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Mixed Adlayer of Alkanethiol and Peptide on GaAs(100): Quantitative Characterization by X-ray Photoelectron Spectroscopy

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Homogeneous and mixed adlayers composed of an alkanethiol (1-octadecanethiol, ODT) and a peptide (CGISYGRKKRRRQRRR) on GaAs(100) were formed in two different solvent systems: phosphate-buffered saline (PBS) and *N,N*-dimethylformamide (DMF). The chemical composition of each adlayer was characterized by X-ray photoelectron spectroscopy (XPS). The data showed that the makeup of the adlayer and its stability largely depends on the solvent used. Angle-resolved XPS also revealed that the adlayer thickness and tilt angles were different from values obtained from ellipsometry measurements and vastly varied between the two solvents used. The coverage data extracted from the XPS measurements indicated that homogeneous adlayers of peptide in PBS buffer form a multilayered film. Homogeneous alkanethiol adlayers exhibited monolayer coverage under all solvent treatments. Coadsorbed layers containing both alkanethiol and peptide have fractional monolayer coverage in both solvents.

Introduction

Surface gradients can be of great importance for a variety of studies that aim to understand the function and properties of composite materials or constructs.¹ Surface gradients can be easily fabricated without expensive equipment through the formation of mixed self-assembled monolayers.² In particular, mixed monolayers containing a specific biomolecule of interest are worth studying because they can potentially modify substrates with preprogrammed and reproducible coverage and be incorporated in cell-based *in vitro* studies.³ In addition, the use of mixed monolayers can facilitate the preservation of the biological activity of analytes such as DNA.⁴ Experiments have been performed to understand the properties and function of mixed monolayers composed of alkanethiols and DNA on gold surfaces.⁵ Researchers have utilized Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and electrochemical methods and have proven the techniques' utility to obtain quantitative information with regard to composition and coverage. Despite these promising data on gold films,⁶ relatively few reports have used surface characterization tools to understand and quantify the properties of homogeneous or mixed adlayers containing biomolecules on other surfaces.^{7–10}

In recent years a number of research groups have pointed out the importance of doing systematic surface studies on technologically important semiconductor materials such as GaAs.^{11–15} Recent reports have contributed to an improved understanding of what factors can play a role in interfacial and intermolecular ordering on the bare semiconductor surface when alkanethiols are utilized as adsorbates.^{16–18} The latest studies have presented more complete and thorough information due to improvements in the analytical techniques and instrumentation that were employed. Among the latest studies of molecular layers on GaAs surfaces, relatively few reports have used biomolecules as adsorbates on this material.^{19,20}

In this report we utilize XPS to gather quantitative information with regard to the composition, thickness, coverage, and tilt angles of mixed adlayers composed of an alkanethiol and a peptide on GaAs(100). The peptide used to form the mixed adlayer was chosen for its specific recognition properties. This peptide sequence is derived from the TAT protein and has been shown to bind with high affinity to the stem–loop region of TAR-RNA.²¹ The mixed adlayers were originally designed and prepared

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in order to test the feasibility of using GaAs junction field-effect transistors as part of a label-free detection scheme.²² Our previous studies showed that protection of the surface via adlayer formation is important for the reproducible and reliable response of the device. The quantitative information we extract in the present study with regard to the composition of the mixed layer is very important in terms of designing and optimizing surface passivation strategies that can result in GaAs-based devices with good reproducibility, stability, specificity, and selectivity.

Experimental Section

Reagents and Materials. n-Type GaAs(100) wafers doped with $(0.5-5) \times 10^{18} \text{ cm}^{-3}$ Si were purchased from Wafer Technology Ltd. (Payson, AZ). 1-Octadecanethiol (ODT, 98%) was purchased from Aldrich. All other solvents were purchased from Mallinckrodt Chemicals. The peptide, CGISYGRKKRRQRRR, was synthesized by AnaSpec (San Jose, CA). The sequence was purified by HPLC and then analyzed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectroscopy.

Surface Cleaning and Modification. Small pieces of GaAs ($0.5 \times 0.5 \text{ cm}^2$) were consecutively cleaned by ultrasonication with three solvents: acetone, 2-propanol, and pure ethanol. Immediately after cleaning, each surface was immersed in concentrated HCl solution for 1 min to remove the native oxide layer on the surface. The GaAs substrates were then rinsed multiple times with water and pure ethanol. In order to study the effect of solvent on the formation of homogeneous adlayers, we prepared two separate solutions (1 mM each) of the peptide in phosphate-buffered saline (PBS) solution and *N,N*-dimethylformamide (DMF). The cleaned GaAs wafers were incubated in the two types of peptide solutions for 24 h at 4–8 °C. Following this treatment, the wafers were rinsed several times with water to remove unbound molecules. Homogeneous adlayers of ODT were formed by immersing the surface in a 1 mM solution prepared in either ethanol or DMF. All samples were thoroughly washed with the solvent used to make the 1 mM solution and dried under nitrogen gas. Mixed adlayers were prepared by first incubating the samples in ODT in either ethanol or DMF, and subsequently placing each sample in a peptide solution of either PBS buffer or DMF for 24 h. Subsequently the wafers pieces were rinsed with solvent and dried under nitrogen gas.

X-ray Photoelectron Spectroscopy. XPS data were obtained by a Kratos Ultra DLD spectrometer using monochromatic Al K α radiation ($h\nu = 1486.58 \text{ eV}$). The survey and high-resolution spectra were collected at fixed analyzer pass energy of 160 and 20 eV, respectively. The spectra were collected at angles 0°, 30°, 45°, 60°, and 75° with respect to the surface normal. Atomic concentrations of the chemical elements on the near-surface region were estimated after subtraction of a Shirley-type background, with the corresponding Scofield atomic sensitivity factors and inelastic mean free path (IMFP) of photoelectrons taken into account by standard procedures in the CasaXPS software. The binding energy (BE) referring to the Fermi level were corrected by use of the C 1s value at 284.80 eV for surfaces treated with adsorbates in DMF solvent. BE for surfaces treated with adsorbates in PBS buffer was corrected by use of the As 3d value at 40.95 eV. A commercial Kratos charge neutralizer was used to achieve a resolution of 0.6–0.7 eV measured at the full width at half-maximum (fwhm) of the As 3d and Ga 3d deconvoluted spin-orbital split doublets. The XPS spectra were fitted with the CasaXPS software, with the assumption of a Gaussian–Lorentzian line shape.

Quantitative XPS Analysis. As described by Fadley,²³ the photoemission intensity from a semi-infinite and atomically clean surface can be written as

$$N_s^0(\theta) = I_0 \Omega_0(E_s) A_0(E_s) D_0 \rho \frac{d\sigma_s}{d\Omega} \Lambda_e(E_s) \cos \theta \quad (1)$$

where $N_s^0(\theta)$ is the peak intensity of the substrate, I_0 is the intensity of the X-ray flux, Ω_0 is the acceptance solid angle of the electron analyzer, A_0 is the effective area of the specimen over which $\Omega_0 \neq 0$, and D_0 is the instrument detection efficiency. D_0 is independent of the kinetic energy of the photoelectrons if the energy analyzer operates in the constant pass energy regime. In addition, θ is the photoemission angle between the surface normal and the electron emission direction; $d\sigma_s/d\Omega$ is the differential cross section, which can be calculated from tabulated Scofield cross-sections and the Reilman asymmetric parameter; $\Lambda_e(E_s)$ is the electron attenuation length of the substrate photoelectron. The electron attenuation length (EAL) is a function of the kinetic energy of the photoelectrons and is also dependent on the properties of the material, where the photoelectrons propagate. The EAL values can be calculated by a software package, NIST SRD-82,²⁴ utilizing the kinetic energy (KE) of the electrons and the photoionization asymmetry parameters (β).

A uniform overlayer of thickness t results in an attenuation of the signal from the substrate as

$$N_s(\theta) = I_0 \Omega_0(E_s) A_0(E_s) D_0 \rho \frac{d\sigma_s}{d\Omega} \Lambda_e(E_s) \cos \theta \exp\left(\frac{-t}{\Lambda_e(E_s) \cos \theta}\right) \quad (2)$$

The intensity ratio between the clean substrate and the substrate covered with a uniform overlayer can be used to calculate the adlayer thickness:

$$\frac{N_s(\theta)}{N_s^0(\theta)} = \exp\left[\frac{-t}{\Lambda_e(E_s) \cos \theta}\right] \quad (3)$$

The plot of $\ln [N_s(\theta)/N_s^0(\theta)]$ versus $1/\cos \theta$ should have the slope equal to $-t/\Lambda_e(E_s)$. We believe that using a graphic approach is more reliable than a single point measurement, in which significant experimental error can arise even from the background subtraction. On the other hand, graphic interpretation of the angle-resolved XPS data allows us to even minimize the roughness effects.²⁵ For $N_s^0(\theta)$, the peak intensity of the clean substrate, the signal from the Ar-sputtered GaAs(001) surface was used. We took the photoemission from the As 2p_{3/2}, Ga 2p_{3/2}, As 3d, and Ga 3d core levels as the signal from the substrate.

Adsorbate coverage was calculated by use of a nonattenuating adlayer approximation proposed by Fadley,²³ in which the intensity overlayer/substrate ratio can be described by eq 4:

$$\frac{N_l(\theta)}{N_s(\theta)} = \frac{\Omega_0(E_l) A_0(E_l) D_0(E_l) \frac{d\sigma_l}{d\Omega} d}{\Omega_0(E_s) A_0(E_s) D_0(E_s) \frac{d\sigma_s}{d\Omega} \Lambda_e^{\text{subst}}(E_s) \cos \theta} \left(\frac{s_{\text{over},l}}{s_{\text{subst}}}\right) \quad (4)$$

Here, in addition to the parameters described above, $s_{\text{over},l}$ is the mean surface density of atoms in which the peak l is expressed per square centimeter, s_{subst} is the mean surface density of the substrate atoms expressed per square centimeter, $s_{\text{over},l}/s_{\text{subst}}$ is the fractional adlayer coverage of the atomic species in which the photoemission peak l originates, and d is the mean separation between layers with density s in the substrate. For the substrate signal we used C 1s, N 1s, and S 2p peaks.

The oxide overlayer signal can be represented by the following formula:

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$$N_i(\theta) =$$

$$I_0 \Omega_0(E_i) A_0(E_i) D_0 \rho_i \frac{d\sigma_i}{d\Omega} \Lambda_e^{\text{over},l}(E_i) (\cos \theta) \left[1 - \exp\left(\frac{-t}{\Lambda_e^{\text{over},l}(E_i) \cos \theta}\right) \right] \quad (5)$$

where $\Lambda_e^{\text{over},l}(E_i)$ is the electron attenuation length of the photoelectron in the overlayer. Since the kinetic energy difference between the photoelectron emitted from the substrate and from the overlayer is a few electronvolts, the electron attenuation length for the substrate and overlayer photoelectron might be assumed to be equal. The analogue of the Hill equation²⁵ can be obtained by dividing eq 2 by eq 5:

$$t = \Lambda_e(E_k)(\cos \theta) \ln \left[1 + \frac{N_i(\theta) \rho_s}{N_s(\theta) \rho_i} \right] \quad (6)$$

The difference between eq 6 and the original Hill equation²⁵ is the term ρ_s/ρ_i , which represents the density difference between the substrate and the overlayer.

Results and Discussion

This section focuses on assessing differences in the properties of homogeneous and mixed adlayers composed of an alkanethiol (ODT) and a short synthetic peptide (CGISYGRKKRRQRRR) sequence when two different solvent systems were used. The quantitative characterization is done by XPS, which has been shown to be useful in assessing the properties of biomolecules on surfaces.^{10,26} The XPS data were initially utilized to verify the presence of the chosen adsorbates on the GaAs(100) surface and to monitor the oxidation of the surface. Angle-resolved XPS data and curve-fitting were employed in order to elucidate the type of bonding between the surface and the adsorbates. The same data were also analyzed to calculate the thicknesses of the homogeneous and mixed adlayers. The tilt angles were estimated on the basis of these thickness values and the length of each molecule used. The numbers of C-, N-, and S-containing species on the surface were calculated from Fadley's formalism.

Oxidation States of GaAs(100). Prior work has shown that compounds like ODT can successfully passivate the GaAs surface but prolonged exposure to water-based solutions leads to gradual etching.²⁷ For our device to work, we prepared mixed adlayers in buffer and DMF.²² We started the detailed XPS characterization by first assessing whether there are any differences in terms of the chemical species on the surface when the two solvents were used. Data were collected on surfaces functionalized with homogeneous adlayers containing (i) ODT, (ii) peptides, and (iii) mixed adlayers of ODT and peptides in PBS buffer and DMF. We wanted to assess to what extent the stability and chemical makeup of the surface are affected by the presence of additional ions in the buffer solution. Figures 1 and 2 show the Ga 2p_{3/2}, As 3d, and Ga 3d core-level spectra obtained for (1) GaAs(100) cleaned in HCl, (2) GaAs(100) functionalized with ODT in ethanol and in DMF, (3) GaAs(100) functionalized with the peptide, and (4) GaAs functionalized with the mixed adlayer of ODT and peptide. The As 3d spectra were fitted with three pairs (spin-orbital splitting) of components: one pair was for As-Ga, the other pair was for individual As,²⁸ and the third pair was for As₂O₃. Typically, the contribution of the individual As component was very minor. The Ga 3d spectra were fitted with a pair for Ga-As and another pair for Ga₂O₃. The Ga 2p_{3/2} and As 2p_{3/2} spectra were fitted with two components for Ga-As and for oxides. The fingerprint components of Ga₂O₃ and As₂O₃ were detected in the As 3d and Ga 3d spectra at 20.3 and ~44.5

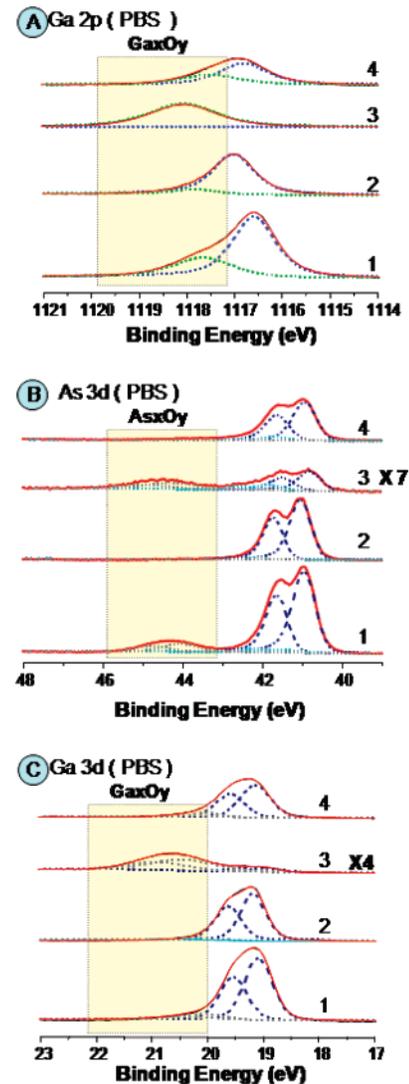


Figure 1. High-resolution XPS spectra of (a) Ga 2p_{3/2}, (b) As 3d, and (c) Ga 3d regions on GaAs surfaces treated in PBS buffer: (1) clean surface, (2) ODT functionalized in ethanol, (3) peptide functionalized, and (4) ODT-peptide functionalized.

eV, respectively, when the GaAs(100) surface etched in HCl was examined. The oxide layer most likely forms during the transfer to the XPS chamber. The thickness of the oxide layers was calculated from eq 6, and the results are shown in Table 1. After immobilization of ODT on the surface by use of either solvent, the oxide was hardly detectable in the As 3d and Ga 3d spectra. In order to increase the surface sensitivity, the As 2p_{3/2} and Ga 2p_{3/2} peaks were used. The kinetic energies of the photoelectron emitted from As 3d and Ga 3d via Al K α radiation ($h\nu = 1486.58$ eV) are ~1445 and 1467 eV, respectively. The corresponding values for As 2p_{3/2} and Ga 2p_{3/2} are 164 and 370 eV, respectively. Therefore, IMFPs for the 3d and 2p photoelectrons in GaAs are 29.8/30.2 Å (As/Ga) and 6.7/10.9 Å (As/Ga).²⁹ The large IMFP values for the 3d lines make them less effective to monitor the oxidation. On the other hand, comparison between the bulk-sensitive 3d lines and the surface-sensitive 2p photoemission peaks can provide valuable information about the oxide layer morphology. As shown in Table 1, the oxide layer thickness is approximately 1 Å for surfaces treated in ethanol (PBS). Surfaces treated in DMF solution were the least effective

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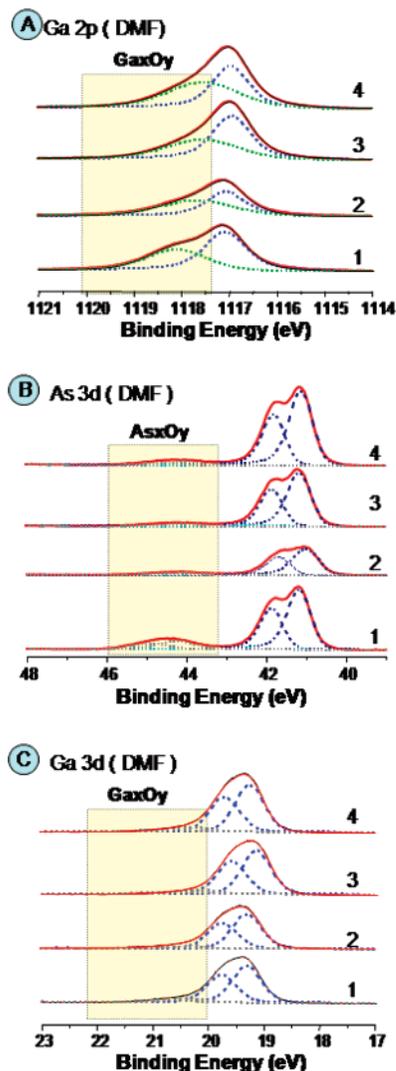


Figure 2. High-resolution XPS spectra of (a) Ga $2p_{3/2}$, (b) As 3d, and (c) Ga 3d regions on GaAs surfaces treated in DMF: (1) clean surface, (2) ODT functionalized in DMF, (3) peptide functionalized, and (4) ODT-peptide functionalized.

Table 1. Oxide Layer Thickness Formed on Surfaces after Different Functionalizations in DMF and PBS^a

	Ga ₂ O ₃ , Å (based on Ga 3d)	As ₂ O ₃ , Å (based on As 3d)
PBS Buffer Solution ^b		
clean	9.3 ± 0.0	14.1 ± 0.6
ODT	1.4 ± 0.2	1.3 ± 0.5
peptide	43.7 ± 13.2	61.3 ± 15.8
ODT/peptide	6.2 ± 2.0	10.3 ± 2.3
DMF Solvent		
clean	12.1 ± 0.8	18.1 ± 2.1
ODT	6.3 ± 0.9	10.0 ± 1.4
peptide	7.1 ± 0.5	11.2 ± 1.2
ODT/peptide	6.1 ± 0.0	9.8 ± 0.4

^a Thickness was averaged through the different photoemission angles excluding 75° due to noticeable elastic scattering of photoelectrons.²⁵ The As $2p_{3/2}$ peak was not acquired. ^b ODT was prepared in ethanol.

in terms of successful passivation with ODT. The thicknesses were calculated on the basis of four photoemission peaks: Ga 3d, As 3d, Ga $2p_{3/2}$, As $2p_{3/2}$. The values demonstrate a consistent trend and the details are discussed below.

The oxide layer thicknesses in the mixed adlayers prepared in PBS buffer and DMF solutions are in the range of 6 Å and are similar to values obtained after the analysis of surfaces functionalized with ODT in DMF. This proves that the coadsorbed layer can effectively protect the surface. On the other hand, the

Table 2. Percentages of Ga and As after Different Treatments^a

	Ga, ^b %	As, ^b %
PBS Buffer Solution ^c		
clean	48.6	51.4
ODT	53.1	46.9
peptide	76.1	23.9
ODT/peptide	54.1	45.9
DMF Solvent		
clean	49.8	50.2
ODT	52.6	47.4
peptide	51.6	48.4
ODT/peptide	52.3	47.7

^a Calculated for the normal photoemission. ^b Based on Ga 3d and As 3d. ^c ODT was prepared in ethanol.

surface functionalized with the peptide can be easily oxidized. Moreover, after treatment of the substrate with peptide in PBS solution, the surface is coated with an oxide layer of approximately 50 Å. Likely, the big and flexible peptide molecules lack the ability to form a dense layer and therefore cannot protect the surface from oxidation.

It is remarkable that the surface ratio between arsenic and gallium changes depending on the treatments. The As/Ga proportions are shown in Table 2. The GaAs(100) surface after etching with HCl is characterized by approximately 1:1 Ga/As ratio with a small excess of arsenic on the surface, whereas upon treatment with the adsorbates the Ga/As balance changes. After the functionalization with peptide in PBS buffer as a solvent, without any prior passivation with ODT, the abundance of arsenic decreases to 24%. This result is consistent with previous reports that have explained how unprotected GaAs exposed to water and oxygen allows the corrosion of the surface to take place, releasing H₂AsO₃⁻.²⁷ The other treatments led to significantly less depletion of As from the surface. The abundance of arsenic in the oxide layer was also depleted. The mismatch between the oxide thicknesses calculated on the basis of bulk-sensitive 3d lines and surface-sensitive 2p lines (Table 1) supports the notion that the oxide film is not a flat layer. Likely, the oxide propagates to the bulk as pits. The oxide pits are thought to form at surface defects such as steps. The oxidation of the surface protected with the adsorbed molecules should occur through the defects in the adsorbed layer. As soon as the oxide pit appears, arsenic starts to be washed out as H₂AsO₃.

Adsorbed Layer Composition. We applied the curve-fitting analysis to the C 1s, N 1s/Ga Auger, and S 2p/Ga 3s regions in order to identify the adsorbed species. For the C 1s region, shown in Figure 3, the analysis we used was similar to the one described in ref 10: the number of chemical states of the carbon atom was determined from the peptide structure and the constraint was built accordingly. There are six different carbon species that one expects to find on the basis of the peptide structure: (1) carbon bonded only to carbon and/or hydrogen, (2) carbon coordinated with one nitrogen atom along with a carbon and/or a hydrogen atom, (3) carbon atom with a single bond to an oxygen atom, (4) carbon from an amide group, (5) carbon atom with a double bond to oxygen atom, and (6) carbon coordinating with three nitrogen atoms, as in arginine. Different chemical shifts of the C 1s peak are expected, dependent on the presence of certain carbon species on the surface. The intensities of the components should be proportional to the abundance of the chemical state. The number of carbon chemical states and the expected ratios between the corresponding components of the peptide constraint are shown in Table 3. The components for residual hydrocarbons and ODT (C–C contamination and C–C from ODT) were included in the curve-fitting. The C 1s spectra along with the curve-fitting analysis are shown in Figure 3. The components amide, C–N, and CN₃ components were detected on the peptide and ODT-peptide treated surfaces, confirming the presence of the peptide on the GaAs(100) surface. The curve-fitting procedure

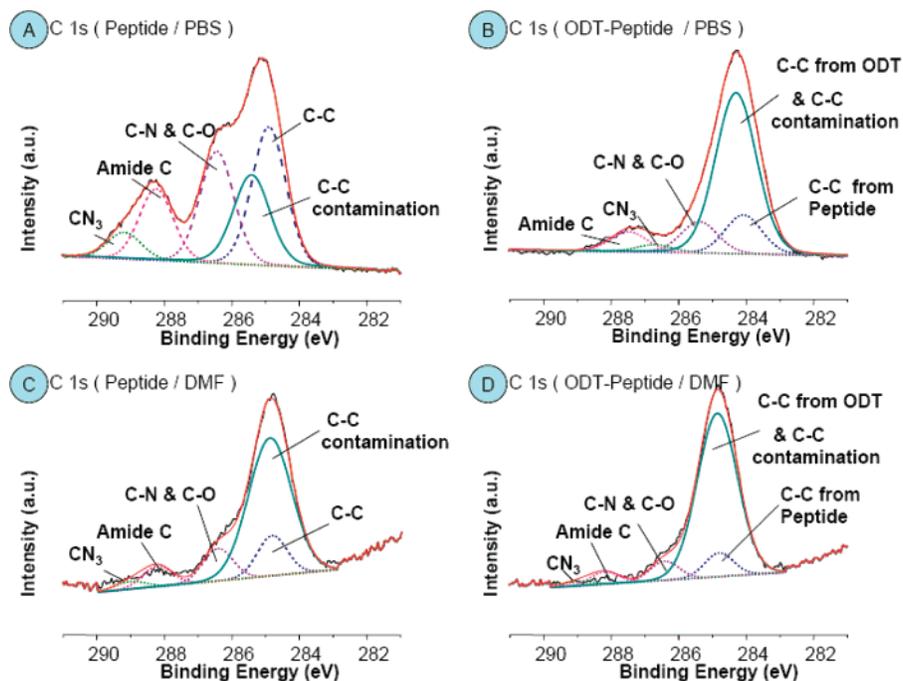


Figure 3. High-resolution XPS C 1s spectra obtained at the photoemission angle of 0° for GaAs(100) modified in PBS buffer or DMF: (A) peptide functionalization in PBS, (B) ODT-peptide sequential treatment in ethanol and PBS buffer, (C) peptide functionalization in DMF, and (D) ODT-peptide sequential treatment in DMF.

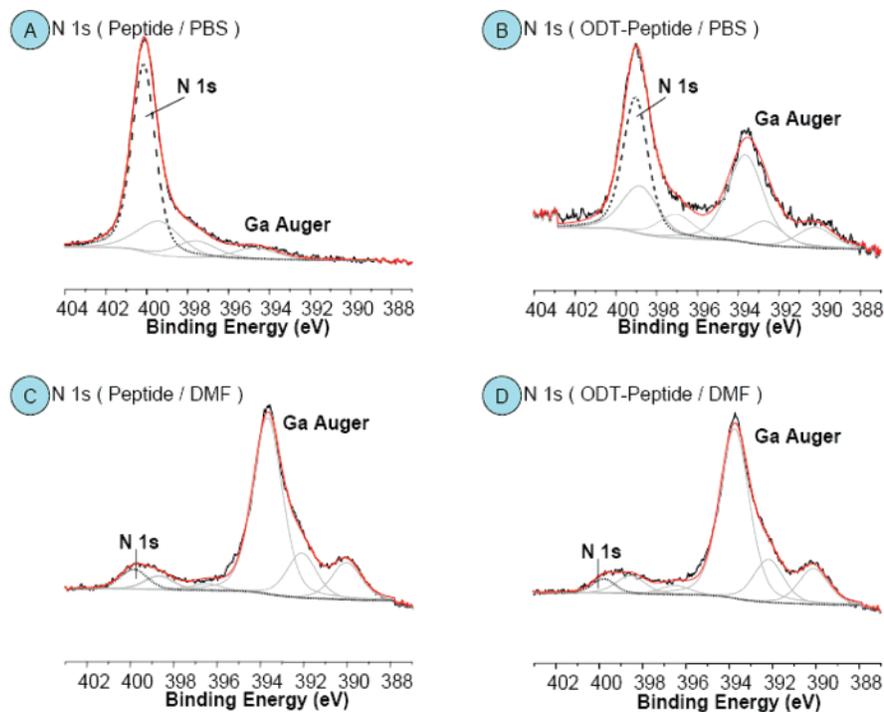


Figure 4. High-resolution N 1s spectra obtained at the photoemission angle of 0° for GaAs(100) modified in PBS or DMF: (A) peptide functionalization in PBS, (B) ODT-peptide sequential treatment in ethanol and PBS, (C) peptide functionalization in DMF, and (D) ODT-peptide sequential treatment in DMF.

Table 3. Summary of Chemical States of Carbon in the Peptide Structure and Expected Ratios between the Components in the Peptide Constraint

	C-C	C-N and C-O	amide C	CN ₃
no. of bonds	31	25	16	6
ratio	1	0.81	0.52	0.19

was verified by comparing the theoretically expected ratio between the peptide carbon and nitrogen with the values obtained from the XPS measurements. As shown in Table 4, the curve-fitting

Table 4. Comparison between XPS Results and Theoretically Expected Values

	C/N ratio		
	theory	PBS	DMF
peptide	2.16	2.83	2.50
ODT/peptide		2.98	2.97

gave reasonable results for both solvents and we concluded that these data can be used for the calculation of coverage and adlayer thickness.

Table 5. Summary of the Calculated Film Thickness Values

	film thickness, Å			
	PBS buffer		DMF	
	As 3d	Ga 3d	As 3d	Ga 3d
ODT ^a	38.11	44.86	5.62	16.58
peptide	121.25	89.09	17.76	19.57
ODT/peptide				
from ODT	48.50	52.66	19.31	19.76
from peptide	46.15	50.11	18.37	18.81

^a Data presented on the left side of the table were calculated from adsorption layers prepared in pure ethanol.

The curve-fitting procedure also was used to calculate the amount of nitrogen. The N 1s peak overlaps with the Ga Auger multi-peak. To extract the N 1s component, the shape of the Ga Auger multi-peak was investigated on the clean surface and subsequently the constraint we obtained was used for the curve-fitting, as shown in Figure 4. A significant amount of nitrogen was detected on the surface of GaAs(100) functionalized in PBS, while the samples modified in DMF exhibited a much smaller amount of nitrogen.

The high-resolution S 2p spectra are shown in Figure 5. Curve-fitting was performed in order to separate the S 2p components and the Ga 3s contribution. A single S 2p doublet, in which the S 2p_{3/2} component is centered at ~162 eV, was observed after functionalization of the surface with homogeneous and mixed adlayers in both solvents. The peak at this binding energy confirms the presence of a covalent bond between the thiol groups and the surface. To verify the absence of other sulfur-containing species, angle-resolved experiments were performed. At the photoemission angle of 75°, the intensity of the S 2p peaks was comparable to the intensity of the Ga 3s peak but no extra S 2p peaks were detected.

Adsorbed Layer Thickness. The film thickness was calculated from eq 3 as described in the Experimental Section and the results are presented in Table 5. The values for the ODT film thickness in ethanol were consistent regardless of which photoemission lines (As 3d or Ga 3d) were used in the calculations. These values were higher than the ellipsometric thickness values (21 ± 2 Å) previously reported.¹¹ For ODT films prepared in DMF, the thickness extracted from the Ga 3d data was the closest to the ellipsometric values reported before. For the homogeneous peptide films, there was a large difference between the thickness values in each solvent system. The electron attenuation length

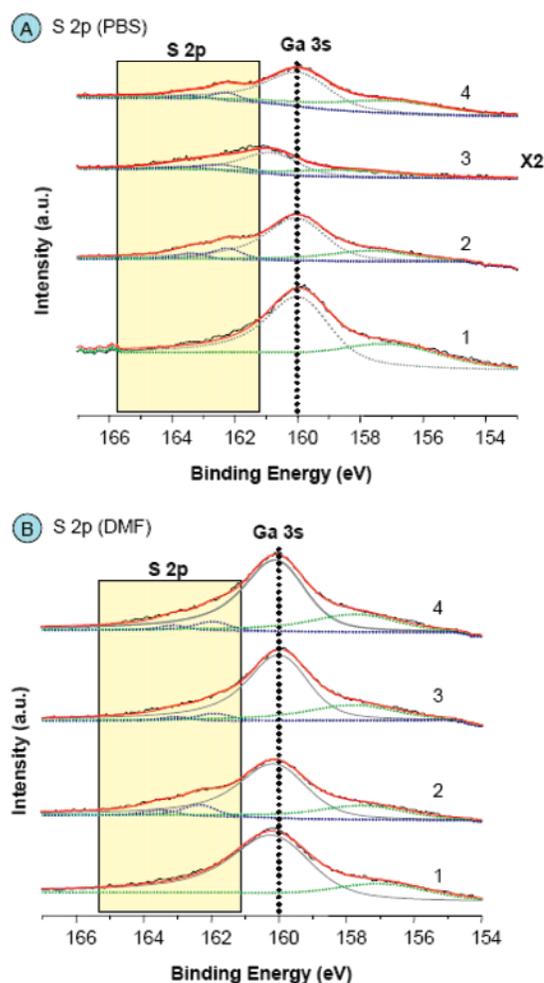


Figure 5. High-resolution S 2p/Ga 3s spectra obtained at the photoemission angle of 0° for GaAs(100) samples treated in (A) PBS buffer or (B) DMF: (1) clean surface, (2) ODT functionalized, (3) peptide functionalized, and (4) ODT-peptide functionalized.

(EAL) for each individual adsorbate (ODT or peptide) was used to calculate the thickness of the ODT/peptide coadsorbed layer and this did not result in any large differences.

Surface Coverage. The surface coverage of adsorbates was calculated from eq 4 as described in the Experimental Section and the results are summarized in Table 6. The C 1s, N 1s, and

Table 6. Summary of the Surface Coverages by Fadley's Formalism

	surface coverage (molecules/nm ²)					
	C 1s, ML		N 1s, ML		S 2p, ML	
	As 3d	Ga 3d	As 3d	Ga 3d	As 3d	Ga 3d
	PBS Buffer ^a					
ODT	1.47 ± 0.16 (18.46 ± 2.05)	1.33 ± 0.18 (16.70 ± 2.23)			1.42 ± 0.16 (17.89 ± 1.96)	1.28 ± 0.11 (16.13 ± 1.43)
peptide ^b	5.04 ± 0.23 (63.44 ± 2.94)	1.23 ± 0.49 (15.50 ± 6.24)	3.38 ± 0.47 (42.59 ± 5.88)	0.86 ± 0.38 (10.84 ± 4.81)	10.18 ± 3.86 (128.27 ± 48.65)	2.39 ± 0.16 (30.05 ± 2.05)
ODT/peptide ^c	4.07 ± 0.98 (51.28 ± 12.30)	3.14 ± 0.50 (39.50 ± 6.33)	0.24 ± 0.01 (2.96 ± 0.09)	0.19 ± 0.01 (2.33 ± 0.09)	1.51 ± 0.43 (18.96 ± 5.43)	1.16 ± 0.24 (14.62 ± 3.03)
	DMF Solvent					
ODT	0.99 ± 0.08 (12.44 ± 1.06)	0.94 ± 0.06 (11.88 ± 0.76)			0.89 ± 0.17 (11.18 ± 2.19)	0.85 ± 0.13 (10.65 ± 1.58)
peptide ^b	0.04 ± 0.01 (0.54 ± 0.06)	0.04 ± 0.01 (0.54 ± 0.06)	0.03 ± 0.01 (0.41 ± 0.12)	0.03 ± 0.01 (0.41 ± 0.12)	0.32 ± 0.06 (4.03 ± 0.73)	0.31 ± 0.04 (3.87 ± 0.52)
ODT/peptide ^c	0.72 ± 0.04 (9.03 ± 0.44)	0.66 ± 0.03 (8.32 ± 0.33)	0.02 ± 0.01 (0.29 ± 0.07)	0.02 ± 0.00 (0.25 ± 0.00)	0.40 ± 0.11 (5.08 ± 1.36)	0.37 ± 0.10 (4.66 ± 1.22)

^a The ODT adlayer was prepared in ethanol. ^b We could not determine the surface coverage from S 2p because the curve-fitting procedure has ~10% error, and the accuracy is critical for low signals such as S 2p. ^c The ODT/peptide adlayer surface coverage of C species was determined from amide C, C–N, and CN3 species because they can originate only from the peptides on the surface.

S 2p photoemission peaks were used as representatives of the overlayer, whereas the Ga 2p_{3/2}, As 3d, and Ga 3d peaks were used for the substrate. The results were consistent for all of the variously treated substrates. Judging from the coverage calculations based on C 1s and S 2p, ODT formed a monolayer in both solvents. This also validates our fitting procedure for the C 1s and S 2p spectra. The peptides immobilized on the surface with PBS buffer also likely form multilayered films, but in DMF the coverage is significantly lower. The ions in the PBS may have changed the properties of the GaAs surface and thus caused a different packing and coverage of peptides in the film. ODT/peptide coverage is a fraction of monolayer when DMF is used as a solvent. However, it is remarkable that from the S 2p peak the coverage is 0.5–0.6 ML and in fact these are mainly sulfur atoms from ODT. Also ODT and peptide attach to the surface through sulfur atoms, and therefore sulfur coverage should be underestimated due to screening. Taking into account that the surface is partially covered with the oxide pits, we can speculate that ODT coverage is close to 1 ML. The peptide coverage is represented by the figure calculated on the basis of N 1s. As shown in Table 6, when DMF is used as a solvent, the nitrogen coverage is 3–4% for the peptide adlayer as well as for coadsorbed ODT/peptide layer. This similarity might point to the fact that the peptide requires specific adsorption sites on the surface, the

concentration of which is approximately equal for DMF-based immobilization. ODT is a smaller molecule than the peptide and therefore ODT could form a monolayer around the peptide molecules, protecting the surface from oxidation. In PBS buffer, beyond monolayer coverage was observed for ODT and ODT/peptide adlayers. This might be a consequence of ionic solution effect and/or depletion of the arsenic concentration on the surface. As shown in Table 2, PBS buffer has a stronger effect in removing As than the DMF solvent.

Conclusion

The study reports the quantitative characterization of adlayers on GaAs(100). The results support the notion that XPS can be used to quantitatively compare the composition of homogeneous and mixed adlayers composed of an alkanethiol and a biomolecule. The data showed that the solvent used to form each adlayer can play an important role in terms of composition, coverage, and oxide formation susceptibility.

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