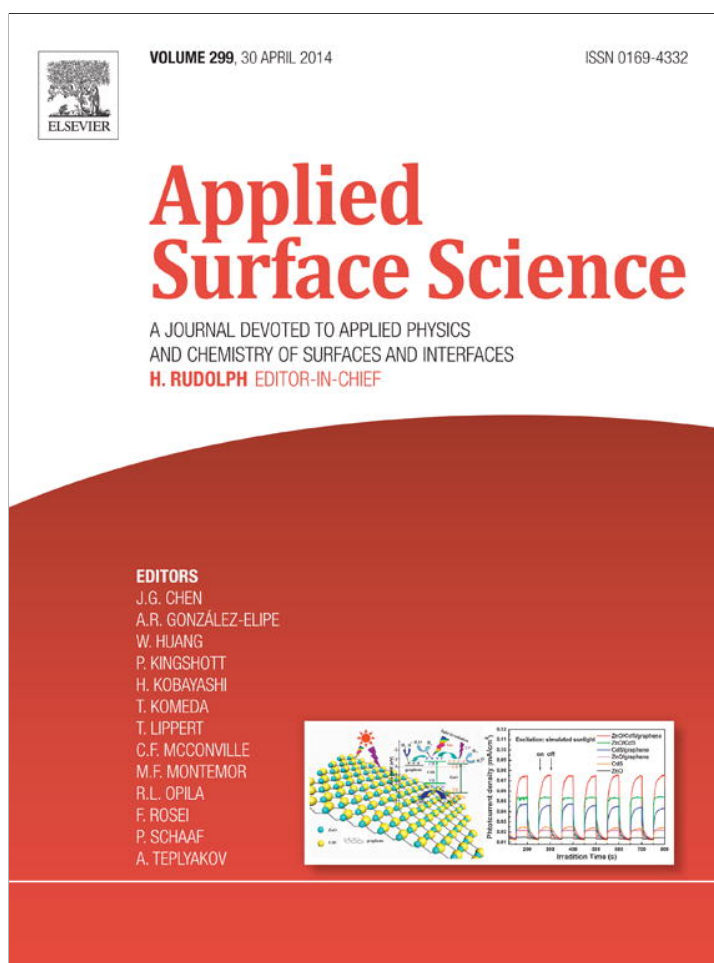


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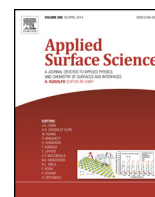
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Solvent-mediated self-assembly of hexadecanethiol on GaAs (001)



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ABSTRACT

We have investigated the influence of solvents on the quality of hexadecanethiol (HDT) self-assembled monolayers (SAM) formed on GaAs (001) in chloroform, ethanol and ethanol/water 1:1 characterized by their increasing dielectric constants from 4.8 (chloroform) to 24.5 (ethanol) and water (80.1). Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) data show that the incubation in ethanol/water 1:1 solution creates conditions favouring inter-molecular interaction leading to the formation of an outstanding quality HDT SAM on GaAs (001). Incubation in low-dielectric constant solvents is not offering advantageous conditions for growing HDT SAM on GaAs. The chloroform environment, while weakening the thiol–thiol interaction, induces the oxidation of the GaAs surface and, in particular, formation of Ga₂O₃. This reduces the concentration of surface defects responsible for non-radiative recombination and leads to an enhanced photoluminescence emission, despite the fact that HDT SAM formed in chloroform are highly disordered, exhibiting the worst chemical passivation among the investigated samples.

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1. Introduction

The formation of self-assembled monolayers (SAM) of organic thiols on semiconductor surfaces has attracted much attention in last 20 years due to their prospective applications in surface passivation [1,2], chemical and bio-sensing [3–5], and hybrid molecule-semiconductor devices [6,7]. The structural ordering of SAM is essential for these applications. For unprotected or poorly protected III–V semiconductor surfaces, their electrical and optical properties could degrade remarkably after exposure to oxygen and air atmosphere [2]. Thus, the development of a well-ordered and densely packed monolayer to maintain a stable response over an extended period of time is of great importance. In comparison to gold surfaces, the formation of organic thiol SAM on GaAs is more complex and diverse, and is not well understood. Long-chain alkanethiols are more likely to form crystalline-like packing SAM due to the intermolecular forces that drive the formation of ordered structures [8]. It has been observed that varying the type of terminal groups, from hydrophilic to hydrophobic, could increase the passivation performance of the (001) GaAs surface as judged by the intensity of the GaAs-related photoluminescence signal [9]. The intermolecular reaction is not only dependent on the length of the alkane chain, but also on the solvent environments surrounding thiol molecules [10–13].

Aqueous solutions have been reported to enhance the inter-molecular reaction of long chain alkanethiols on Au surface [11–14]. Besides the intermolecular forces, the interfacial affinity between sulphur head groups and substrate binding sites (e.g., As and/or Ga) is another key factor to the formation of high-quality SAM [15,16]. Lebedev et al. have argued that the reactivity of solvated HS[−] ions correlates with the dielectric constant of the bulk solvent [17–19]. Their results suggest that water is unfavourable for the interfacial binding of sulphur to GaAs surface. However, our recent results concerning 16-mercaptohexadecanoic acid (MHDA) monolayer formation on GaAs in ethanol/water solutions confirmed that water exerts a positive effect on the monolayer conformation [20]. Thus, it is reasonable to anticipate that the final monolayer structure is the result of a delicate balance between inter-molecular chain reactions, as well as the substrate-head group and substrate-terminal group interactions.

To explore the role of solvent in the formation of a high quality SAM designed for both electronic and chemical passivation of GaAs (001), we have investigated the formation of conventional long-chain hexadecanethiol (HDT) SAM on GaAs (001) in chloroform, ethanol and ethanol/water 1:1 solvents characterized by their increasing dielectric constants from 4.8 (chloroform) to 24.5 (ethanol) and 80.1 (water). In addition to studying the quality of SAM by the Fourier-transform infrared spectroscopy (FTIR), we have also investigated the photoluminescence effect (PL) that is known to be extremely sensitive to the surface presence of non-radiative recombination centres [9,21].

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2. Experimental

2.1. Reagents

HDT was purchased from Prochimia Surfaces (Gdansk, Poland). Two sides polished semi-insulating (SI) GaAs wafer was used in order to accommodate transmission FTIR measurements with low signal attenuation. The same wafer was used for X-ray photoelectron spectroscopy (XPS). A nominally undoped GaAs/Al_{0.35}Ga_{0.65}As multilayer structure grown by molecular beam epitaxy (MBE) on a semi-insulating (001) GaAs substrate was employed for photoluminescence (PL) measurements. The wafer (V0879) comprised a 500 nm thick epilayer of GaAs overlaid with 100 and 10 nm thick Al_{0.35}Ga_{0.65}As barriers confining a 6.0 nm thick GaAs quantum well. The microstructure was capped with a 10 nm thick GaAs.

Semiconductor grade Optic-clear (National Diagnostics, USA), acetone (ACP Chemicals, Canada), isopropyl alcohol (Anachemia, Canada), ammonium hydroxide (28%, Anachemia, Canada), anhydrous chloroform (Fisher Scientific, USA) and anhydrous ethanol (Brampton, Canada) were used without further purification. To remove residual oxygen, degassed water and ethanol solution (typically 250 mL) was prepared by flushing with a 3 SCFH high-purity (99.999%) nitrogen stream (Praxair, Canada) for 4 h. Chloroform, characterized by the relatively low vapour pressure (5.9 kPa) at 20 °C, was used directly without degassing.

2.2. Fabrication of monolayers

Prior to SAM deposition, SI-GaAs (001) samples (4 mm × 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 HDT chloroform or ethanol solutions (2 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 N₂ in the dark for later analysis.

As the solubility of HDT in aqueous solution is low, the deposition of SAM was carried out from a solution of HDT in ethanol/water 1:1. Previously, we used a similar ethanol/water 1:1 solution for the growth of high-quality MHDA SAMs on GaAs (001) [20]. The final concentration of 0.5 mM was prepared by diluting a 1 mM ethanolic HDT solution at 1:1 ratio with deionized water (degassed) by volume. The solution was sonicated for 5 min before use.

2.3. Interface and surface characterization

FTIR and XPS were used to assess the quality of HDT monolayers formed on GaAs surface. The information about the instruments and experimental details can be found elsewhere [20,22].

Photoluminescence measurements were used to elucidate on the electrical character of the HDT-GaAs interface. For these measurements, we used exclusively GaAs/Al_{0.35}Ga_{0.65}As multilayer structures grown by MBE. The measurements were carried out with a Hyperspectral Imaging PL Mapper (HI-PLM) custom designed by Photon, etc. (Montreal) [21]. The HI-PLM instrument accommodates samples up to 7 mm × 7 mm, and it allows the acquisition of PL maps with a spatial resolution of 5 μm approximately. The full sample area was excited with a 532 nm CW laser of uniform intensity at ~50 mW/cm². The mapping of the investigated samples was carried out for the 871 nm emission peak. To define this peak, the

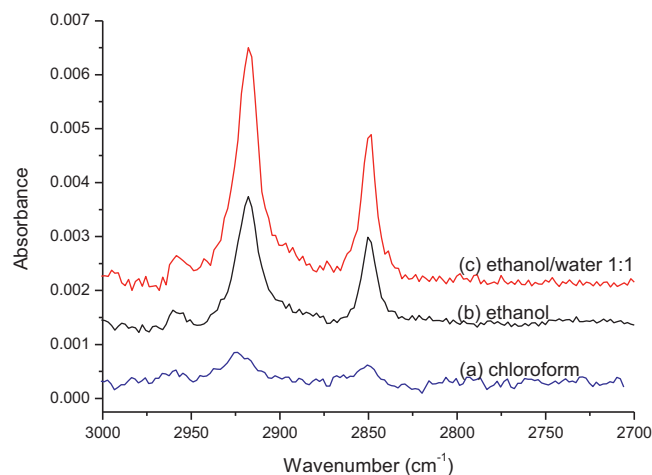


Fig. 1. Transmission FTIR spectra of HDT SAMs formed in (a) chloroform, (b) ethanol and (c) ethanol/water 1:1.

spectra were taken with a 2 nm wavelength step size in the range between 856 and 876 nm.

3. Results

3.1. FTIR study

Infrared spectroscopy has been widely applied to determine the chain orientation and ordering of *n*-alkanethiols on solid substrates [9,23,24]. Previous study has demonstrated that the energy of the asymmetric CH₂ stretching vibration band ($\nu_{\text{CH}_2^{\text{as}}}$) is strongly affected by the order of the alkyl chains [25–27], and the red shift of $\nu_{\text{CH}_2^{\text{as}}}$ is related to the improvement of the crystal structure of the monolayer. In addition, it can be used to infer on the amount of *gauche* defects [23,28,29]. Fig. 1 shows FTIR absorption of HDT SAM formed in (a) chloroform, (b) ethanol and (c) ethanol/water 1:1 solutions. It can be seen that the absorbance amplitude of the SAM formed in chloroform is relatively weak, and the frequency of its $\nu_{\text{CH}_2^{\text{as}}}$ peak is the greatest ($2923.2 \pm 0.4 \text{ cm}^{-1}$) among the investigated SAM. This result suggests that the methylene chains of SAM fabricated from chloroform solution are in *gauche* conformation and the surface coverage of HDT molecules is relatively low [29,30]. The HDT SAM formed in ethanol show medium absorbance ($2.21 \pm 0.03 \times 10^{-3}$), and the $\nu_{\text{CH}_2^{\text{as}}}$ frequency of $2918.3 \pm 0.2 \text{ cm}^{-1}$ is comparable to the results reported before [21,24]. The SAM formed in ethanol/water 1:1 exhibits the strongest absorbance ($3.82 \pm 0.02 \times 10^{-3}$) and the lowest frequency of $\nu_{\text{CH}_2^{\text{as}}}$ peak ($2917.5 \pm 0.3 \text{ cm}^{-1}$). Furthermore, the full-width-at-half-maximum (FWHM) of this peak ($14.2 \pm 0.3 \text{ cm}^{-1}$) is the narrowest among the investigated samples. In Table 1, we summarize the FTIR results obtained for a series of three independently fabricated samples grown in different solvents. These results compare favourably with the characteristics of HTD SAM prepared on Au surface in ethanol and aqueous micellar solutions of hexaethylene glycol monododecyl ether [31].

Table 1

Absorbance, wavenumber and FWHM of asymmetric vibrations of CH₂ FTIR peaks in HDT SAM on the GaAs (001) surface grown in (a) chloroform, (b) ethanol and (c) ethanol/water 1:1. The error values have been calculated based on measurements of three samples prepared independently.

	Absorbance ($\times 10^{-3}$)	Wavenumber _{AS} (cm^{-1})	FWHM _{AS} (cm^{-1})
(a)	0.55 ± 0.01	2923.2 ± 0.4	24.1 ± 0.2
(b)	2.21 ± 0.03	2918.3 ± 0.2	15.1 ± 0.2
(c)	3.82 ± 0.02	2917.5 ± 0.3	14.2 ± 0.3

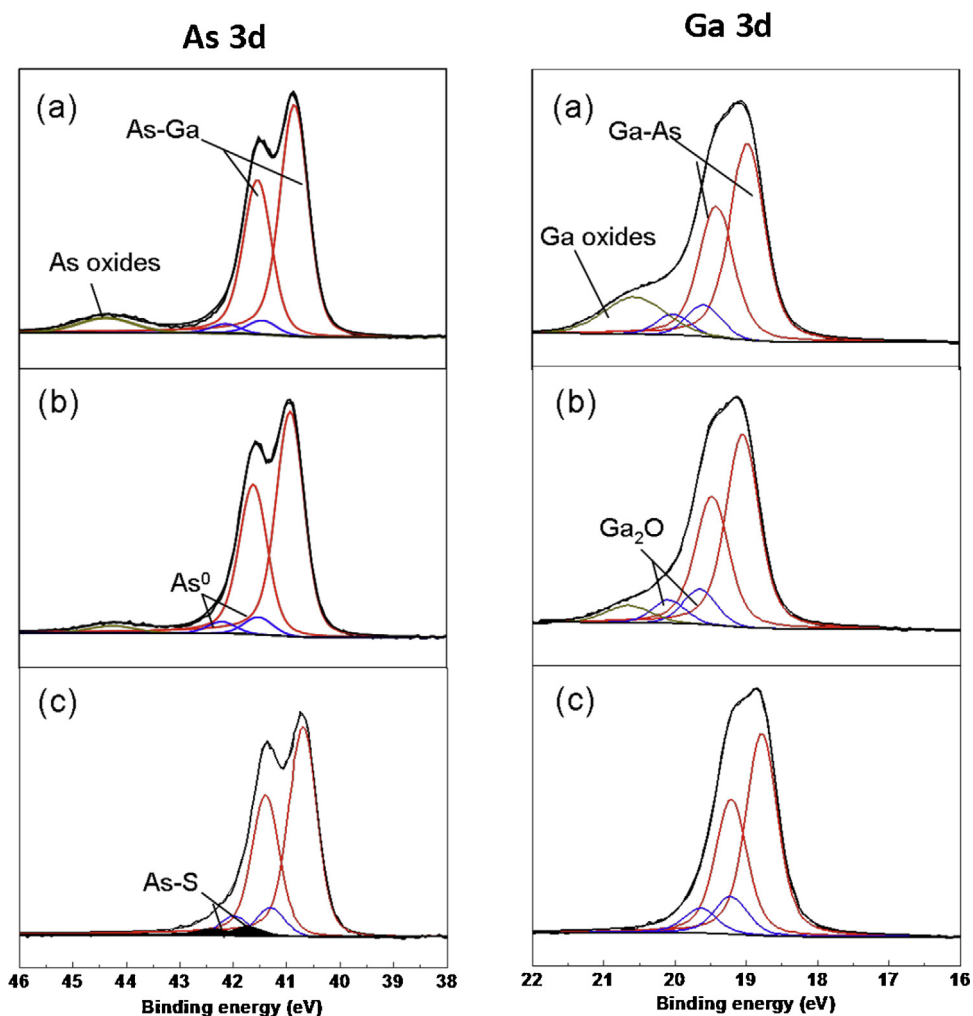


Fig. 2. XPS As 3d and Ga 3d components of HDT monolayers grown on GaAs (001) in (a) chloroform, (b) ethanol and (c) ethanol/water 1:1 solutions.

3.2. XPS study

The Ga 3d and As 3d XPS of HDT monolayers formed in (a) chloroform, (b) ethanol and (c) ethanol/water 1:1 solutions are shown in Fig. 2. The Ga/As ratios of these samples are 1.30, 1.25 and 1.09, respectively. The Ga 3d spectra have been deconvoluted into bulk GaAs, Ga suboxide (Ga_2O), and other Ga oxides dominated by the Ga_2O_3 peak at ~ 20.4 eV, while 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 further considered in detail [32,33]. The parameters for all the individual component peaks in Ga 3d and As 3d spectra, e.g., binding energy, assignments, FWHM, spin-orbit splitting and branching ratio are referred to our recently published results [20].

In the As 3d spectra, the sample grown in chloroform (a) shows the significant presence of As oxides, whereas reduced concentration of As oxides is observed in the sample incubated in ethanol (b). Even further reduced level of oxides is observed in the sample grown in ethanol/water 1:1 (c). A doublet peak assigned to As–S bonding at ~ 42.0 eV has been identified in the XPS spectrum of the sample (c). This doublet, of a significantly weaker intensity, has also been observed in the sample incubated in ethanol (b), as indicated by the black shaded area. However, no 42.0 eV doublet could be identified in the spectra of sample (a), suggesting that more thiols

immobilize on the GaAs surface by As–S binding in ethanol and, especially, in the ethanol/water 1:1 solution.

In the Ga 3d spectra, a doublet of Ga–S is expected to appear since Ga–S bonds are energetically more favourable than As–S bonds [34,35]. However, no such peak could be resolved because of its close proximity to the Ga suboxide (Ga_2O) peak at 19.8 eV [32,36]. Nevertheless, the existence of Ga–S cannot be completely excluded [37]. The sample (a) exhibits the most remarkable presence of Ga oxides, further corroborating the FTIR observation that the monolayer formed in chloroform is defective. In contrast, the sample (c) grown in ethanol/water 1:1 shows a negligible presence of Ga oxides expected at high binding energy (>19.8 eV). For clear comparison, we have listed the composition of each component in the Ga 3d and As 3d spectra in Table 2. We have separated S 2p region by subtracting Ga 3s (at ~ 160 eV) and As plasmon (at ~ 157 eV) according to the previous work [33]. As shown in Fig. 3, S 2p spectrum exhibits a single doublet at the binding energy of ~ 162.6 eV (ratio 2:1, splitting 1.18), which is characteristic of thiolate species [36,38]; while for the multilayer or otherwise weakly bound thiols, the doublet binding energy is at 163.7 eV [39]. The fitting results suggest that a negligible fraction of the unbound thiols is present in these samples. For the samples grown in chloroform (a), ethanol (b) and ethanol/water 1:1 (c), a relative ratio of the S 2p emission intensity is (a):(b):(c) = 1:1.5:2.6.

Table 2

Atomic concentrations of As–S, As⁰, As oxides, Ga₂O oxide and all other Ga oxides for samples (a), (b) and (c) shown in Fig. 2.

	As 3d ^a			Ga 3d ^b	
	As–S (%)	As ⁰ (%)	As oxides (%)	Ga ₂ O (or/and Ga-S) (%)	Ga oxides (%)
(a) Chloroform	0	5.04	5.46	17.16	13.06
(b) Ethanol	1.12	6.29	3.17	12.51	5.10
(c) Ethanol/water 1:1	2.76	9.44	0	16.51	0

^a Concentrations of As–S, As⁰ and As oxides are calculated for each component area and compared to the whole spectral area of As 3d.

^b Concentrations of Ga₂O and all other Ga oxides are calculated for each component area and compared to the whole spectral area of Ga 3d.

3.3. Photoluminescence study

The analysis of the PL effect has frequently been used to study the SAM passivation efficiency and electrical characteristics of III–V semiconductors surfaces and interfaces [1,2,22]. Fig. 4 illustrates

room temperature PL peak intensities of GaAs/AlGaAs samples as a function of the sample storage time in air. All samples in this experiment were excited at nominally identical conditions. Initially, for the HDT SAM formed in chloroform (a), a 3.2 (±0.1) times PL intensity increase is observed in comparison to the signal from an unprotected sample exposed for several weeks to an atmospheric environment. Combined with FTIR and XPS analysis reported above, we suspected that this PL increase is related to the enrichment of the surface with Ga oxides that are known to reduce concentration of surface defects responsible for non-radiative recombinations [40]. In order to evaluate this hypothesis, we prepared a series of samples that were etched with ammonium hydroxide and incubated in chloroform only (without thiols). We observed that in this case PL intensity increased by 2.5× (±0.12), suggesting that, indeed, the oxidation process in chloroform leads to a reduced density of surface states responsible for non-radiative recombination (see Fig. A1 in Appendix comparing XPS As 3d and Ga 3d spectra of an etched (d) and an etched and 18 h incubated in chloroform (e) samples). The initial PL intensity increase of 1.7× (±0.1) observed for samples with HDT SAM deposited in ethanol/water solution (c) is comparable to the 1.9× (±0.1) increase observed for samples with HDT SAM deposited in ethanol (b). Combined with the surface components revealed by the XPS analysis (see Table A1 in Appendix), it is reasonable to conclude that it is the richness of elemental As that is responsible for the weak PL increase of sample (c) [41,42]. However, as illustrated in Fig. 4, the samples incubated in ethanol/water, in comparison to those incubated in

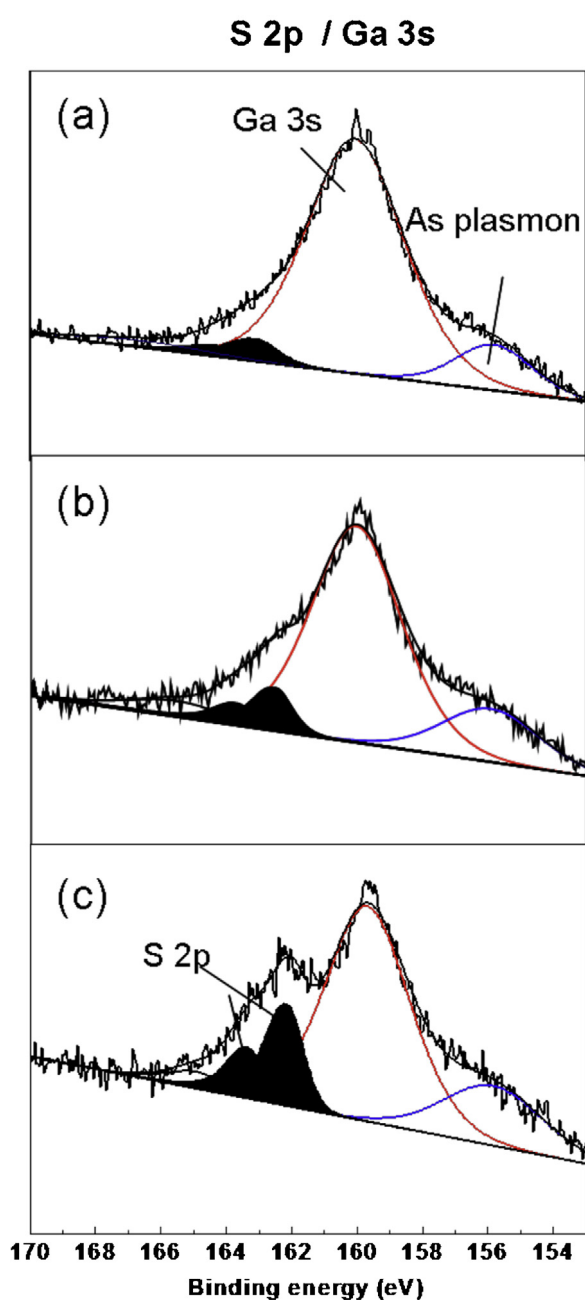


Fig. 3. XPS S 2p and Ga 3s components of HDT monolayers grown on GaAs (001) in (a) chloroform, (b) ethanol and (c) ethanol/water 1:1 solutions.

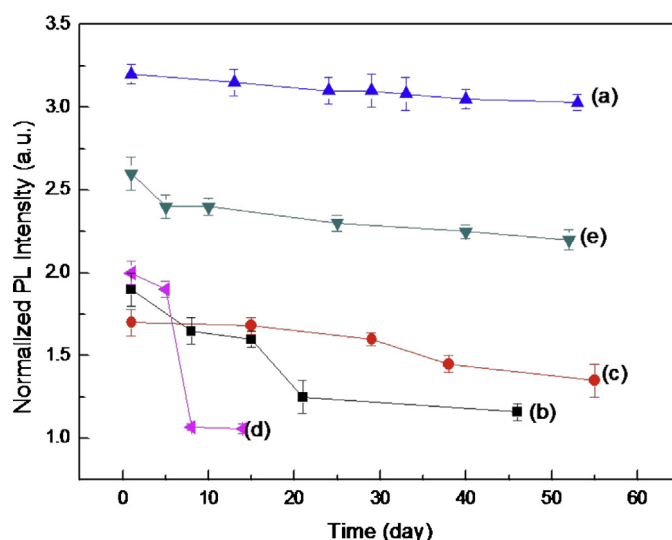


Fig. 4. Room temperature GaAs PL peak intensity as a function of storage time in air of HDT SAM-GaAs samples prepared in chloroform (a), ethanol (b), ethanol/water 1:1 (c), etched only sample (d), and etched and 18 h incubated in chloroform sample (e). The error values have been calculated based on measurements of three samples prepared independently. Data collected under nominally identical excitation conditions and normalized to the PL intensity of a heavily oxidized GaAs (001) sample.

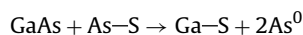
ethanol, exhibit an enhanced photonic stability upon the exposure to an atmospheric air. Sample (b) shows an almost 63% decreased PL signal in 50 days, whereas sample (c) is evidently more stable with its PL reduced only by 25% after the same period of time. The likely reason of this enhanced stability is the presence of a more densely packed HDT SAM on GaAs incubated in the ethanol/water solution. Note that the PL intensity of a freshly etched sample (d) has doubled in comparison to that of an oxidized sample, but its PL signal has decreased again within approximately 8 days to near its initial intensity. Among the investigated samples, the best photonic stability (a 7% PL intensity decrease in 50 days) exhibited SAM coated samples incubated in chloroform (a). The most likely reason for this behaviour is that, in addition to the formation of Ga–S sites, this chemical environment promotes the formation of a thermodynamically stable Ga₂O₃/GaAs interface that is known to suppress the process of formation of non-radiative recombination centres on the surface of GaAs [43]. This result compares to the 18% decay of the PL signal in the samples incubated in chloroform only, for the same period of exposure to an atmospheric environment.

4. Discussion

A theoretical study in our group concerning adsorption kinetics of thiols on GaAs (001) surfaces in vacuum has suggested that hydrogen desorption of –SH is an unfavourable process, and during the thiolation step, hydrogen remains on the GaAs surface upon S–H cleavage [35]. Numerous thiolation experiments have been carried out in a liquid phase with relatively low concentration of thiols (1–10 mM) in different solvents, and it has been reported that the binding process between thiols and surface sites can gain the additional energy associated with solvation [44–47]. Compared to solvents with a low dielectric constant (chloroform, ethanol), water is more prone to accept the hydrogen cleaved from S–H and stabilize the forming dipole [15,48]. At the same time, due to the unfavourable interaction of water molecules with hydrocarbon chains of HDT molecules, and the strong, attractive hydrophobic interactions of the hydrocarbon chains in the presence of water [49], there must be a greater energetic restriction to have defects within the water–ethanol–borne SAM due to increased surface area of the contact between the hydrocarbon chains of the alkanethiols and water molecules [31]. Therefore, SAMs prepared in aqueous solution are likely to crystallize into a better-defined domain structure with relatively fewer defects. In contrast, in chloroform, the strong interaction between chloroform and the nonpolar alkane chain of HDT deteriorates the driving force of forming ordered SAM, i.e., the intermolecular force between alkane chains, resulting in a defective monolayer. Our results show that the quality of HDT monolayers formed in three solvents follows the sequence: ethanol/water 1:1 > ethanol > chloroform, which coincides with the solvents' dielectric constants, and further confirms that the intermolecular force plays an important role in the self-assembly, especially of long chain alkanethiols.

Although densely packed HDT SAM are formed on GaAs in ethanol/water 1:1, their presence has not led to a satisfactory improvement of the electronic properties of the GaAs surface. Considering interfacial binding, i.e., the affinity between sulphur and surface binding sites (Ga and/or As), –SH groups of HDT are less nucleophilic and tend to interact with less-polarizable As sites through As–S bonding in ethanol/water 1:1 [50–52]. However, the As–S bonding does not reduce the surface states, as an As–S antibonding state appears within the energetic gap of GaAs [34]. At the same time, our XPS analysis exhibits that the samples incubated in ethanol/water 1:1 are As⁰ rich. This is known to produce mid-gap levels that deteriorate the electronic properties of GaAs [41,42]. The

enrichment with As⁰ may be due to the following transformation that is thermodynamically stable at the GaAs/sulphide interface [53]:



In the low dielectric constant solvent – chloroform, the solvation effect will increase the hardness of sulphur that is prone to interact with more-polarizable Ga sites by nucleophilic attack [51], and lead to the decreased surface-state densities due to Ga–S bonding [34]. As the HDT SAM formed in chloroform is defective due to the reduced intermolecular (thiol–thiol) interaction, the partial oxidation process is inevitable. Chloroform will also increase the hardness of oxygen atoms dissolved in it, resulting in their tendency to interact with the hard region of the GaAs surface according to the hard and soft acids and bases principle [54,55]. Consequently, Ga₂O₃ is formed on the GaAs surface, reducing the surface state density that pin Fermi level or/and increasing the surface gap of the semiconductor, as suggested by ab initio quantum chemical calculations [51,56]. It is feasible that due to this effect the samples incubated in chloroform only (without HDT) could exhibit a significantly increased intensity of the PL emission, as observed in Fig. 4. In addition to Ga oxides, the formation of As oxides and elemental As takes place during GaAs exposure to chloroform (see Table A1 in Appendix). Thus, the PL efficiency in this case is slightly compromised in comparison to that of a molecular beam epitaxially grown GaAs sample in situ capped with a thin layer of Ga₂O₃ [40].

5. Conclusion

We have investigated the influence of solvents on the formation of HDT SAM on GaAs (001) by studying both chemical and electronic properties of the SAM–GaAs interface. The results confirm that ethanol/water 1:1 mixture largely improves the conformational order and surface coverage of the long chain alkanethiol monolayer on GaAs that has originally been reported for MHDA SAMs on GaAs [20]. A comparison of PL and XPS results for samples incubated in chloroform and ethanol shows a significant reduction of the surface electronic states for the samples incubated in chloroform (a low dielectric constant solvent). However, the HDT monolayer formed in chloroform is highly disordered due to the strong interaction between chloroform and the nonpolar alkane chain of HDT, which deteriorates the intermolecular forces between alkane chains. It is clear that HDT and other long-chain SAM formed on GaAs investigated for achieving surface functionality, may not necessarily provide the best electronic passivation of the GaAs surface. One approach to address this problem could involve post-treatment of SAM/GaAs samples with ammonium sulphide as suggested in the literature [22].

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Appendix.

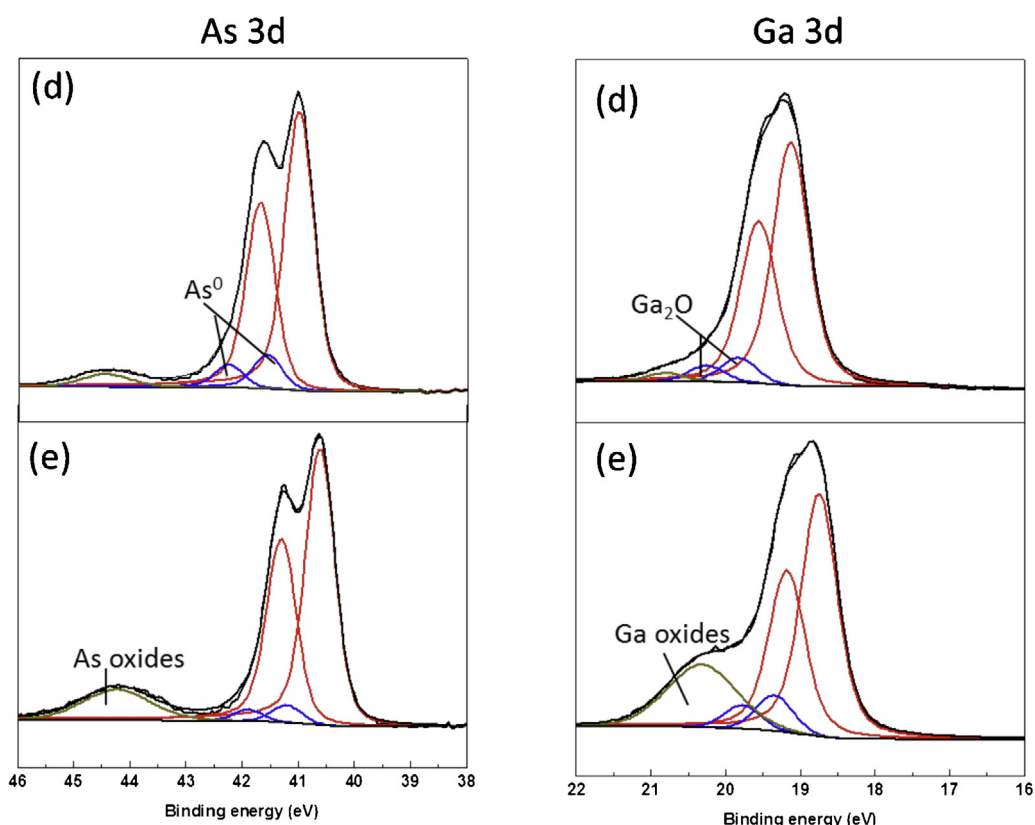


Fig. A1. XPS As 3d and Ga 3d spectra of (d) etched GaAs (001) and (e) etched GaAs, followed by an 18 h incubation in chloroform (without hexadecanethiol). Enhanced formation of Ga and As oxides is observed on the surface of a sample incubated in chloroform.

Table A1

Atomic concentrations of As–S, As⁰, As oxides, Ga₂O and Ga oxides for the samples (d) and (e) shown in Fig. A1.

	As 3d ^a			Ga 3d ^b	
	As–S (%)	As ⁰ (%)	As oxides (%)	Ga ₂ O (%)	Ga oxides (%)
(d) Etched GaAs	0	10.66	3.38	7.67	1.65
(e) Etched GaAs and 18 h incubated in CHCl ₃	0	4.38	10.55	9.02	18.00

^a Concentrations of As–S, As⁰ and As oxides are calculated for each component area and compared to the whole spectral area of As 3d.

^b Concentrations of Ga₂O and all other Ga oxides are calculated for each component area and compared to the whole spectral area of Ga 3d.

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