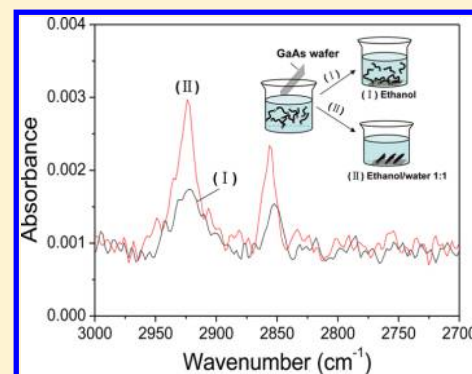


Water-Mediated Self-Assembly of 16-Mercaptohexadecanoic Acid on GaAs (001)

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ABSTRACT: Self-assembled monolayers (SAMs) of alkanethiols have been widely investigated to generate both specific functionality and increased chemical/photonic stability of III–V semiconductor surfaces. Because of the availability of the COOH terminal group, the 16-mercaptohexadecanoic acid (MHDA) has often been investigated to engineer interfaces involving proteins, nucleic acids, and other biomolecules. Typically, MHDA SAMs have been deposited by incubating semiconductor substrates in MHDA/ethanol solutions. We have investigated the role of water on the process of MHDA SAM formation on the GaAs (001) surface, and we report on the formation of increasing quality MHDA SAM in proportion of the concentration of water mixed with ethanol, up to 50%. The transmission Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and water contact angle measurements suggest that MHDA SAM obtained from the ethanol/water 1:1 solution represent a superior quality carboxylic acid-terminated SAM on GaAs (001) reported to date.



1. INTRODUCTION

GaAs is an important semiconductor with intrinsic physicochemical properties, making it attractive for the development of both electronic and photonic devices. Because of the high surface state density ($N_s \geq 10^{12}/(\text{cm}^2 \text{ eV})$) in this material, a substantial surface Fermi level pinning has been observed,¹ which could impair the performance of some GaAs-based devices. To address this problem, the synthesis of a passivation layer on GaAs has been sought to modify its surface electronic properties and protect the freshly etched or cleaved surface from oxidation and/or adsorption of foreign atoms.² Alkanethiol monolayers on GaAs surface, referred to as single, closely packed layers of molecules,³ have drawn substantial attention since the pioneering work by Sheen and Allara et al. in constructing self-assembled monolayer (SAM) on GaAs from an alkanethiol molten at high temperatures.⁴ Organized alkanethiol monolayers have frequently been prepared on GaAs surfaces under mild reaction conditions,^{5–8} while wet etching has been widely applied as a preprocessing step in SAM fabrication on GaAs surfaces.^{9,10} Frequently, in order to create an oxide-free surface, deposition from ethanolic solutions containing aqueous ammonia at 2–20% per volume has been applied when processing GaAs^{6,8,11} or InAs.^{12,13} To this end, it has been argued that the entire removal of oxide is not required to enable the attachment of thiols, e.g., to the InAs surface.¹⁴

Solvents have a profound effect on surface coverage and orientation of alkythiol SAMs on GaAs.¹⁵ In that context, the use of water as solvent has been regarded less attractive than alcohol, primarily due to its relatively high dielectric constant and resulting reduced hardness of SH^- ions that prevents electron transfer from SH^- to the GaAs surface.^{16–18} In

contrast, aqueous solutions have shown to have a positive effect on the formation of alkythiol SAMs on Au surfaces.^{19–22} Compared with ethanol, the use of ethanol–water (1:1) solvent for the formation of protein binding alkythiolate monolayers on Au surfaces results in accelerated alkythiolate monolayer formation and improvement in monolayer integrity.²¹ It has been argued that in aqueous solutions the long alkyl chains associate via van der Waals and hydrophobic interactions that promote organization of stable SAMs on the Au surface.²²

In our earlier research of alkanethiol SAM formation on the GaAs (001) surface, we reported that SAMs could routinely be fabricated by using degassed ethanol or isopropyl alcohol solutions.^{23–26} Recently, we have observed that water washed samples of hexadecanethiol (HDT) SAMs on GaAs showed an increased photoluminescence (PL) intensity in comparison to that from isopropyl alcohol only washed samples.²⁷ In addition, we have observed that HDT SAM-coated GaAs samples showed an enhanced long-term photonic stability if, before exposure to the ammonium sulfide solution, they were washed with water.²⁷ This suggests that water could enhance the properties of SAMs and/or those of the GaAs surface on which SAMs are formed.

To investigate the role of water in the process of SAM formation on GaAs, we focused on 16-mercaptohexadecanoic acid (MHDA) SAM, as this material is attractive for engineering interfaces involving proteins, nucleic acids, and other biomolecules. Also, among known long-chain alkane-

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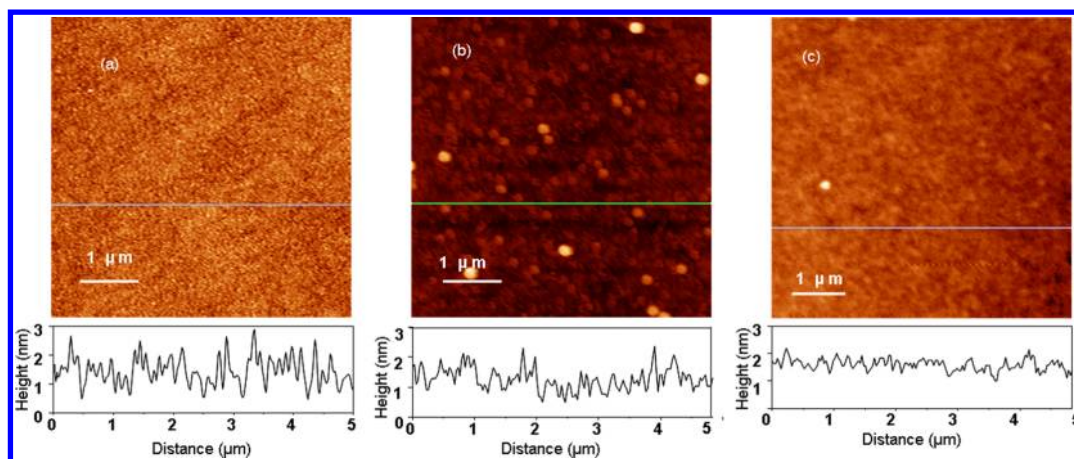


Figure 1. AFM images and cross-sectional profiles along the indicated lines of the GaAs (001) surface: (a) after NH_4OH etching; (b) after MDHA SAM assembly in ethanol; (c) after MDHA SAM assembly in ethanol/water 1:1 solution.

thiols, MHDA with a polar terminal group is relatively well soluble in water, making it desirable for the undertaken study.

2. EXPERIMENTAL SECTION

2.1. Reagents. Two-side polished semi-insulating (SI) GaAs (001) wafers (Wafer Technology Ltd.) were used in order to accommodate Fourier transform infrared (FTIR) spectroscopy transmission measurements with low signal attenuation. The same wafers were used for atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and contact angle measurements. Semiconductor grade Opticlear (National Diagnostics), acetone (ACP Chemicals, Canada), isopropyl alcohol (Anachemia, Canada), ammonium hydroxide (28%, Anachemia, Canada), and anhydrous ethanol (Brampton, Canada) were used without further purification. To remove residual oxygen, a degassed water and ethanol solution (typically 250 mL) was prepared by flushing with a 3 SCFH high-purity nitrogen stream (Praxair Canada) for 4 h. MHDA was purchased from Prochimia Surfaces (Gdansk, Poland).

2.2. Fabrication of Monolayers. Prior to SAM deposition, SI-GaAs (001) samples (4 mm \times 4 mm) were cleaned in an ultrasonic bath sequentially with Opti-Clear, acetone, and isopropanol for 5 min each. The samples were dried using a flow of compressed nitrogen and etched with a solution of concentrated ammonium hydroxide for 2 min at room temperature to remove surface native oxides. The samples were, thereafter, rinsed with freshly deoxygenated ethanol and immediately incubated in MHDA solution (1 mM, degassed) at room temperature for 20 h. After thiolation, the samples were rinsed with ethanol thoroughly to get rid of superfluous thiol molecules physically adsorbed to the substrate, dried in a flow of nitrogen gas for immediate characterization, or packaged under N_2 in the dark for later analysis.

A 1 mM MHDA water–ethanol (1:1) solution was prepared by diluting a 2 mM ethanolic MHDA solution at 1:1 ratio by volume with deionized and degassed water. For the solution with various water concentrations, a measured mass of MHDA was dissolved in ethanol and then diluted with deionized water to the appropriate volume and concentration.²⁸ The final solution was sonicated for 5 min before use. It was found that MHDA molecules yield a white precipitate in solvent compositions greater than 50% of water and there would be interference in SAM formation due to insoluble thiol molecules.

The well-known negative excess volume characteristic of water–ethanol mixtures is ignored.²⁹

2.3. Interface and Surface Characterization. 2.3.1. AFM.

The surface morphology of processed samples was investigated using a Nanoscope IIIa microscope (Digital Instruments, Inc.) operating in a tapping mode. Rotated monolithic silicon probes (BS-Tap 300, Budget Sensors, Sophia, Bulgaria) were used. The cantilever spring constant and the resonance frequency were 40 N/m and 300 kHz, respectively. All the AFM measurements were carried out in an air environment. The root-mean-square roughness (RMS) values of the investigated surfaces refer to an area of 5.0 $\mu\text{m} \times 5.0 \mu\text{m}$. The root-mean-square surface roughness, σ_{RMS} , of the investigated samples was determined as the standard deviation of Z in the given region:

$$\sigma_{\text{RMS}} = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{\text{av}})^2}{N}}$$

where Z_{av} is the average Z value in this region, Z_i is the i th Z value, and N is the point within this region.

2.3.2. FTIR Spectroscopy. The FTIR spectra were collected by using an FTIR Nicolet Nexus 470. The signal was collected by a liquid N_2 cooled HgCdTe (MCT) broadband detector. The spectral resolution was set at 4 cm^{-1} . The probing spot size was approximately 3 mm in diameter. The measurements were started 5 min after mounting the sample to allow the chamber to purge. A sample etched by ammonia and incubated in ethanol for 20 h was used as a reference (background), so that the resulting difference spectrum revealed features specific to the SAM only.

2.3.3. Contact Angle. Contact angle measurements were carried out using a Rame-Hart NRL Model 100 goniometer at room temperature and ambient humidity. A sessile drop of Milli-Q water was placed on the surface using a manual syringe fixture. A minimum of two independent measurements were made for each surface (5 mm \times 5 mm). The static angles reported are the averages of more than three batches of samples. Contact angles were measured within 20 s following contact in case of the solvent-induced conformational reorganization of the SAM.³⁰

2.3.4. XPS. Following their exposure to thiol solutions, SAM-coated GaAs samples were immediately rinsed with ethanol and dried with high-purity nitrogen (99.999%). Subsequently, within 5 min, the samples were transferred to the vacuum

chamber of the XPS (Kratos Analytical, AXIS Ultra DLD) system with a base pressure of 1×10^{-9} Torr. The surface survey scans and high resolution scans were observed with a 150 W Al K α source operating in constant energy modes at 50 and 20 eV pass energy, respectively. The XPS results were analyzed by CASA XPS 2.3.15. The data were collected for a takeoff angle of 60° with respect to the surface normal.²⁴ Symmetric and asymmetric lines were used to peak fit the spectra envelopes into their constituent chemical states. The cross-section corrected ratio of the bulk photoemission components As–Ga/Ga–As equal to 1 should be expected. To compensate for the surface charging effect, all the binding energies were referenced to adventitious saturated hydrocarbon at the peak energy of 285.0 eV. To fit the S 2p and Ga 3s region, a nonstandard approach was used to create the irregular shape of the background of inelastic scattering according to Marshall's model.²⁴

3. RESULTS AND DISCUSSION

3.1. GaAs Surface Morphology. Figure 1 shows AFM images of the surface morphology of (a) freshly etched bulk GaAs, (b) MHDA SAM-coated sample fabricated in ethanol, and (c) MHDA SAM-coated sample fabricated in ethanol/water 1:1. For each sample, the AFM measurements were performed in three different sites of the $5.0 \mu\text{m} \times 5.0 \mu\text{m}$ area. The root-mean-square roughness amplitudes (σ_{RMS}) of samples shown in Figure 1a–c are 7.8 ± 1.1 , 9.6 ± 1.3 , and $6.7 \pm 0.5 \text{ \AA}$, respectively. The formation of high-quality SAMs on partially oxide-covered or oxide-free (freshly etched) GaAs is not expected to lead to the measurable roughening of the surface morphology of this material.³¹ The significant roughening of the surface observed for the sample exposed to MHDA diluted in ethanol (Figure 1b) indicates the formation of a disordered layer on GaAs. In contrast, the sample with SAM incubated in the ethanol/water 1:1 solution shows evidence of surface smoothing (Figure 1c). This suggests that, if an MHDA SAM is indeed formed in that case, it must be well organized.

3.2. FTIR Spectroscopy Data. A series of transmission FTIR spectra shown in Figure 2 were collected for a sample incubated in a pure solution of MHDA in ethanol (a) and for samples incubated in MHDA ethanolic solution diluted with 10 (b), 25 (c), and 50% (d) of water. Easily identifiable peaks at 2917–2923 and 2850–2851 cm^{-1} are assigned to asymmetric

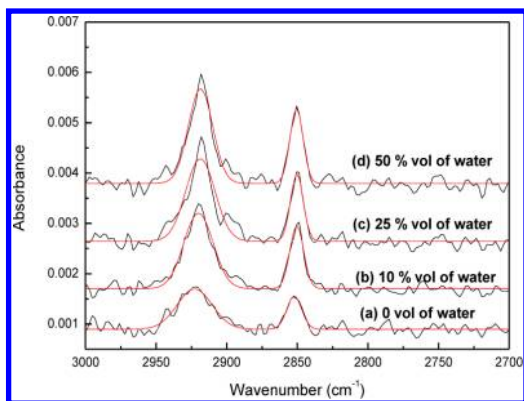


Figure 2. Transmission FTIR spectra of MHDA monolayers grown in ethanol (a) and in ethanol with (b) 10, (c) 25, and (d) 50 vol % of water. The black lines are experimental data, and the red lines are the fitted results (Gaussian).

CH_2 ($\nu_{\text{CH}_2^{\text{as}}}$) and symmetric CH_2 ($\nu_{\text{CH}_2^{\text{s}}}$) stretching vibration modes, respectively.³² It is well-known that the $\nu_{\text{CH}_2^{\text{as}}}$ band position is strongly affected by the order of the alkyl chains, and the low-frequency shift of the $\nu_{\text{CH}_2^{\text{as}}}$ band indicates enhancement of the monolayer order.^{23,33} For the monolayer prepared in pure ethanol solution, the $\nu_{\text{CH}_2^{\text{as}}}$ peak is observed at relatively high frequency of 2922.7 cm^{-1} . Also, the intensity of that peak is quite weak, which suggests that the methylene chains are in the *gauche* conformation.^{34,35} In Table 1, we compare FTIR

Table 1. Absorbance, Wavenumber, and FWHM of Asymmetric Vibrations of CH_2 FTIR Peaks in MHDA SAMs on the GaAs (001) Surface Grown in Ethanol (a) and in Ethanol with (b) 10, (c) 25, and (d) 50 vol % of Water

	absorbance ($\times 10^{-3}$)	wavenumber _{AS} (cm^{-1})	fwhm _{AS} (cm^{-1})
(a)	0.78 ± 0.03	2922.7 ± 0.9	27.3 ± 0.4
(b)	1.43 ± 0.04	2920.0 ± 0.7	22.5 ± 0.5
(c)	1.65 ± 0.05	2918.6 ± 0.7	21.7 ± 0.3
(d)	1.86 ± 0.02	2918.5 ± 0.5	18.7 ± 0.4

amplitudes and full width at half-maxim (fwhm) values of $\nu_{\text{CH}_2^{\text{as}}}$ vibration modes observed for the investigated samples. In comparison with the sample obtained in a pure solution of MHDA in ethanol, a significantly increased FTIR absorption amplitude is observed for the sample incubated in ethanolic solution diluted with 10% of water. At the same time, the fwhm of the $\nu_{\text{CH}_2^{\text{as}}}$ vibration modes decreased from 27.3 to 22.5 cm^{-1} . This trend continues, although with some evidence of the saturation, for the samples incubated in solutions with increasing water content. The 1.86×10^{-3} absorbance of the MHDA SAM incubated on GaAs in ethanol/water (1:1) is comparable to the absorbance of the $\nu_{\text{CH}_2^{\text{as}}}$ mode observed for high-quality HS-(CH_2)₁₅-CH₃ SAMs on GaAs (001).²³

The systematic narrowing of the $\nu_{\text{CH}_2^{\text{as}}}$ modes (decreased fwhm) is illustrated in Table 1 for samples obtained in ethanolic solutions with increasing water content. These results clearly demonstrate that adding water to the ethanolic solution of MHDA creates conditions favoring the formation of high quality of MHDA SAM on the GaAs (001) surface.

3.3. Contact Angle Measurements. Water contact angle measurements were investigated to probe the general structural and chemical characteristic of the wetting surface. Etching with aqueous ammonia gave a shiny hydrophilic surface, e.g., in agreement with Lebedev et al.¹⁰ Also, the water contact angle of $65 \pm 1^\circ$ that we observed for the MHDA layer formed in pure ethanol is comparable with 68° reported by Cho.³⁶ The partially hydrophobic surface suggests that an incomplete or disordered SAM is formed in ethanol. The hydrophobic character of the sample is likely related to the excessive exposure of the CH_2 groups to water.^{32,37} As the water volume fraction in the mixture solution increased, a decreasing water contact angle was observed, as shown in Table 2. The contact angle of $44 \pm 2^\circ$ observed for MHDA monolayer formed in the ethanol–water 1:1 solution indicates formation of a relatively hydrophilic surface of GaAs. Thus, these results corroborate the FTIR observations concerning the increased quality SAMs formed in ethanolic solutions with increasing concentration of water.

3.4. XPS Study. The measured XPS spectra were decomposed into individual components and fitted self-consistently with a series of doublets and fitting parameters chosen by using the full set of spectra. The results of the

Table 2. Contact Angle of Bare GaAs before/after Etching and the Samples Coated with MHDA Monolayers Prepared under Different Volume Fractions of Water in Ethanol Solvent

sample	contact angle (deg)	sample	contact angle (deg)
bare GaAs substrate	70 ± 2	10 vol % of water	59 ± 2
GaAs after etching	57 ± 1	25 vol % of water	53 ± 1
0 vol % of water	65 ± 1	50 vol % of water	44 ± 2

previous work on SAM-GaAs samples were taken into account to verify the fitting parameters.^{24,31,38}

The Ga 3d and As 3d XPS of MHDA layers formed by incubation in ethanol and in ethanol/water 1:1 are shown in Figures 3a and 3b, respectively. The Ga/As ratios of these

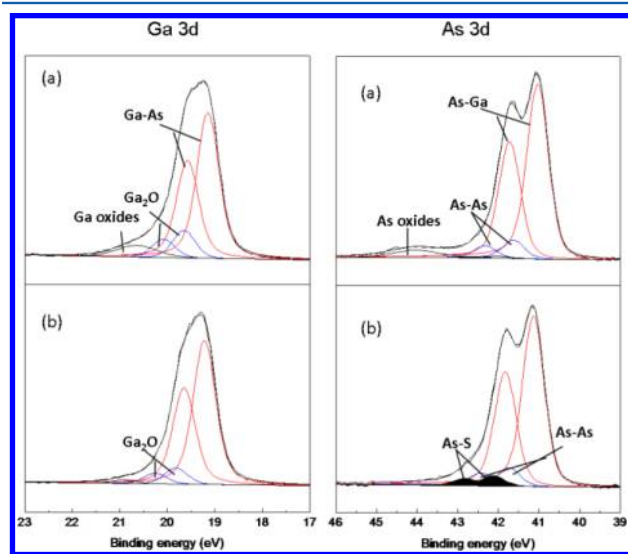


Figure 3. Ga 3d and As 3d XPS of MHDA monolayers grown (a) in ethanol and (b) in ethanol/water 1:1 mixture.

samples are 1.21 ± 0.04 and 1.03 ± 0.01 , respectively. The Ga 3d spectra have been deconvoluted into bulk GaAs, Ga suboxide (Ga_2O), and Ga oxides, and the As 3d spectra have been deconvoluted into bulk GaAs, elemental As (As^0), S–As, and As oxides. The broad maxima at high binding energy related to Ga and As oxides were not considered in detail.³⁸ The parameters for all the individual components peaks in Ga 3d and As 3d spectra, e.g., binding energy, assignments, full width at half-maximum (fwhm), spin–orbit splitting, and branching ratio are shown in Table 3.

Table 3. Parameters of the Individual Peaks in the Ga 3d and As 3d Spectra in Figure 3^a

	binding energy(eV)	assignments	fwhm (eV)	spin–orbit splitting (eV)	branching ratio
Ga 3d	19.2 ± 0.1	GaAs	0.53 ± 0.01	0.43	3/2
	19.8 ± 0.2	Ga suboxide (Ga_2O)			
	>19.8	Ga oxides			
As 3d	41.0 ± 0.1	GaAs	0.61 ± 0.01	0.69	3/2
	41.7 ± 0.1	elementary As (As^0)			
	42.0 ± 0.1	As–S			
	>43.8	As oxides			

^aFor simplicity, only the energy of the main component in each doublet is reported.

In the As 3d spectra, the MHDA monolayer grown in ethanol (Figure 3a) show more As oxides than the sample incubated in ethanol/water 1:1 at high binding energy (Figure 3b). Particularly, for the doublet peak assigned to As–S bonding at 42.0 eV (black), the emission intensity of the former is weaker than the latter, which suggests that more thiols are immobilized on the surface by As–S binding for the sample incubated in ethanol/water 1:1.

In the Ga 3d spectra, there are more Ga oxides at high binding energy (>19.8 eV) for the sample grown in MHDA ethanol solution (Figure 3a) than the monolayer grown in ethanol/water 1:1 (Figure 3b). Besides a doublet at 19.8 eV assigned to Ga suboxide (Ga_2O), no specific peaks for Ga–S bonding could be resolved because of their close proximity to that peak.

The Ga 3s and S 2p spectra overlap as shown in Figure 4, and the region of Ga 3s (~160 eV) is determined by calibration

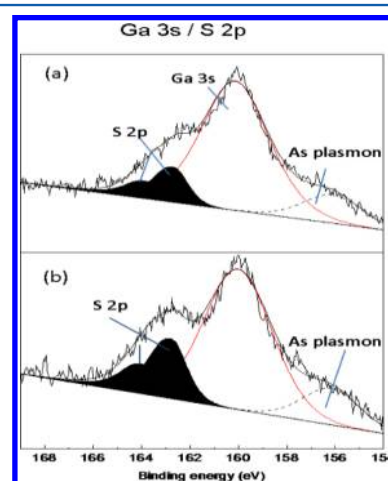


Figure 4. S 2p and Ga 3s XPS of the MHDA monolayers grown (a) in ethanol and (b) in an ethanol/water 1:1 mixture.

to the Ga 3d spectra according to the differences in relative sensitivity factor (RSF).²⁴ The As plasmon loss component is assigned at 156.2 ± 0.1 eV according to the literature.^{8,39} A single doublet peak at ~162.5 and ~163.7 eV (branching ratio 2:1) is assigned to S $2p_{3/2}$ and S $2p_{1/2}$ (dark shade), which is characteristic for thiolate species, consistent with a direct S–substrate bonding.³⁸ The absence of S 2p intensity at high binding energy indicates a negligibly small fraction of weakly bound MHDA molecules (physisorption) on the surface.³⁹ For the monolayer assembly in ethanol/water 1:1, the emission intensity of sulfur is 1.47 ± 0.04 times higher than the sample grown in ethanol.

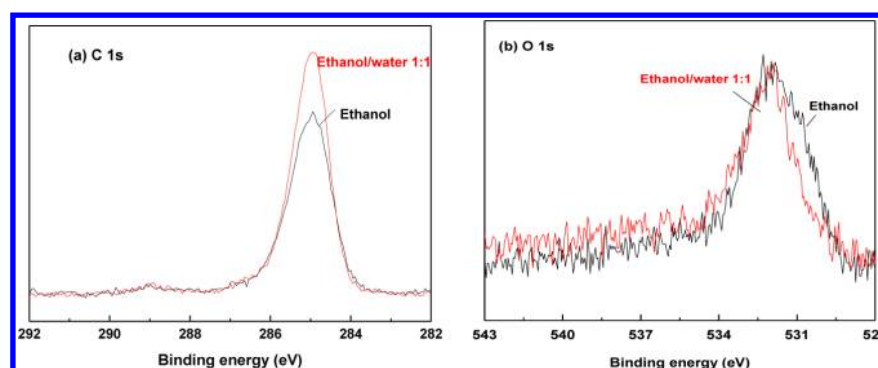


Figure 5. (a) C 1s and (b) O 1s XPS signal of the MHDA monolayers grown in ethanol versus ethanol/water 1:1 mixture.

Additionally, the comparison of XPS C 1s signals (Figure 5a) exhibit that the MHDA monolayer grown in ethanol/water 1:1 has smaller fwhm value than the one grown in ethanol (1.04 vs 1.18), and the carboxyl group ($-\text{COOH}$) emission intensity is 1.41 ± 0.05 times higher than that of the sample grown in ethanol (fitting results). This suggests that the structure of the former is more densely packed. At the same time, for the sample grown in ethanol/water 1:1, the fwhm value of O 1s spectra is also smaller than that of the sample grown in ethanol (1.84 vs 2.57), further confirming that more ordered MHDA monolayer with less oxides is formed in ethanol/water 1:1 solution (Figure 5b).

Our XPS experiments revealed that, compared with the SAM obtained in ethanol, the thiolation process in the ethanol/water 1:1 solution leads to the formation of material with distinctively lower surface concentration of As oxides and Ga oxides. The difference for As oxides becomes less evident within a 7 day atmospheric exposure (results not shown here). However, the concentration of Ga oxides in sample fabricated in the ethanol-only solution remains significantly greater for the same period of time. As illustrated in Figure 6, within the first 2 days, the concentration of Ga oxides in the ethanol solution made sample increases at a rate of $0.86 \pm 0.03\%$ per day, while that in the ethanol/water 1:1 solution made sample at a slightly reduced rate of $0.73 \pm 0.03\%$ per day. Thus, the GaAs surface processed in the ethanol/water 1:1 solution seems to have lower

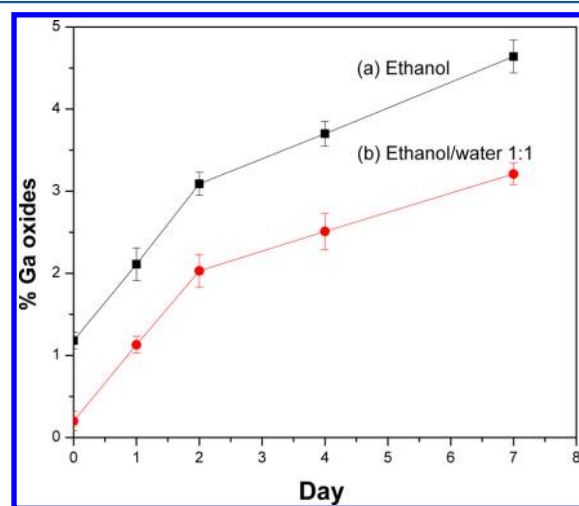


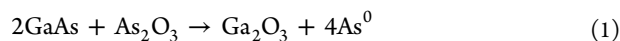
Figure 6. Time-dependent surface concentration of Ga oxides in MHDA-SAM-GaAs fabricated in ethanol-only (a) and in ethanol/water 1:1 (b) solutions.

concentration of surface oxides, and it ages in an atmospheric environment at a slightly lower rate than that processed in ethanol-only solution. However, it is important to emphasize that the thiolation procedure is not expected to provide an ultimate surface stability of GaAs because in the most favorable case, as suggested by theoretical modeling,⁴⁰ only 50% of surface atoms are expected to bind with thiolates.

To understand the role of water in the formation of high-quality MHDA SAMs on the GaAs surface, a discussion is required of the problem related to the source of the formation of disordered MHDA SAMs. After etching with ammonia, the polarizable, electron-deficient binding sites are formed on the GaAs surface and attacked by nucleophiles, such as $-\text{SH}$ and $-\text{COOH}$ groups.^{41,42} The two-site adsorption makes the MHDA molecules lie down on the surface and induce the collapsed-site defects when incubation is carried out in ethanol.^{42,43} At the same time, the hydrogen bond between neighboring carboxylic groups is another factor inducing the formation of highly disordered films, as it has been observed on the Au surface.³⁵ Our previous results showed that MHDA films formed in ethanol have evidently different crystalline-like packing structure from that formed by methyl-terminated thiols with the same number of CH_2 units (HDT).⁴⁴ The dimers of two $-\text{COOH}$ groups present in the ethanolic solution do not separate during the adsorption process, yielding highly disordered molecular films on the GaAs surface.^{34,45} In the presence of water, the carboxylic acid dimers will be “broken” due to the formation of hydrogen bonds between water molecules and individual carboxylic acid groups.⁴⁶

Lebedev et al. have investigated the role of solvent played in the adsorbate interaction of inorganic sulfide anions (HS^-) with surface binding sites.^{18,47} They argued that due to the different influence of the solvation shell, the anions solvated by less dielectric constant solvent (alcohol) are strongly nucleophilic; i.e., they can easily donate electrons to surface atoms.⁴⁷ In our case, compared with MHDA molecules solvated by ethanol, the thiols solvated by water/ethanol 1:1 are less nucleophilic, and they tend to interact with less-polarizable As sites.¹⁴ This results in an increase of As-S binding as indicated by the XPS results. At the same time, for the assembly of relatively long-chain MHDA alkanethiols, the intermolecular forces between the alkane chains become more significant due to hydrophobic interactions between the alkane chains.^{48,49} Thus, even though the average molecular spacing is incommensurate with the lattice spacing of GaAs (001),⁴⁰ the enhanced intermolecular forces may induce short-range ordering of MHDA SAMs, resulting in the formation of a relatively densely packed monolayer.

In addition to the mediating role water plays in the surface–admolecule and intermolecular reactions, water could also affect the chemical state of the GaAs surface exposed to MHDA solution. Both As_2O_3 and Ga_2O_3 form on the clean surface of GaAs exposed to oxygen, with Ga_2O_3 being a thermodynamically favored compound that forms through the following transformation:^{50,51}



Formation of Ga oxide-enriched surface in samples exposed to ethanolic solution of MHDA has been observed in XPS experiments (see Figure 3). Although some oxides could be formed during the transfer of investigated samples to the XPS chamber, a distinctive presence of As oxides is evident in the sample incubated in ethanolic solution of MHDA but not in that exposed to ethanol/water solution. It is feasible that the exposure to a water environment helped to remove As oxides as they are known to be relatively easily soluble in water.⁵² The absence of As_2O_3 on the surface of samples incubated in ethanol/water solution reduces, in turn, the channel for Ga oxide formation as suggested by eq 1.

4. CONCLUSIONS

We have investigated the influence of water on the formation of MHDA SAMs on the GaAs (001) surface, and we demonstrate that deposition from an ethanolic solution of MHDA mixed with water leads to the formation of superior quality of SAMs when compared to those obtained from a pure ethanolic solution. The MHDA SAM obtained from an ethanol/water 1:1 MHDA solution is characterized by the FTIR peak related to the asymmetric mode of CH_2 vibrations, $\nu_{\text{CH}_2}^{\text{as}}$, located at 2918.5 cm^{-1} . The fwhm of that peak is 18.7 cm^{-1} , and its amplitude of absorption is at 1.86×10^{-3} . This compares with a slightly stronger absorption of $\sim 2.2 \times 10^{-3}$ from the $\nu_{\text{CH}_2}^{\text{as}}$ peak of HDT SAMs (same CH_2 chain length) on GaAs located at 2918 cm^{-1} ²³ and with 4×10^{-3} absorption from the $\nu_{\text{CH}_2}^{\text{as}}$ peak of MHDA SAM on Au (also observed at 2918 cm^{-1}).⁵³ In comparison to the absorption of this peak from MHDA SAMs on GaAs obtained in ethanolic solutions, the amplitude of the $\nu_{\text{CH}_2}^{\text{as}}$ peak observed in this work is 5 times greater than that reported previously.⁵⁴ Furthermore, the relatively low vibrational energy of the $\nu_{\text{CH}_2}^{\text{as}}$ peak observed in this work suggests that it originates from a high-quality MHDA SAM. We argue that, in comparison to alcohol-based solvents, the deposition of MHDA SAMs from an ethanol/water 1:1 mixture largely improves the chain conformational order of MHDA molecules on the GaAs surface. In addition to moderating the intermolecular and admolecule–surface interactions, our results suggest that water also plays an important role in improving the conformation of MHDA molecules by dissolving surface As oxides and, thus, creating conditions favoring attachment of thiols via the –SH group. An increased surface coverage with sulfur has been observed in the investigated samples, as indicated by transmission FTIR, contact angle, AFM, and XPS measurements. It is reasonable to expect that the method presented here will be attractive for the development of MHDA SAM architectures on GaAs, and likely on surfaces of other semiconductors, designed for biosensing and related nanoelectronic applications.

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Notes

The authors declare no competing financial interest.

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