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Oriented self-assembled monolayers of bifunctional molecules on InAs

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ABSTRACT

We describe the formation and characterization of oriented self-assembled monolayers (SAMs) of bifunctional molecules on InAs. Cysteamine, a small molecule with thiol and amine termini, can be efficiently deposited on InAs(001) from a basic aqueous solution. Analysis of the deposited films using X-ray photoelectron spectroscopy (XPS) reveals that cysteamine forms a monolayer, in which molecules are oriented and attached to the InAs surface exclusively via their thiol termini. The free amine ligands presented at the interface of the resulting oriented SAM should provide a convenient pathway for subsequent surface functionalization. In addition, cysteamine deposition efficiently removes InAs native oxides; the resulting cysteamine SAM provides surface passivation, protecting the InAs substrate from reoxidation after short-term exposures to air and aqueous solutions.

1. Introduction

Deposition of self-assembled monolayers (SAMs) [1,2] is a promising approach for surface passivation and functionalization of III–V semiconductors [3–12]. Much of the recent progress focused on chemical and electronic surface passivation provided by thiol-based SAMs, which have been observed to inhibit surface oxidation [13–17] and to enhance photoluminescence [18–20] of III–V materials. Many passivation effects of SAMs are similar to those observed for III–V surfaces treated by inorganic and organic sulfides [4,21–30]. In contrast to the numerous demonstrations of III–V surface passivation, relatively few studies have reported successful functionalization of III–V surfaces by SAMs, e.g., via the deposition of bifunctional SAMs [10–13]. Creating SAMs that present reactive ligands at the interface is critical for functional applications, including the construction of multilayers or attachment of biological molecules.

Producing oriented bifunctional monolayers on InAs and other III–V materials, however, has proven to be challenging. Whereas on coinage metals the thiol-down orientation of SAMs is largely independent of their terminal functionality [1,2], the same rule does not hold for thiols on III–V surfaces. Our examination of XPS spectra from previous studies [11,13] indicates, for example, that III–V surfaces exposed to alkanethiols with oxygen-containing functional groups (hydroxyls and carboxyls) show considerable oxidation, presumably because oxygen-containing ligands readily interact with III–V semiconductors. The resulting oxygen-based attachment chemistry not only leads to disordered monolayers, but also produces surface oxidation that can have detrimental effects on electronic properties of the interface [3,4,14,21,22].

Surprisingly, the use of thiol molecules functionalized with amines rather than oxygen-based ligands has been largely left unexamined on InAs or other III–V materials. Here, we present a comprehensive XPS analysis of cysteamine monolayers formed on InAs, and show that oriented films can be produced presenting amine ligands suitable for further chemical or biological functionalization. These monolayers also offer surface passivation, protecting the InAs substrate from reoxidation after short-term exposures to air and aqueous solutions.

2. Experimental

InAs (0 0 1) samples were diced from a commercial single side polished wafer. Cysteamine ($HSC_2H_4NH_2$, 98% purity) was purchased from Sigma–Aldrich (St. Louis, MO). Prior to treatment, InAs samples were degreased by soaking in hexanes for 24 h, then sonicated sequentially in hexanes, acetone, and ethanol, for 5 min in each solvent. Samples were then rinsed with ethanol and dried under flowing nitrogen.

Cysteamine solution consisted of 10 mM cysteamine in a 1:9 mixture of NH_4OH (29.7% stock solution, Fisher Scientific) in absolute ethanol. The alkaline component of the solution strips the native oxide from the InAs sample and simultaneously de-protonates the thiol group, thus activating it for covalent attachment to the surface [7,14,17]. Monolayers were deposited by immersing InAs samples in the cysteamine solution for 30 min, in glass scintillation vials placed in a water bath at 55 °C. After treat-

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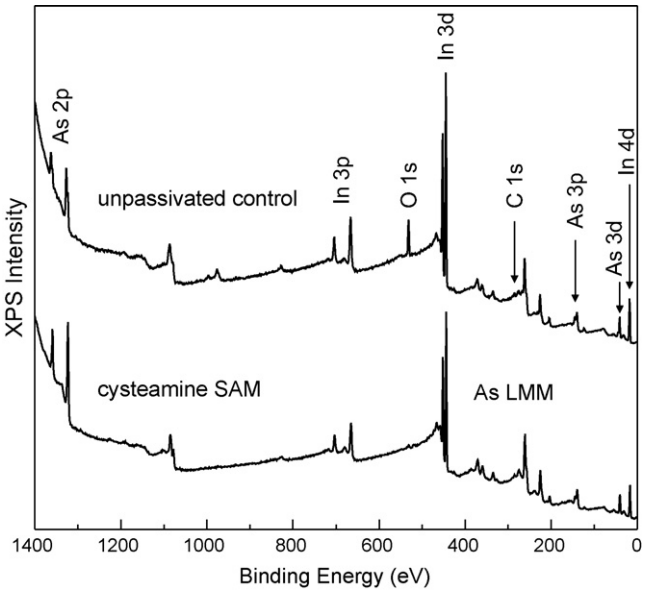

Fig. 1. Survey spectra of InAs samples treated in basic solutions with and without cysteamine. The basic solution without cysteamine was used to remove native oxides from the unpassivated control (top spectrum), the cysteamine SAM (bottom spectrum) was deposited from a similar basic solution containing cysteamine. Exposure to air for ≤10 min before XPS analysis reoxidized only the unpassivated control (O 1s peak in top spectrum).

ment, samples were rinsed in copious amounts of deionized water and dried with flowing nitrogen.

The basic solution used for cysteamine deposition removes native oxide from InAs substrates, therefore samples stripped of their native oxide using a similar treatment (but without cysteamine in solution) are most appropriate as controls for determining the chemical effects of the cysteamine deposition and for separating them from the effects of the basic solution. The use of dilute NH_4OH to produce high-quality oxide-free GaAs substrates for deposition of SAMs [7,14] suggested a similar method for InAs. The InAs control samples (also denoted as "unpassivated" controls hereafter) were stripped of native oxide by placing them for 10 min into a solution of 15% NH_4OH in deionized water. Samples were then rinsed with deionized water and dried under flowing nitrogen, immediately prior to transferring them into the vacuum chamber for XPS analysis.

XPS characterization was performed in a commercial XPS system equipped with a monochromatic Al Kα source, a magnetic lens, and a hemispherical electron energy analyzer (58° angle between the monochromator and analyzer) [30–32]. XPS measurements were carried out without any additional sample treatment, at room temperature in a UHV chamber with base pressure $<1 \times 10^{-9}$ Torr. Nominal X-ray spot size and analyzer field of view were $\leq 1\,mm^2$, the nominal acceptance angles were 4° and 30° (along the energy dispersive and nondispersive directions, respectively), no effort was made to ensure a particular azimuthal alignment of samples. The binding energies (BE) are reported with 0.1 eV precision, based on a two-point analyzer energy calibration described in detail elsewhere [30–32]. The elemental XPS data (nominal analyzer resolution of 0.36 eV) were acquired in angle-integrated normal emission mode and analyzed following previously described procedures [28–32].

3. Results and discussion

3.1. XPS surveys

The XPS surveys in Fig. 1 compare the surface compositions of two InAs samples that were treated in similar basic solutions and briefly exposed to deionized water and ambient air before XPS measurements. The O 1s intensity is clearly dramatically higher for the "unpassivated" control sample (top spectrum in Fig. 1), the surface of which was etched in a basic solution but left apparently unprotected against subsequent reoxidation. In contrast, the spectrum of the sample treated by a cysteamine-containing basic solution (bottom spectrum in Fig. 1) exhibits a much weaker O 1s peak, indicating that the cysteamine deposition not only removed the native oxide but also provided short-term passivation against reoxidation.

In addition to direct surface oxidation, water adsorption can also contribute to the O 1s signal, particularly because cysteamine deposition is expected to produce a hydrophilic surface [33]. The low O 1s signal intensity makes any detailed peak fitting in that region ambiguous, but the overall width of 3–4 eV for the O 1s spectral envelope indicates that multiple chemical states of oxygen are present on the surface. A definitive assignment of some O 1s intensity as adsorbed water is prevented by the lack of reliable reference data on O 1s BEs for this system. The total O 1s signal, however, is comparable, within the experimental uncertainties, to the total signal from the surface oxides, which suggests ≈1 monolayer (ML) as the upper limit on the total amount of adsorbed water molecules, based on our previous coverage estimates for passivated InAs surfaces [30]. The low limit on the amount of surface-bound water in UHV, of course, does not rule out the presence of water on these surfaces under ambient conditions, but rather indicates that physisorbed water molecules are effectively removed from cysteamine-treated surfaces under UHV conditions.

Overall, both surveys in Fig. 1 are dominated by major peaks of the substrate elements, In and As. In fact, As-based III–V materials provide particularly convenient internal references for semi-quantitative evaluation of spectroscopic signatures of small-thiol adsorbates, because the substrate As LMM Auger and As 3p XPS peaks are adjacent to the C 1s and S 2p regions, respectively. In general, even a complete monolayer of small thiol-containing molecules will produce C 1s and S 2p peaks that are much weaker than the substrate peaks, so the low intensity of cysteamine spectroscopic signatures in the bottom survey in Fig. 1 is expected, rather than surprising. The barely noticeable C 1s peaks in Fig. 1 also indicate that nonspecific adsorption of organic contaminants was not significant for either of the two samples.

In order to directly examine the spectroscopic signatures of cysteamine and the associated InAs interface chemistry, in the following sections we consider the high-resolution elemental spectra (Fig. 2) and peak fitting results (Tables 1 and 2) for the two samples introduced in Fig. 1. The spectra in Fig. 2 are normalized to the bulk As 3d component *for each sample*, to enable direct semi-quantitative

Table 1
Fitting parameters of major XPS peaks for a cysteamine monolayer on InAs.

Peak	Component	BE (eV)	FWHM (eV)	
			Lorentzian	Gaussian
As $2p_{3/2}$	As–In	1322.8	0.5	1.0
	As–S	1324.0	0.5	1.5
	As^{3+} oxide	1326.2	0.5	1.5
	As^{5+} oxide	1327.3	0.5	1.5
In $3d_{5/2}$	In–As	444.5	0.3	0.5
	In–S	445.0	0.3	0.5
	In–O	445.3	0.3	1.2
N 1s	N–C	400.0	0.2	1.3
S $2p_{3/2}$	Thiolate	162.5	0.1	1.1
	Chemisorbed sulfur	161.0	0.1	1.1
As $3d_{5/2}$	As–In	40.9	0.1	0.6
	As–S	41.9	0.1	0.6
	As–O	44.2	0.1	1.2