# Enhanced Photonic Stability of GaAs in Aqueous Electrolyte Using Alkanethiol Self-Assembled Monolayers and Postprocessing with Ammonium Sulfide

Palani Arudra, Gregory M. Marshall, Neng Liu, and Jan J. Dubowski*

Laboratory for Quantum Semiconductors and Photon-based Bio-Nanotechnology, Department of Electrical and Computer Engineering, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada

S *Supporting Information*

ABSTRACT: The photonic stability of sulfurized GaAs(001) exposed to phosphate buffered saline (PBS) solution was investigated by in situ photoluminescence (PL). Results show that samples first coated with hexadecanethiol (HDT) self-assembled monolayers (SAMs), and post-treated with ammonium sulfide, exhibited a dramatic stability increase in PBS solution. The initial PL intensity was observed to be about 3 times higher relative to samples prepared with HDT SAMs alone. X-ray photoelectron spectroscopy measurements showed the presence of increased sulfur content in accordance with the observed enhancement of PL intensity. Infrared spectroscopy measurements indicate that HDT SAMs remain well-ordered following ammonium sulfide treatment. This hybrid passivation method of GaAs is potentially attractive to the development of biosensing architectures based on PL emission from III−V quantum semiconductors.
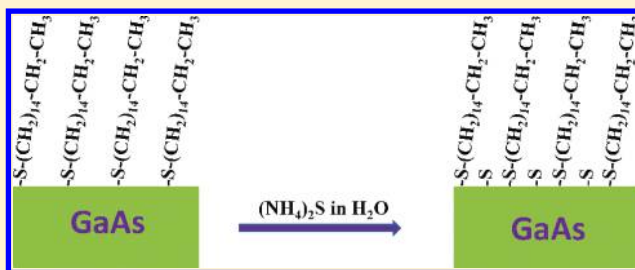
INTRODUCTION

Traditionally, III−V semiconductor surfaces have been discussed in terms of their electronic characteristics and the development of junction-based devices. More recently, these surfaces have attracted research interest resulting from their sensitivity to molecular adsorbates and electrochemical environments, often in the context of sensor development. For instance, we have used GaAs to observe the decomposition of thimerosal, an important pharmaceutical antiseptic/antifungal-agent, in phosphate-buffered physiological saline (PBS) solution.[1] A significant problem hindering the use of GaAs and other III−V semiconductors in the development of functional interfaces for biodetection concerns an effective means of surface passivation and stabilization in physiological environments, while maintaining a high degree sensitivity. Chemically, passivation acts to remove the native oxide layer replacing it with a stabilizing layer that inhibits reoxidation in situ. The application of self-assembled monolayers (SAMs) using long-chain alkanethiols,[2−8] alkane phosphates,[9] or exposure to various inorganic sulphide treatments, including sodium and ammonium sulphides (AS),[10−20] are surface modification techniques that have been explored as a means to passivate GaAs(001). In the context of biosensitive devices, alkanethiol SAMs can serve two practical requirements: surface passivation via thiol coupling and chemical specificity via terminal-group functionalization. From an electronic point of view, passivation corresponds to a decrease in the surface recombination velocity (SRV) of minority carriers, which has been a significant factor contributing to photoluminescence (PL) enhancements in sulfide and thiol treated GaAs.[11,21,22]

Adlkofer and Tanaka reported that deposition of octadecylthiol (ODT) monolayers on highly doped *n*-GaAs improves its stability in air and in aqueous electrolytes as observed in electrochemical impedance spectroscopy experiments.[23] However, other reports have indicated that thiol-GaAs coupling alone does not render an effective degree of electronic passivation.[22,24,25] Recent theoretical calculations show that thiols bind to both Ga and As but cover only 50% of the available surface sites.[5,21] Thus, if SAMs are to be employed as a means to functionalize the GaAs surface in sensor applications, a new strategy is required in order to improve the site coverage and increase the quality of passivation. To address this problem, we report on a hybrid approach that achieves enhanced photonic stability of GaAs(001) through an initial passivation using alkanethiol SAMs, followed by AS treatment.

EXPERMENTAL DETAILS

Reagents. AS (40−48% in H_2O), hexadecanethiol (HDT), and PBS were obtained from Sigma-Aldrich, Canada. The water used for all experiments was purified with a Milli-Q system. Optic-clear (National diagnostics, USA), acetone (ACP chemicals, Canada), isopropyl alcohol (IPA) (Anachemia, Canada), and NH_4OH (Anachemia) were used without further purification.

Sample Preparation. A nominally undoped GaAs capped AlGaAs/GaAs multilayer structure, the details of which are reported elsewhere,[26] was grown by molecular beam epitaxy on a semi-insulating GaAs(001) substrate and used for all PL measurements. Otherwise, an undoped double-side polished semi-insulating GaAs(001) wafer was employed. The formation of HDT SAMs was carried out on the oxide-free surface of GaAs(001) using standard protocols as follows.[26] Wafers were cleaned by an ultrasonic bath for 5 min sequentially in each of the Optic-clear, acetone, and isopropanol solvents. The wafers were then dried with nitrogen and etched in NH_4OH (28%) solution for 2 min. The etched samples were immediately washed with degassed ethanol and kept in a 2 mM solution of HDT in ethanol for 20 h. Two sets of samples were prepared by rinsing the wafers with either distilled water or IPA and subsequently exposing them to AS solution (20% $(NH_4)_2S$ in H_2O) for 15 min. The processed samples were immediately exposed to degassed PBS solution and kept in a windowed reaction chamber suitable for PL measurements without exposure to air.

Photoluminescence Measurements. PL measurements were carried out with a custom-designed Hyperspectral Imaging PL Mapper (HI-PLM). The computer-based interface of the HI-PLM system automated the collection of a time series of PL maps in 10 min intervals. Sample illumination was controlled by a computer-programmed shutter that opened during PL integration time only. A fused silica window reflected 4% of the excitation source to a Centronic OSD100-7Q calibrated silicon photodiode for power normalization, establishing PL stability within 3% variation. PL excitation was achieved by flooding the sample area with a homogenized beam using a 532 nm laser. To avoid possible laser-induced degradation of the thiol−GaAs interface, the excitation power was kept in the low-injection regime, not exceeding 120 mW/cm^2.[26] The acquisition time to obtain a PL map in the spectral region of interest ($\lambda \approx 870$ nm) was about 70 s. The HI-PLM instrument allows the collection of PL maps on samples of dimension up to 7 mm × 7 mm with a spatial resolution of 5 μm. However, for the purpose of this experiment, the PL signal was averaged over the entire sample surface. An increase in PL intensity provides qualitative evidence of improved passivation by means of the chemical and electronic effects referred to above. The PL measurements were carried out either immediately after drying the processed samples with nitrogen or in situ by observing the PL intensity from samples exposed directly to PBS solution over a 5 h period.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) spectra were recorded in UHV ($<10^{-9}$ Torr) with an Axis Ultra DLD (Kratos Analytical Ltd., UK) utilizing a monochromatic Al Kα source (1486.6 eV) and analyzer pass energy of 20 eV. The analysis area (700 μm × 300 μm) was defined by an aperture in the transfer lens column. The data were collected for a takeoff angle of 60° with respect to the surface normal. The binding energy reference to untreated GaAs wafer was positioned at the As 3d5/2 peak at 41.37 eV,[6] which was subsequently used as a nominal calibration. No charge neutralization current was applied. Peak fitting and quantification analysis were performed, using the software package CasaXPS,[27] in terms of the chemical states and atomic percentages of thiol species present on the GaAs surface.

Fourier Transform Infrared (FTIR) Spectroscopy. Mid-IR spectra were recorded in transmission using a Bruker Optics Hyperion 2000 IR microscope coupled to a Bruker Optics Tensor 27 FTIR spectrometer. The probing spot size was approximately 2 mm in diameter and the spectral resolution was set at 4 cm^{-1}. Analysis focused on the spectral region of the C−H stretching modes associated with the alkane CH_2 asymmetric (2918 cm^{-1}) and symmetric (2850 cm^{-1}) vibrations. The position and full width at half-maximum (FWHM) of absorption peaks relates to the molecular orientation and ordering of the SAMs.[6,22]

■ RESULTS AND DISCUSSION

The increase of PL signal and its saturation was observed in situ for GaAs samples exposed to thiol solution similarly to the results reported earlier.[26] The dynamics of this process suggests that both saturation of the surface coverage and minimization of the thiolate conformational disorder take place within less than, typically, 20 h. The PL intensity of HDT SAM coated GaAs samples, rinsed with IPA or H_2O, and subsequently processed in AS solution is summarized in Table 1. For

Table 1. PL Measurements of Dried GaAs(001) Samples Coated with HDT or AS Treated, and Post-Processed As Indicated

sample treatment	PL peak intensity
HDT with IPA wash	160 (1.0)
HDT with H$_2$O wash	222 (1.39)
AS with H$_2$O wash	288 (1.80)
AS with HDT and IPA wash	189 (1.18)
HDT with IPA wash and AS	528 (3.30)
HDT with H$_2$O wash and AS	579 (3.62)

comparison, the PL response from samples exposed to AS and HDT only is also shown along with the response from samples first exposed to AS, then thiolated with HDT and rinsed as indicated. It can be seen that the HDT SAM coated sample, if washed with H_2O, yields a PL signal 40% stronger than the HDT coated (reference) sample that was washed with IPA. The PL intensity of the hybrid processed sample, i.e., HDT SAM coated, washed with IPA, and exposed to AS solution, is 3.3 times higher compared to that of the reference sample, but the hybrid HDT SAM/AS treated sample, if washed with H_2O, shows an even greater PL enhancement (3.62). The mechanism behind the increased PL intensity of samples washed with H_2O is not clear. It is known that HDT is not highly soluble in H_2O; thus, it is possible that in contrast to IPA, water rinsing leaves some physisorbed thiols on the GaAs surface. The presence of physisorbed material could introduce an additional physical barrier to oxidation and other atmospheric reactions in the dried samples and thus contribute to enhanced PL signal. Note that the AS treated and H_2O rinsed sample yielded a PL signal that was 80% more intense relative to the HDT coated and IPA rinsed reference. However, a similar AS treated sample subsequently exposed to HDT solution and washed with IPA, showed only a marginally increased PL signal (1.18). This minor increase of the PL intensity seems to suggest that the AS treatment of a fresh GaAs surface does not saturate the surface with S atoms, leaving it partially oxidized. This observation is consistent with the limited surface coverage achieved with AS dissolved in H_2O, as reported by Bessolov et al.[15]

In all cases, the PL intensity of HDT SAM coated samples that were also exposed to AS increased by more than 3 times when compared to the reference sample. We attribute this

behavior to the reduction of the surface states, such as Ga dangling bonds that are responsible for the formation of PL reducing gap states. Reduction of As dangling bonds is of minor importance in that context as it is known that As−S antibonding states appear within the GaAs gap.[28,29] Increased PL intensity could also be related to reduced band-bending in the near-surface region of GaAs. Our experiments have suggested that SAM formation only minimally affects band-bending in GaAs(001) due to Fermi level pinning[22] and that the PL enhancement, which is typically about 1.5 times, is due to a maximized reduction of SRV.[24] Therefore, it is expected that further enhancement of the PL intensity following AS treatment of SAM coated samples is accounted for by a reduction of the GaAs surface state density to a level below the pinning threshold, which results in a more significant band-bending reduction.

The environmental stability of samples immersed in PBS solution at pH = 7.4 was investigated by collecting PL signal from HDT SAM coated samples and comparing to that of the AS only treated sample. A series of time-dependent PL intensity (I_{PL}) runs up to 300 min has been presented in Figure S1 of the Supporting Information. In Table 2, we present absolute values

Table 2. In situ PL Intensity (I_{PL}) from Processed GaAs Samples Immersed in PBS Solution at pH 7.4^a

sample treatment	I_{PL} at a given time (min)		
	0	180	240
AS with H$_2$O wash	125	0	0
HDT with IPA wash	61	0.25	0.02
HDT with H$_2$O wash	97	0.29	0.04
HDT with IPA wash and AS	336	0.32	0.16
HDT with H$_2$0 wash and AS	387	0.65	0.20

^{a}For each case, data are normalized to I_{PL} at $t = 0$.

of I_{PL} observed at $t = 0$, 180, and 240 min. It can be seen that at $t = 0$, the PL signal from the AS-only treated GaAs sample washed with H$_2$O is approximately 2 and 1.5 times stronger than that from HDT SAM coated samples that were rinsed with IPA and H$_2$O, respectively. However, HDT SAM coated samples, washed with either IPA or H$_2$O and postprocessed in AS solution, show a PL signal enhanced by 2.7 and 3.0 times, in comparison to the AS-only treated GaAs sample. In addition, the hybrid processed samples demonstrate enhanced stability in the PBS environment over time relative to the samples processed with a singular treatment. The dynamics of the PL signal decay indicates that, e.g., the HDT SAMs provide a certain level of passivation against degradation in the PBS environment; however, a decay to 2−4% of its initial value within 4 h for these samples indicates that SAM formation alone is not effective against deterioration in a biological environment on this time scale. It should be noted that a stable photonic response from GaAs could be achieved, e.g., by coating it with SiO$_2$ or other optically transparent dielectric layers. Unfortunately, this would reduce, or even eliminate, the sensitivity of the semiconductor material to surface immobilized biomolecules, such as viruses and bacteria. As indicated in Table 2, for HDT/AS hybrid processing, the H$_2$O washed sample has better short-term stability, but this difference becomes less evident after 4 h. More to the point, the 4 h stability of the hybrid treated samples has been improved at least 5 times compared to HDT processing alone, independent

of the rinsing solvent used. In the following paragraphs, both FTIR and XPS measurements confirm that the enhanced photonic stability of GaAs in PBS is indeed related to the increased concentration of surface sulfur atoms.

The FWHM of both asymmetric (2918 cm^{-1}) and symmetric (2850 cm^{-1}) C−H stretching modes associated with linear alkane (CH$_2$ groups) is shown in Table 3. These results have

Table 3. FWHM of FTIR Peaks Corresponding to Symmetric (∼2850 cm^{-1}) and Asymmetric (∼2918 cm^{-1}) Vibrations of CH$_2$ Molecules and Intensities of FTIR Asymmetric CH$_2$ Peaks (I_{ASY}) in HDT SAMs on the GaAs(001) Surface^a

sample treatment	FWHM$_{SYM}$ (cm^{-1})	FWHM$_{ASY}$(cm^{-1})	$I_{ASY} \times 10^4$
HDT [30 minutes]; IPA wash	11.10(2851)^b	19.01(2920)^b	11.4^b
HDT [14 h]; IPA wash	11.03(2850)^b	17.11(2918)^b	23.7^b
HDT [20 h]; IPA wash	9.42(2850)	16.50(2918)	14.7
HDT [20 h]; H$_2$O wash	8.91(2849)	12.54(2918)	18.4
HDT [20 h]; IPA wash and AS	12.25(2850)	15.33(2918)	3.9
HDT [20 h]; H$_2$O wash and AS	8.51(2850)	12.80(2919)	55.7

^{a}HDT SAM coated samples were IPA or H$_2$O washed with or without AS treatment. The values of FTIR peak positions are shown in curly brackets. ^{b}Reference 26.

been extracted from the FTIR absorption spectra reported in Figure S2 in the Supporting Information. The fwhm of the HDT treated sample decreases as the time of incubation is increased. This suggests that the formation of well-ordered HDT SAM structures takes place on the GaAs surface with increasing time of incubation.[26,30] A greater value of FWHM corresponds to a more disordered structure as reported in the literature.[31] Also, the FWHM of CH$_2$ stretching modes in the HDT treated sample washed with H$_2$O is narrower than that in the IPA washed sample. This suggests that H$_2$O washing allows achieving a better organized SAM, or alternatively, IPA washing degrades the SAM to some degree. As shown in Table 3, the effect of H$_2$O washing is illustrated by higher FTIR peak intensities corresponding to asymmetric C−H modes of the HDT samples. In particular, the AS treated water washed HDT sample shows the FTIR peak intensity 3-times greater in comparison to the water washed only HDT sample (I_{ASY} = 55.7 × 10^{-4} vs 18.4 × 10^{-4}).

The Ga 3s spectra of the GaAs surface treated with (i) AS only, (ii) HDT and postprocessed with AS, and (iii) AS processed and HDT SAM coated are shown in Figure 1. It shows the S 2p doublet, with 162.15 and 163.35 eV peaks assigned to S 2p3/2 and S 2p1/2, respectively.[32−35] The atomic percentage of sulfur in each sample was calculated using the XPS data. The sample treated with AS shows 4.30% of sulfur, whereas the HDT SAM coated and AS post-treated sample shows 5.95% of sulfur. In contrast, the HDT SAM coated sample that was pretreated with AS, shows only 4.05% of atomic sulfur. This lower sulfur concentration suggests that SAM formation on even a partially sulfurized GaAs surface is limited due to the presence of chemisorbed sulfur atoms. It is also possible that the AS treatment leaves zones of the oxidized GaAs surface, which would reduce the efficiency of SAM formation. Our XPS data corroborate the observation of an increased photonic stability of GaAs in aqueous
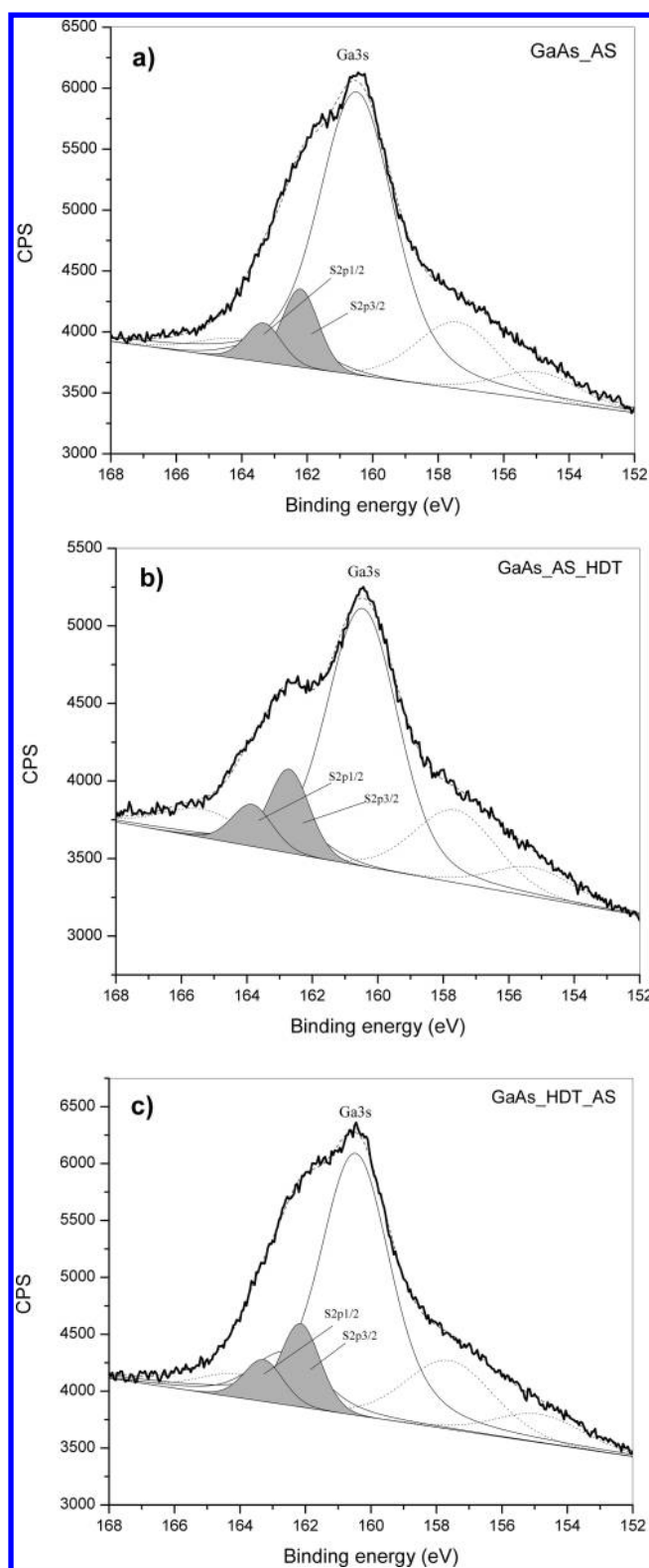
Figure 1. Angle-resolved XPS data of the Ga 3s peak region for GaAs(001) surface (a) treated with AS only, (b) AS + HDT treated sample, and (c) HDT + AS treated sample. The inelastic scattering is shown by the broken line.

solution, and clearly show that the AS post-treatment of HDT SAM samples increases the concentration of surficial sulfur atoms that are responsible for the improved surface passivation.

In summary, to address the deficiency of SAM formation processes on the GaAs(001) surface, we have introduced the additional step consisting of treatment of HDT SAM coated samples in the AS solution. This hybrid approach allows increasing density of sulfur atoms reacting with Ga and As, as indicated by the XPS measurements, which drastically increases photonic stability of such material in hydrous environment of PBS. The FTIR analysis of both asymmetric and symmetric stretching modes of the alkanethiol SAM CH_2 group confirms that the AS treatment does not affect significantly the quality of formed SAMs; however, it increases the overall concentration of S atoms on the GaAs surface. Although further improvement of the stability of this material in aqueous electrolytes seems feasible, the reported here results demonstrate the feasibility of new PL-based experiments aiming detection of surface immobilized biomolecules in a variety of biological fluids.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

In situ PL intensity (IPL) from processed GaAs samples immersed in PBS solution at pH 7.4. FTIR absorption spectra of HDT SAMs on GaAs surface washed with IPA or H_2O and followed by AS treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Tel: 819-821-8000. Fax: 819-821-7937. URL: http://www.dubowski.ca.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Palani, A.; Nguiffo-Podie, Y.; Frost, E.; Dubowski, J. J. Decomposition of Thimerosal and Dynamics of Thiosalicylic Acid Attachment on GaAs(001) Surface Observed with in Situ Photoluminescence. *J. Phys. Chem. C* **2010**, *114*, 13657−13662.

(2) McGuiness, C. L.; Shaporenko, A.; Mars, C. K.; Uppili, S.; Zharnikov, M.; Allara, D. L. Molecular Self-Assembly at Bare Semiconductor Surfaces: Preparation and Characterization of Highly Organized Octadecanethiolate Monolayers on GaAs(001). *J. Am. Chem. Soc.* **2006**, *128*, 5231−5243.

(3) McGuiness, C. L.; Blasini, D.; Masejewski, J. P.; Uppili, S.; Cabarcos, O. M.; Smilgies, D.; Allara, D. L. Molecular Self-Assembly at Bare Semiconductor Surfaces: Characterization of a Homologous Series of *n*-Alkanethiolate Monolayers on GaAs(001). *ACS Nano* **2007**, *1*, 30−49.

(4) Voznyy, O.; Dubowski, J. J. Adsorption Kinetics of Hydrogen Sulfide and Thiols on GaAs(001) Surfaces in a Vacuum. *J. Phys. Chem. C* **2008**, *112*, 3726−3733.

(5) Voznyy, O.; Dubowski, J. J. Structure of Thiol Self-Assembled Monolayers Commensurate with the GaAs(001) Surface. *Langmuir* **2008**, *24*, 13299−13305.

(6) Marshall, G. M.; Lopinski, G. P.; Bensebaa, F.; Dubowski, J. J. Surface Dipole Layer Potential Induced IR Absorption Enhancement in *n*-Alkanethiol SAMs on GaAs(001). *Langmuir* **2009**, *25*, 13561−13568.

(7) McGuiness, C. L.; Diehl, G. A.; Blasini, D.; Smilgies, D. M.; Zhu, M.; Samarth, N.; Weidner, T.; Ballav, N.; Zharnikov, M.; Allara, D. L. Molecular Self-Assembly at Bare Semiconductor Surfaces: Cooperative Substrate−Molecule Effects in Octadecanethiolate

Monolayer Assemblies on GaAs(111), (110), and (100). *ACS Nano* **2010**, *4*, 3447−3465.

(8) Zhou, C.; Walker, A. V. UV Photooxidation and Photopatterning of Alkanethiolate Self-Assembled Monolayers (SAMs) on GaAs (001). *Langmuir* **2007**, *23*, 8876−8881.

(9) Artzi, R.; Daube., S. S.; Cohen, H.; Naaman, R. Adsorption of Organic Phosphate as a Means To Bind Biological Molecules to GaAs Surfaces. *Langmuir* **2003**, *19*, 7392−7398.

(10) Carpenter, M. S.; Melloch, M. R.; Lundstrom, M. S.; Tobin, S. P. Effects of Na_2S and $(NH_4)_2S$ Edge Passivation Treatments on the Dark Current−Voltage Characteristics of GaAspn Diodes. *Appl. Phys. Lett.* **1988**, *52*, 2157−2159.

(11) Lunt, S. R.; Ryba, G. N.; Santangelo, P. G.; Lewis, N. S. Chemical Studies of the Passivation of GaAs Surface Recombination Using Sulfides and Thiols. *J. Appl. Phys.* **1991**, *70*, 7449−7465.

(12) Lebedev, M. V. Sulfur Adsorption at GaAs: Role of the Adsorbate Solvation and Reactivity in Modification of Semiconductor Surface Electronic Structure. *J. Phys. Chem. B* **2001**, *105*, 5427−5433.

(13) Bessolov, V. N.; Lebedev, M. V.; Ivankov, A. F.; Bauhofer, W.; Zahn, D. R. T. Electronic Properties of GaAs(100) Surface Passivated in Alcoholic Sulfide Solutions. *Appl. Surf. Sci.* **1998**, *133*, 17−22.

(14) Bessolov, V. N.; Lebedev, M. V.; Ivankov, A. F.; Bauhofer, W.; Zahn, D. R. T. Sulphide Passivation of GaAs: The Role of the Sulphur Chemical Activity. *Semicond. Sci. Technol.* **1998**, *13*, 611−614.

(15) Bessolov, V. N.; Konenkova, E. V.; Lebedev, M. V. A Comparison of the Effectiveness of GaAs Surface Passivation with Sodium and Ammonium Sulfide Solutions. *Phys. Solid State* **1997**, *39*, 54−57.

(16) Carpenter, M. S.; Melloch, M. R.; Cowans, B. A.; Dardas, Z.; Delgass, W. N. Investigations of Ammonium Sulfide Surface Treatments on GaAs. *J. Vac. Sci. Technol.* **1989**, *B7*, 845−850.

(17) Konenkova, E. V. Modification of GaAs(100) and GaN(0001) Surfaces by Treatment in Alcoholic Sulfide Solutions. *Vaccum* **2002**, *67*, 43−52.

(18) Spindt, C. J.; Liu, D.; Miyano, K.; Meissner, P. L.; Chiang, T. T.; Kendelewicz, T.; Lindau, I.; Spicer, W. E. Vacuum Ultraviolet Photoelectron Spectroscopy of Ammonium Sulfide-Treated Gallium Arsenide (100) Surfaces. *Appl. Phys. Lett.* **1989**, *55*, 861−863.

(19) Lebedev, M. V.; Mayer, T.; Jaegermann, W. Sulfur Adsorption at GaAs(100) from Solution: Role of the Solvent in Surface Chemistry. *Surf. Sci.* **2003**, *547*, 171−183.

(20) Saravanan, S.; Soga, T.; Jimbo, T.; Umeno, M. Deep Levels Reduction in $(NH_4)_2S$ Treated and Annealed GaAs Epilayer on Si Substrate. *Mater. Sci. Eng., B* **2001**, *B84*, 195−199.

(21) Dubowski, J. J.; Voznyy, O.; Marshall, G. M. Molecular Self-Assembly and Passivation of GaAs(001) with Alkanethiol Monolayers: A View Towards Bio-Functionalization. *Appl. Surf. Sci.* **2010**, *256*, 5714−5721.

(22) Marshall, G. M.; Bensebaa, F.; Dubowski, J. J. Surface Barrier Analysis of Semi Insulating and n+-type GaAs(001) Following Passivation with *n*-Alkanethiol SAMs. *Appl. Surf. Sci.* **2011**, *257*, 4543−4546.

(23) Adlkofer, K.; Tanaka, M. Stable Surface Coating of Gallium Arsenide with Octadecylthiol Monolayers. *Langmuir* **2001**, *17*, 4267−4273.

(24) Marshall, G. M.; Bensebaa, F.; Dubowski, J. J. Electro-optic Investigation of the Surface Trapping Efficiency in *n*-Alkanethiol SAM Passivated GaAs(001). *Nanotechnology* **2011**, *22*, 235704.

(25) Moumanis, K.; Ding, X.; Dubowski, J. J.; Frost, E. Aging and Detergent Washing Effects of the Surface of (001) and (110) GaAs Passivated with Hexadecanethiol. *J. Appl. Phys.* **2006**, *100*, 034702.

(26) Kim, C. K.; Marshall, G. M.; Martin, M.; Bisson-Viens, M.; Wasilewski, Z.; Dubowski, J. J. Formation Dynamics of Hexadecanethiol Self-Assembled Monolayers on (001) GaAs Observed with Photoluminescence and Fourier Transform Infrared Spectroscopies. *J. Appl. Phys.* **2009**, *106*, 083518.

(27) Fairley, N. *CasaXPS*, version 2.3.10, 1999−2005.

(28) Ohno, T.; Shiraishi, K. First-Principles Study of Sulfur Passivation of GaAs(001) Surfaces. *Phys. Rev. B* **1990**, *42*, 11194−11197.

(29) Voznyy, O.; Dubowski, J. J. Structure, Bonding Nature, and Binding Energy of Alkanethiolate on As-Rich GaAs(001) Surface: A Density Functional Theory Study. *J. Phys. Chem. B* **2006**, *110*, 23619−23622.

(30) Marshall, G. M.; Bensebaa, F.; Dubowski, J. J. Observation of Surface Enhanced IR Absorption Coefficient in Alkanethiol Based Self-Assembled Monolayers on GaAs(001). *J. Appl. Phys.* **2009**, *105*, 094310.

(31) Wang, L.; Reehal, H. S.; Martínez, F. L.; Andrés, E. S.; Prado, A. D. Characterization of Nitrogen-Rich Silicon Nitride Films Grown by the Electron Cyclotron Resonance Plasma Technique. *Semicond. Sci. Technol.* **2003**, *18*, 633−641.

(32) Shaporenko, A.; Adlkofer, K.; Johansson, L. S. O.; Ulman, A.; Grunze, M.; Tanaka, M.; Zharnikov, M. Spectroscopic Characterization of 4'-Substituted Aromatic Self-Assembled Monolayers on GaAs(100) Surface. *J. Phys. Chem. B* **2004**, *108*, 17964−17972.

(33) Szuber, J.; Bergignat, E.; Hollinger, G.; Polakowska, A.; Koscielniak, P. XPS Study of the Surface Fermi Level of $(NH_4)_2Sx$-passivated GaAs(100) Surface. *Vacuum* **2002**, *67*, 53−58.

(34) Kang, M.-G.; Park, H.-H. Effect of Prepared GaAs Surface on the Sulfidation with $(NH_4)_2Sx$ Solution. *J. Vacuum Sci. Technol., A* **1999**, *17*, 88−92.

(35) Lee, J.-L. Sulfur Doping of GaAs with $(NH_4)_2Sx$ Solution. *J. Appl. Phys.* **1999**, *85*, 807−811.