, 1246, 1165, 1097, 1057, 1030, 959, 786, 645. Diethyl (6-bromohexyl) phosphonate (**2b**): Yield 89%. ^{1}H NMR ($CDCl_3$) δ 4.11 (q, J = 7.2 Hz, 4H, OCH_2), 3.41 (t, J = 6.8 Hz, 2H, $BrCH_2$), 1.9−1.4 (m, 10H, $(CH_2)_5$), 1.35 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ 61.62 (d, J = 7 Hz), 33.97 (d, J = 9 Hz), 32.67 (d, J = 5 Hz), 29.88 (d, J = 17 Hz), 27.67 (d, J = 35 Hz), 25.78 (d, J = 140 Hz), 22.52, 16.70 (d, J = 6 Hz). IR (cm^{-1}): 2980, 2935, 2863, 1457, 1443, 1392, 1369, 1241, 1164, 1098, 1056, 1027, 962, 799, 642. Diethyl (9-bromononyl) phosphonate (**2c**): Yield 90%. ^{1}H NMR ($CDCl_3$) δ 4.10 (q, J = 6.8 Hz, 4H, OCH_2), 3.41 (t, J = 6.8 Hz, 2H, $BrCH_2$), 1.9−1.3 (m, 16H, $(CH_2)_8$), 1.34 (t, J = 6.4 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ 61.57 (d, J = 6 Hz), 34.27, 32.96, 30.76 (d, J = 17 Hz), 29.36, 29.18, 28.88, 28.30, 26.56, 25.15, 22.60, 16.70. IR (cm^{-1}): 2980, 2929, 2855, 1465, 1458, 1442, 1391, 1369, 1247, 1164, 1098, 1057, 1029, 958, 786, 644.

(*b*) *Synthesis of 1,3-Alkadiynes* (**3a−3c** *in Scheme 1*).[37,38] An ether solution of methyllithium−lithium bromide complex (6.7 mL; 10 mmol) was added dropwise to a solution of 1,4-bis(trimethylsilyl)-1,3-butadiyne (10 mmol) in anhydrous THF (20 mL) at −78 °C and then stirred for 5 h at room temperature under argon protection. Subsequently, 1-bromoalkane (12 mmol) in fresh distilled HMPA (20 mL) was added dropwise at −78 °C and stirred for 30 min at room temperature. After the pH was adjusted to 7.0 by adding 3 M HCl at 0 °C, the mixture was extracted with ethyl acetate. After the solvent was evaporated, potassium fluoride dihydrate (20 mmol) in DMF (20 mL) was added, stirred for 1 h at room temperature, poured into 3 M HCl (15 mL) with stirring at 0 °C, and then extracted with ethyl acetate. The organic layer was washed with 3 M HCl, brine, saturated $NaHCO_3$ solution, and saturated NaCl solution and then dried over $MgSO_4$. Removal of the solvent gave a brown liquid, which was used for next step directly.

(*c*) *Synthesis of Diethyl Alkadiyn-1-phosphonates* (**4a−4c** *in Scheme 1*). To crude 1,3-alkadiyne (**3**; nominally 2.0 mmol) in anhydrous THF (8 mL) was added dropwise 1.5 mL of *n*-butyllithium (a 1.6 M solution in hexane; 2.4 mmol) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C under argon, and then a HMPA solution (8 mL) of diethyl (ω-bromoalkyl)phosphonate (**2**; 2.4 mmol) was added. The mixture was stirred for 30 min at 0 °C and then for 2 h at room temperature followed by extraction with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$ solution, water, and saturated NaCl solution and dried over $MgSO_4$, and then the solvent was evaporated. The crude product was purified by silica gel column chromatography with 20:1 ethyl acetate/hexane as eluent to give light-yellow liquid. 4,6-Nonadecadiyn-1-phosphonate (**4a**): Yield 72%. ^{1}H NMR ($CDCl_3$) δ 4.08 (q, J = 6.4 Hz, 4H, OCH_2), 2.24 (t, J = 6.8 Hz, 4H, C−CH_2), 1.8−1.2 (m, 30H, CH_2 and $OCH_2C\underline{H_3}$), 0.90 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 65.39, 65.33, 61.56, 61.50, 32.02, 30.86, 30.71, 29.62, 29.46, 29.41, 29.29, 29.23, 29.06, 28.99, 28.53 (d, J = 6 Hz), 26.57, 25.16, 22.90, 22.60 (d, J = 3 Hz), 19.35, 16.67 (d, J = 6 Hz). IR (cm^{-1}): 2977, 2928, 2854, 1456, 1391, 1248, 1164, 1099, 1058, 1029, 960, 815, 788, 722. 7,9-Nonadecadiyn-1-phosphonate (**4b**): Yield 75%. ^{1}H NMR ($CDCl_3$) δ 4.11 (q, J = 6.8 Hz, 4H, OCH_2), 2.23 (t, J = 6.8 Hz, 4H, C−CH_2), 1.8−1.3 (m, 30H, CH_2 and $OCH_2C\underline{H_3}$), 0.90 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 65.42, 65.36, 61.59, 61.53, 32.05, 30.86, 30.71, 29.64, 29.47, 29.40, 29.30, 29.24, 29.06, 28.99, 28.53 (d, J = 6 Hz), 26.57, 25.17, 22.87, 22.70 (d, J = 3 Hz), 19.39, 16.70 (d, J = 7 Hz). IR (cm^{-1}): 2979, 2929, 2855, 1457, 1392, 1244, 1164, 1097, 1057, 1031, 960, 818, 786, 702. 10,12-Nonadecadiyn-1-phosphonate (**4c**): Yield 62%. ^{1}H NMR ($CDCl_3$) δ 4.10 (q, J = 7.2 Hz, 4H, OCH_2), 2.24 (t, J = 6.8 Hz, 4H, C−CH_2), 1.8−1.2 (m, 30H, CH_2 and $OCH_2C\underline{H_3}$), 0.90 (t, 6.8 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 65.42, 65.37, 61.59, 61.53, 32.07, 30.86, 30.71, 29.64, 29.47, 29.41, 29.30, 29.24, 29.06, 28.99, 28.53 (d, J = 6 Hz), 26.54, 25.15, 22.87, 22.59 (d, J = 3 Hz), 19.32, 16.70 (d, J = 7 Hz). IR (cm^{-1}): 2979, 2927, 2855, 1465, 1391, 1245, 1164, 1098, 1058, 1030, 959, 824, 788, 723.

(*d*) *Synthesis of Diacetylenic Alkylphosphonic Acids* (*Alkadiyn-1-phosphonic Acids;* **1a−1c** *in Scheme 1*).[39] Trimethylsilylbromide (1.56 mmol) was added to an anhydrous CH_2Cl_2 solution (5 mL) of diethyl alkadiyn-1-phosphonate (**4**, 0.26 mmol) at 0 °C and then stirred overnight at room temperature. After the solvent was evaporated under reduced pressure, water (15 mL) was added and stirred for 24 h. The reaction mixture was extracted with ethyl acetate, washed with water and saturated NaCl solution, and then dried over $MgSO_4$. Removal of the solvent gave a white solid. 4,6-Nonadecadiyn-1-phosphonic acid (**1a**): Yield (from **4a**) 79%. ^{1}H NMR ($CDCl_3$) δ 2.26 (t, J = 7.2 Hz, 4H, C−CH_2), 1.8−1.2 (m, 24H, CH_2), 0.89 (t, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 65.63, 65.39, 32.07, 29.64, 29.48, 29.30, 29.06, 28.54, 22.88, 19.40, 14.33. IR (cm^{-1}): 2955, 2922, 2849, 1465, 1419, 1340, 1293, 1233, 1223, 1070, 1009, 989, 938, 724. Exact MS: m/z calculated for $C_{19}H_{32}O_3P$ (M − H), 339.2089; found, 339.2080. 7,9-Nonadecadiyn-1-phosphonic acid (**1b**): Yield (from **4b**) 82%. ^{1}H NMR ($CDCl_3$) δ 2.23 (t, J = 6.8 Hz, 4H, C−CH_2), 1.8−1.2 (m, 24H, CH_2), 0.89 (t, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 65.54, 65.38, 32.10, 29.65, 29.49, 29.31, 29.25, 29.10, 29.03, 28.59, 22.89, 19.41, 14.34. IR (cm^{-1}): 2955, 2921, 2849, 1465, 1420, 1340, 1293, 1232, 1223, 1065, 1009, 989, 938, 723. Exact MS: m/z calculated for $C_{19}H_{34}O_3P$ (M − H), 339.2089; found, 339.2089. 10,12-Nonadecadiyn-1-phosphonic acid (**1c**): Yield (from **4c**) 79%. ^{1}H NMR ($CDCl_3$) δ 2.24 (t, J = 6.4 Hz, 4H, C−CH_2), 1.8−1.2 (m, 24H, CH_2), 0.88 (t, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 65.60, 65.31, 32.07, 29.66, 29.49, 29.31, 29.22, 29.06, 29.00, 28.55, 22.65, 19.41, 14.35. IR (cm^{-1}): 2954, 2920, 2848, 1464, 1420, 1342, 1293, 1233, 1222, 1072, 1011, 989, 935, 727. Exact MS: m/z calculated for $C_{19}H_{32}O_3P$ (M + H), 341.2246; found, 341.2242.

Preparation and Characterization of Group-III Nitride Samples. Group-III nitride samples coated with phosphonate SAMs were prepared according to our previous report.[18] In short, GaN or AlGaN substrates (ca. 5 × 5 mm^2) were soaked in 50% HCl for 1 min, rinsed with water, dried under an Ar stream, and then treated by UV/O_3 for 30 min in a Novascan PSD-UVT UV/

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ozone system. The resulting UV/O_3-treated substrates were immersed in a 0.1 mM toluene solution of an organic compound for 17 h, thoroughly washed with toluene, and dried under an Ar stream. Diacetylenic alkylphosphonate SAMs were polymerized with a low intensity UV lamp (Spectronics model EF-180, 254 nm, 1.9 mW cm^{-2} at 25 cm) at a distance of 10 cm in an Ar-purged glovebag. Water contact angles on group-III nitride samples were measured using a PG-1 pocket contact angle goniometer by reading contact angle values of the two sides of a drop (2 μL) within 30 s after deposition of the drop. To study the stability of diacetylenic alkylphosphonate SAMs on group-III nitrides, SAM-coated substrates were immersed in 0.1 M NaOH for 10−240 min at room temperature, quickly washed with water, and dried under an Ar stream, and their water contact angles were measured. Transmission visible absorption spectra of diacetylenic alkylphosphonate SAMs on $Al_{0.25}Ga_{0.75}N$ substrates deposited onto double-side polished sapphire wafers were recorded on a Varian *Cary*500 spectrophotometer. A UV/O_3-treated substrate was used as a reference, and diacetylenic alkylphosphonate SAMs on the AlGaN after UV irradiation for 0, 2, 5, 6, 8, or 10 min were used as samples. Contact mode AFM images were obtained by contact-mode imaging in air, using a digital instruments multimode atomic force microscope with Nanoscope IIIa electronics. Contact-mode pyramidal AFM tips were purchased from Veeco (model NP-10).

Results and Discussion

Water Contact Angle Measurements of GaN and AlGaN Substrate Surfaces after the Adsorption of a Primary Substituted Hydrocarbon. Prior to investigating the properties of diacetylenic alkylphosphonate SAMs, adsorption of primary substituted hydrocarbons with different terminal functional groups (−OH, −SH, $-NH_2$, −COOH, or $-PO(OH)_2$) onto GaN and AlGaN (x = 0.2, 0.25) was assessed by measuring the water contact angle (θ^{water}). We previously reported the essential contribution of hydrogen bond interactions between polar functional groups and surface oxide layers to the adsorption of these compounds onto GaN substrates.[17,18] Considering that the chemical properties (e.g., hydrogen bond acidity and basicity) of a surface oxide layer would be altered according to the substrate composition, the surfaces of group-III nitride substrates with different Al/Ga ratios may exhibit different adsorptivities of these compounds.

Just after UV/O_3 treatment, the surfaces of AlGaN substrates were hydrophilic ($\theta^{water} < 15°$), as with UV/O_3-treated GaN surfaces,[17,18] suggesting the formation of a hydrophilic surface oxide layer. After immersion in a 0.1 mM toluene solution for 17 h, which was long enough to reach the adsorption equilibrium, the θ^{water} values of AlGaN surfaces increased (Table 1) due to the adsorption of a primary substituted hydrocarbon onto the surfaces. Regardless of the substrates, the adsorption of n-$C_{18}H_{37}PO(OH)_2$ (ODPA) resulted in hydrophobic surfaces with very high θ^{water} values (> 100°), suggesting ODPA SAM formation on these substrates probably due to the strong hydrogen bond acidity/basicity of the $-PO(OH)_2$ group.[18] In contrast, the other four compounds did not strongly adsorb onto the substrates, as shown by the much lower θ^{water} values (< 80°, Table 1). Interestingly, the θ^{water} values of AlGaN substrates upon the adsorption of these four compounds were significantly smaller than those of GaN substrates. In addition, the difference in θ^{water} values between n-$C_{17}H_{35}COOH$ and n-$C_{18}H_{37}NH_2$ was larger on AlGaN as compared to GaN.

The different molecular adsorption behavior between UV/O_3-treated GaN and AlGaN substrates may be explained on the basis of the difference in their surface chemical compositions. The oxide layer on AlGaN surface would consist of the mixture of Al_2O_3 and Ga_2O_3,[40] whereas that on GaN consists only of Ga_2O_3.[41−43] The lower adsorptivity (i.e., smaller θ^{water}) of UV/O_3-treated AlGaN substrates may reflect the lower surface density of hydrogen bonding sites on Al_2O_3 as compared to Ga_2O_3.[44] The stronger adsorption of acidic n-$C_{17}H_{35}COOH$ on the AlGaN substrates over basic n-$C_{18}H_{37}NH_2$ is probably due to the higher basicity and much lower acidity of Al_2O_3 surface.[44,45] These θ^{water} values of the ODPA SAMs on GaN and AlGaN were smaller than those previously reported on the Al_2O_3 surface of sputtered Al.[46] The larger θ^{water} values in the literature may reflect the surface roughness of the Al substrates and may also be due to the use of a different method, the dynamic Wilhelmy method. Indeed, our θ^{water} value of the ODPA SAMs on single-crystal sapphire substrates was 103°, close to our θ^{water} values on GaN and AGaN.

Table 1. Water Contact Angle (deg)[a] of Chemical Modified Group-III Nitride Substrates[b]

	GaN	$Al_{0.2}Ga_{0.8}N$	$Al_{0.25}Ga_{0.75}N$
n-$C_{18}H_{37}OH$	72.7 ± 1.2	63.3 ± 3.1	62.6 ± 1.6
n-$C_{16}H_{33}SH$	71.7 ± 0.8	54.8 ± 1.3	56.7 ± 1.0
n-$C_{18}H_{37}NH_2$	71.7 ± 1.4	63.1 ± 0.8	61.2 ± 2.2
n-$C_{17}H_{35}COOH$	75.0 ± 1.3	70.2 ± 0.7	67.2 ± 3.7
n-$C_{18}H_{37}PO(OH)_2$	104.9 ± 1.2	103.1 ± 0.4	102.9 ± 0.1

[a] Average ± standard deviation from three separate samples. [b] Substrates treated in a UV/O_3 cleaner for 30 min were immersed in a 0.1 mM toluene solution for 17 h.

Comparison of the Stability of Diacetylenic Alkylphosphonate SAMs on GaN in Basic Solution before and after UV Irradiation. The above results suggest that ODPA SAMs can be formed on UV/O_3-treated GaN and AlGaN substrates. As with ODPA (Table 1), the high θ^{water} values of GaN and AlGaN substrates (102−104°) were similarly observed after immersion in a toluene solution containing one of diacetylenic alkylphosphonic acids (**1a**−**1c**). The high θ^{water} values suggest the SAM formation of diacetylenic alkylphosphonic acids on GaN and AlGaN substrates,[18] permitting us to employ these substrates for investigating the properties of diacetylenic alkylphosphonate SAMs.

However, these SAMs without UV irradiation desorbed from the substrates upon immersing in 0.1 M NaOH, as reported for ODPA SAMs on GaN[18,19] and Al_2O_3.[46] For example, Figure 1 (open circles) shows the θ^{water} values of **1b**-coated GaN substrates at different immersion times. Within 10 min, the θ^{water} values decreased from 103° to ca. 65° and then did not change upon immersion for an extended time. In contrast, the desorption of **1b** SAMs on GaN substrates in 0.1 M NaOH was reduced by UV irradiation at 254 nm (Figure 1, filled circles). The UV irradiation led to a slight decrease in θ^{water} from 103° to 96°, as shown by the data at t = 0 min. The θ^{water} of SAMs of **1a**−**1c** on GaN and AlGaN similarly decreased upon UV irradiation from 102−104° to 95−96°, maybe due to changes in molecular packing and/or partial degradation of the SAMs induced by the UV light.[47] More importantly, after the initial decrease from 96° within the first 10 min, the θ^{water} values did not change to be ca. 82° upon prolonged

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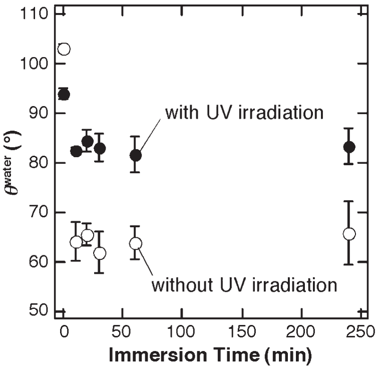

Figure 1. Water contact angles (θ^{water}) of SAMs of diacetylenic alkylphosphoric acid (**1b**) formed on GaN after soaking in 0.1 M NaOH for 0, 10, 20, 30, 60, and 240 min at room temperature. Filled and open circles represent data obtained for SAMs with and without the UV irradiation (254 nm, 6 min), respectively. The plots and error bars indicate the average and standard deviation, respectively, measured using three separate samples.

immersion in 0.1 M NaOH. The significantly higher plateau θ^{water} values of UV-irradiated SAMs would indicate the improved chemical stability of the SAMs due to the photopolymerization of the conjugated diacetylene moieties. On the other hand, the decrease in θ^{water} for the first 10 min of immersion may result from the partial desorption of molecules at defect sites in the SAM (vide infra).

Effect of UV Irradiation Time on the Stability of Diacetylenic Alkylphosphonate SAMs on GaN in Basic Solution. For all the diacetylenic alkylphosphonic acids examined, UV irradiation led to the reduced desorption of their SAMs on GaN in basic solution. Figure 2 summarizes the effect of UV irradiation time (t_{UV}) on the water contact angle of the SAMs of **1a**−**1c** after immersion in 0.1 M NaOH for 4 h (θ_{NaOH}^{water}). Without UV irradiation (i.e., at t_{UV} = 0 min), θ_{NaOH}^{water} was ca. 60° for all the SAMs examined, indicating that these SAMs similarly desorbed in 0.1 M NaOH. With increasing t_{UV}, θ_{NaOH}^{water} increased up to ca. 80°, indicating the reduced desorption of the SAMs due to the photopolymerization of conjugated diacetylene moieties in the SAMs. However, prolonged UV irradiation led to a slight decrease in θ_{NaOH}^{water}, which would be due to the degradation of the SAMs induced by the UV irradiation (vide infra).[48,49] Interestingly, t_{UV} that gave the highest θ_{NaOH}^{water} was longer for **1a**, which has a conjugated diacetylene moiety closer to a terminal phosphonic acid group, probably reflecting the feasibility of the UV-initiated polymerization of diacetylene moieties. The photopolymerization and degradation of the SAMs could be verified from their visible absorption spectra described in the next section.

Visible Absorption Spectra of Diacetylenic Alkylphosphonate SAMs on AlGaN. Figure 3 shows transmission visible absorption spectra of a SAM of **1c** on $Al_{0.25}Ga_{0.75}N$ at different t_{UV}. At t_{UV} = 0 min, except a peak around 580−600 nm due to the AlGaN epilayer,[50,51] there was no peak originating from the diacetylenic alkylphosphonate SAM in the wavelength range of 500−700 nm. Upon UV irradiation, a broad peak around 640 nm appeared. The height of the peak increased up to 6 min and then decreased for longer t_{UV}. The peak around 640 nm could be assigned to $\pi-\pi^*$ electronic transition in the blue form of polydiacetylene.[12,22,27,34] Indeed, the maximum absorbance obtained at t_{UV} = 6 min (ca. 0.002) was similar to that of a polydiacetylene monolayer reported previously.[32,47] On the other hand, a peak around 540 nm due to the red form of polydiacetylene[12,22,27,34] was not observed even for the prolonged t_{UV}, indicating that the decrease in 640 nm peak intensity for the longer t_{UV} would be due to the degradation of the polydiacetylene on AlGaN induced by UV irradiation. The UV-induced degradation of polydiacetylene was reported previously.[48,49]

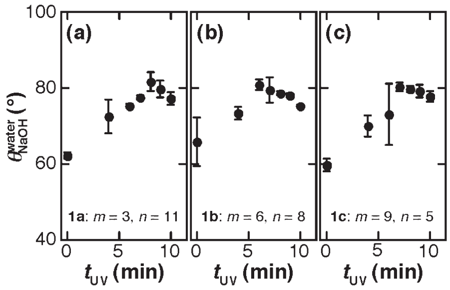

Figure 2. Influence of UV irradiation time (t_{UV}) on water contact angle of diacetylenic phosphonate SAMs on GaN measured after soaking in 0.1 M NaOH for 4 h at room temperature (θ_{NaOH}^{water}): (a) **1a**; (b) **1b**; (c) **1c**. The plots and error bars indicate the average and standard deviation, respectively, measured using three separate samples.

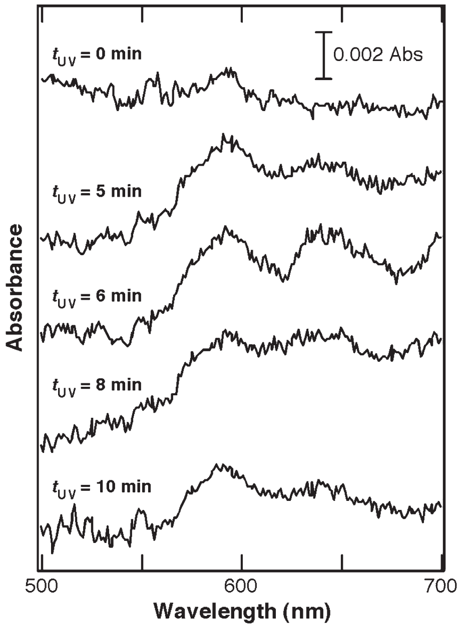

Figure 3. Visible absorption spectra of SAMs of **1c** formed on $Al_{0.25}Ga_{0.75}N$ substrates at different UV irradiation times. A peak around 580−600 nm originated from the substrate, which could not be completely subtracted from the background visible absorption spectrum.

Similar changes in the absorbance at 640 nm upon UV irradiation were observed for SAMs of the diacetylenic alkylphosphonic acids (**1a**−**1c**), as summarized in Figure 4. t_{UV} that gave the maximum absorbance (i.e., the maximum polymerization) was longer in the order of **1a** > **1b** ~ **1c**. This order corresponded to that of t_{UV} required for maximum stability in basic solution (Figure 2), supporting the claim that the improved stability of the diacetylenic alkylphosphonate SAMs (Figure 1) was due to their UV-initiated polymerization. In addition, the order suggests photopolymerization was less efficient as the diacetylene moieties were closer to the substrate (i.e., **1a**), which was consistent to the

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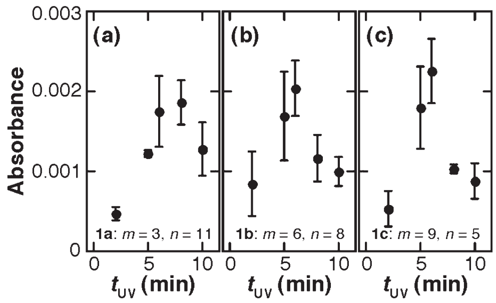

Figure 4. Relationship between the absorbance of diacetylenic phosphonate SAMs formed on $Al_{0.25}Ga_{0.75}N$ at 645 nm and UV irradiation time (t_{UV}): (a) **1a**; (b) **1b**; (c) **1c**. The peak height was determined by Gaussian fitting of a peak. The plots and error bars indicate the average and standard deviation, respectively, measured using three separate samples.

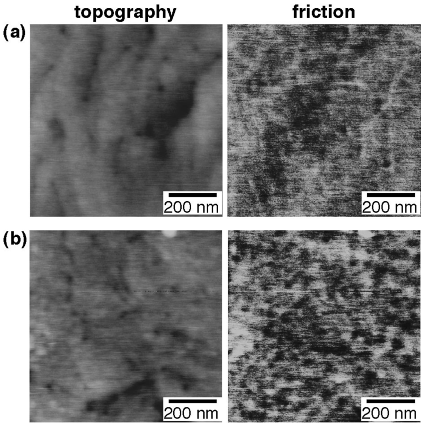

Figure 5. Contact mode topography (left) and friction (right) images of a UV-irradiated (6 min) SAM of diacetylenic phosphoric acid **1b** on GaN (a) before and (b) after soaking in 0.1 M NaOH for 4 h at room temperature. The topography and friction images were taken at the same area simultaneously.

trend observed in the photopolymerization yield of diacetylenic thiolate SAMs on gold.[52] The lower efficiency probably reflected the hindrance of the topochemical polymerization due to the limited flexibility of the diacetylene moieties.[53] In comparison, more efficient photopolymerization was observed in a LB film of an amphiphilic compound having the same total hydrophobic chain length with a diacetylene moiety near a hydrophilic headgroup.[23] In LB films, the head groups were not completely fixed to the air/water interface, and thus the photopolymerization efficiency was mainly determined by molecular packing that was better for compounds with longer alkyl chains.[23]

AFM Images of a Photopolymerized Diacetylenic Alkylphosphonate SAM on GaN before and after Immersion in Basic Solution. In addition, AFM images of a photopolymerized diacetylenic SAM on GaN were measured to understand its partial desorption in 0.1 M NaOH (Figure 1, filled circles). Figure 5 shows topographic and friction images of a UV-irradiated SAM of **1b** on GaN before and after immersion in 0.1 M NaOH for 4 h. The topographic images prior to the immersion (Figure 5a, left) showed step features that reflected the underlying surface structure of a GaN substrate fabricated by the MOCVD method,[9,17] suggesting uniform coverage of the surface with the SAM. In contrast, after immersion in 0.1 M NaOH, a number of pits were observed in the topographic image, especially at the step edges (Figure 5b, left). The surface heterogeneity was more clearly shown in the frictional images (i.e., the right images of Figure 5a and b). The pits were probably formed as a result of the desorption of the SAM molecules that were not highly cross-linked at their defects. The preferential desorption at the step edges may reflect the hindered topochemical photopolymerization of diacetylene moieties at the step edges of the substrate[53] and also the higher accessibility of the basic solution to the resulting defect sites in the SAM.

Conclusions

This paper described the SAM formation of diacetylenic alkylphosphonate SAMs on group-III nitride substrates and their photopolymerization. UV/O_3-treated AlGaN substrates could be used to prepare alkylphosphonate SAMs, as with UV/O_3-treated GaN substrates. They exhibited weaker adsorption of the other primary substituted hydrocarbons as compared to GaN maybe due to the presence of Al_2O_3 having lower hydrogen bond acidity. More importantly, the UV-initiated photopolymerization of diacetylenic alkylphosphonate SAMs reduced their desorption in aqueous basic solution. SAMs containing diacetylene moieties farther from terminal phosphonate groups exhibited more efficient photopolymerization. However, the hindrance of the topochemical polymerization at the III-N surface step edges and the UV-induced degradation of polydiacetylene on group-III nitride surface limited the uniform functionalization with diacetylenic alkylphosphonate SAMs. The results reported here will allow for designing alkylphosphonic acid derivatives suitable to functionalize group-III nitrides and other semiconductor surfaces[14,54] not only for future sensor applications but also for power sources such as dye-sensitized solar cells.[55]

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Supporting Information Available: ^1H NMR, ^{13}C NMR, and IR spectra of compounds **1a**−**c**, **2a**−**c**, and **4a**−**c**, and the mass spectra of compounds **1a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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