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Passivation of GaSb and InAs by pH-activated thioacetamide

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ABSTRACT

We describe the passivation by thioacetamide (TAM) of GaSb and InAs—two III–V semiconductor materials important for fabricating IR devices from Type-II superlattices (T2SLs). We use X-ray photoelectron spectroscopy (XPS) to characterize GaSb and InAs (001) surfaces treated by TAM under both acidic and basic conditions and to analyze the reoxidation of passivated surfaces over time. Both acid- and base-activated TAM treatments produce sulfide layers on GaSb and InAs. The layers produced by base-TAM appear to be of self-limited thickness <1 nm, whereas acid-TAM creates considerably thicker (1–2 nm) sulfide layers. Passivation by both acid- and base-activated TAM offers significant short-term (<1 day) protection against reoxidation, but does not prevent oxide formation after exposure to ambient air for 1–3 days. Based on this comparative study and previous literature reports, the chemical effects of TAM treatments on Ga, Sb, In, and As depend not only on the individual element and reaction conditions, but also on the compound. In other words, our results suggest that passivation chemistry for a common element in two different III–V materials should not, in general, be assumed to be the same.

1. Introduction

We compare the effects of thioacetamide treatments on GaSb and InAs in order to bridge the gap between the fundamental studies of sulfur passivation of III–V materials and the application of methods derived from such studies to passivation of devices. Most published accounts focus on the effects of passivation on device performance without attempting to directly characterize the chemistry of the passivated surface [1–7]. As a result, surprisingly little is known about the chemical effects of various passivation treatments, despite the widespread research on the effects of passivation on performance of III–V devices.

The choice of *two* III–V semiconductors for our study helps to demonstrate another important aspect of applying chemical treatments to device structures. In devices, III–V materials typically are not used separately and independently, but rather as alternating layers in superlattices. For example, Type-II superlattices (T2SLs) of InAs and GaSb are emerging as a promising material system for mid- and long-wavelength IR LEDs [8] and photodetectors [1–5,7,9–14]. In these IR detectors, doped T2SLs are etched through the junction to produce an array of mesa-isolated photodiodes [3,4]; i.e., *both* superlattice materials are exposed to the ambient surroundings in these devices. Therefore, the effects of each passivation method on *both* InAs and GaSb surfaces must be analyzed to fully understand and optimize device passivation.

In unpassivated InAs/GaSb T2SLs, the high surface recombination velocity on the exposed sidewalls of mesa photodiodes results in excess dark current [3,4]. Theoretically, InAs/GaSb T2SLs provide tunable and strong optical absorption, a narrow-gap band structure, large effective masses, and low Auger recombination rates. Therefore, compared with HgCdTe (MCT) devices, effectively passivated T2SLs should be able to operate at higher temperatures.

Sulfur passivation has been used effectively to passivate exposed surfaces of III–V semiconductor devices [15–25], and has been previously attempted for T2SLs [2–4,7]. Historically, most common sulfur passivation treatments have been performed in aqueous solutions of inorganic sulfides, such as $(NH_4)_2S_x$ [16,17,23,26–28] or Na_2S [18,26,27,29]. More recently, an alternative treatment based on thioacetamide (TAM), an organic sulfide, has been proposed and its effectiveness examined in some

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detail [6,7,21,22,24,25]. Surface passivation by TAM compares favorably to that by inorganic sulfides [25] and offers advantages such as milder reaction conditions and the ability to passivate under both acidic and basic conditions. Here, we use X-ray photoelectron spectroscopy (XPS) to characterize GaSb and InAs surfaces passivated by TAM under acidic ("acid-TAM") and basic ("base-TAM") conditions, and to analyze the extent of reoxidation of the passivated surfaces over time.

2. Experimental details

Homoepitaxial GaSb(001) and InAs(001) 0.5 μm-thick undoped epilayers were grown on 5 cm-diameter epi-ready substrates (Wafer Technology Ltd., U.K.) by solid-source molecular beam epitaxy in a Riber compact 21T system equipped with valved arsenic and antimony crackers. The "acid-TAM" or "base-TAM" solutions were prepared by dissolving thioacetamide powder (CH_3CSNH_2, 99.0%, ACS reagent grade) in, respectively, glacial acetic acid (Fisher Scientific), or ammonium hydroxide (29.7% stock solution, Fisher Scientific), diluted 1:10 by volume in deionized water.

In this paper, samples treated by TAM solutions are referred to as "passivated" and compared to "unpassivated" and "untreated" controls. *Passivated* samples were placed for 40 min in 0.18 M TAM solutions (at acidic or basic pH, as described above) held at 70 °C in a water bath. After treatment, samples were rinsed in copious amounts of deionized water, dried with flowing nitrogen, and maintained under ambient atmospheric conditions between XPS measurements. *Unpassivated* control samples were stripped of their native oxide films using AZ400K (Clariant Corporation, Somerville, NJ) for GaSb and 15% NH_4OH for InAs. *Untreated* control samples were as-grown GaSb and InAs films exposed to ambient air for a specified time.

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 [24]. The high-resolution data (nominal analyzer resolution of 0.36 eV) were acquired in angle-integrated normal emission mode and quantitatively analyzed following a previously described procedure [24]. Surface roughness was measured using an atomic force microscope (AFM) operated in contact mode.

3. Results and discussion

3.1. Freshly-passivated surfaces

We find that III–V surfaces treated by TAM solutions at different pH exhibit dramatically different chemistries, as evidenced by XPS data for freshly-passivated GaSb (Fig. 1(b)) and InAs (Fig. 1(c)). The corresponding bulk, sulfide, and oxide components for each element (Table 1) can be identified and quantified by fitting the high-resolution spectra in Fig. 1 [24,30]. A basic TAM solution (spectra marked "base-TAM" in Fig. 1) produces self-limiting thin layers composed primarily of sulfides on both GaSb and InAs. The resulting sulfide components (shaded gray in Fig. 1) are both element- and compound-dependent, with about twice as much Sb–S as Ga–S on GaSb (Fig. 1(b)) and almost exclusively In–S on InAs (Fig. 1(c)).

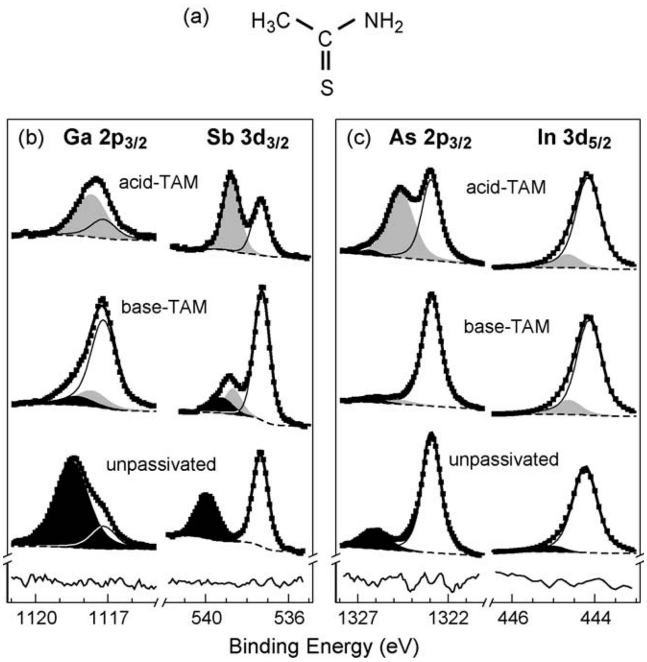

Fig. 1. XPS data for TAM-treated GaSb and InAs samples. Solutions of TAM (a) activated with acid or base were used to passivate GaSb (b) and InAs (c) samples; unpassivated controls were treated only to remove native oxides. Exposure to ambient air before XPS measurements was ≤5 min. Indicated in fits for each element are bulk (thin line, no shading), sulfide (gray shading), and oxide (black shading) chemical components (Table 1). Symbols = data points; thick lines = overall fits; dashed lines = backgrounds; representative fit residuals are shown at the bottom of panels. The minority-spin Sb $3d_{3/2}$ component was used for peak fits in (b) to avoid overlap with O 1s.

Table 1
XPS peak fitting parameters for TAM-treated InAs and GaSb samples.

Peak	Component	BE (eV)	FWHM (eV)		Intensity ratio vs. bulk	
			Lorentzian	Gaussian	Acid-TAM	Base-TAM
In $3d_{5/2}$	In–As	444.2	0.32	0.51	–	–
	In–S	444.7	0.32	0.51	0.15	0.15
	In–O	445.0	0.32	1.2	0	0.007
As $2p_{3/2}$	As–In	1323.0	0.50	0.94	–	–
	As–S	1324.7	0.50	1.5	1.1	0.05
	As–O	1326.2	0.50	1.5	0.06	0.03
Ga $2p_{3/2}$	Ga–Sb	1117.2	0.66	0.83	–	–
	Ga–S	1117.7	0.66	1.1	2.7	0.21
	Ga–O	1118.3	0.66	1.2	0	0.12
Sb $3d_{3/2}$	Sb–Ga	537.3	0.15	0.82	–	–
	Sb–S	538.7	0.15	0.88	1.4	0.27
	Sb–O	539.9	0.15	1.2	0	0.12

Compared to base-TAM, acid-TAM solutions create considerably thicker sulfide layers on GaSb [note the increased sulfide and suppressed bulk components in both Ga and Sb spectra in Fig. 1(b)]. On InAs, roughly the same amount of In–S is formed under acidic and basic conditions, but in acid-TAM there is appreciable As–S formation, approximately 50% higher than the amount of In–S (Fig. 2(b)). The surface termination after acid-TAM treatment, therefore, is a mixture of As–S and In–S, in contrast to the exclusive In–S termination that we have observed after base-TAM treatment, both here and previously [24,25]. We note that both acid- and base-TAM-treated surfaces are relatively smooth (≈4 Å RMS roughness over a 1 μm^2 area), suggesting that there is not a significant differential etch rate under these conditions.

In analyzing the XPS results for the GaSb samples, the spin-orbit minority Sb $3d_{3/2}$ peak was examined instead of the majority $3d_{5/2}$ peak, which partially overlaps with O 1s peak. As surface oxidation progresses, this overlap makes fitting of the Sb $3d_{5/2}$ oxide and sulfide components difficult and can lead to their overestimation.

Significantly, the Ga and As elemental spectra acquired after the acid-TAM passivation of GaSb and InAs, respectively, *do not*