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Use of 3-aminopropyltriethoxysilane deposited from aqueous solution for surface modification of III-V materials

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ABSTRACT

Focal plane arrays of strained layer superlattices (SLSs) composed of InAs/GaSb are excellent candidates for infrared imaging, but one key factor limiting their utility is the lack of a surface passivation technique capable of protecting the mesa sidewall from degradation. Along these lines, we demonstrate the use of aqueous 3-aminopropyl triethoxysilane (APTES) deposited as a surface functionalizing agent for subsequent polymer passivation on InAs and GaSb surfaces following a HCl/citric acid procedure to remove the conductive oxide In_2O_3. Using atomic force microscopy, variable angle spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS), and modeling with density functional theory (DFT), we demonstrate that APTES films can successfully be deposited on III-V substrates by spin coating and directly compare these films to those deposited on silicon substrates. The HCl/citric acid surface preparation treatment is particularly effective at removing In_2O_3 without the surface segregation of In oxides observed from use of HCl alone. However, HCl/citric acid surface treatment method does result in heavy oxidation of both Ga and Sb, accompanied by segregation of Ga oxide to the surface. Deposited APTES layer thickness did not depend on the substrate choice, and thicknesses between 1 and 20 nm were obtained for APTES solution concentrations ranging from 0.1 to 2.5 vol %. XPS results for the N1s band of APTES showed that the content of ionic nitrogen was high (~50%) for the thinnest films (~1 nm), and decreased with increasing film thickness. These results indicate that APTES can indeed be used to form a silane surface layer to cover III-V materials substrates. Such APTES silane layers may prove useful in surface passivation of these materials alone, or as surface functionalizing agents for subsequent covalent binding with polymer overlayers like polyimide.

1. Introduction

Strained layer superlattices (SLSs) composed of InAs/GaSb have a variety of potential uses in meteorology, astronomy, gas detection, fundamental science, and military applications [1–3]. These materials are often employed as photodetectors operating in the long-wave infrared region (8–12 μm). InAs/GaSb SLSs have a comparable absorption coefficient to conventionally used mercury-cadmium-telluride and have additional natural advantages in terms of strong suppression of Auger recombination rates, which reduces dark current [1,4], and lower sensitivity to variations in composition [5].

Many photodetector applications of these superlattice materials require the formation of focal plane arrays for infrared imaging. Part of the fabrication process involves patterning and etching the superlattice to form the individual mesas comprising the focal plane array. During this process, defects arise due to dangling bonds, chemical segregation, and contaminant incorporation on the sidewall surfaces of the mesas, resulting in the formation of various surface states. These surface states are detrimental to device performance as they can fall within the band gap of the superlattice and/or cause band bending at the surface, leading to Fermi level pinning. Furthermore, some of the oxides that spontaneously form on the exposed surface are themselves conductive [4], leading to

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diminished device performance, and excess noise due to surface leakage current [6].

One key factor limiting the performance of these devices is the lack of a surface passivation technique capable of mitigating the surface defects and protecting the sidewall from further degradation [7]. Specifically, there is a lack of chemical and electronic control of the surface properties due to the complex oxides, which spontaneously form on the exposed surfaces [8]. A variety of techniques has been employed to passivate the surfaces of III-V materials, and they can broadly be placed into three categories: (i) strategies employing an inorganic overlayer, (ii) strategies that attempt to bond sulfur directly to the III-V material, and (iii) organic strategies that involve coating surfaces with polymers.

Inorganic passivation strategies involve the deposition of some type of inorganic layer over the III-V material. For example, Rehm et al. reported that epitaxial overgrowth of $Al_xGa_{1-x}As_ySb_{1-y}$ was capable of suppressing leakage current in InAs/(GaIn)Sb superlattices [6]. Other inorganic strategies have involved deposition of silicon in the form of SiN_x [2,4,9,10] and SiO_2 deposited by plasma-enhanced chemical vapor deposition [2–4,7,10–12]. Razeghi et al., however, showed that SiO_2 passivated devices required a graded doping profile and a shallow etch technique. Another strategy, highlighted by Szmulowicz and Brown, is the use of GaSb itself to passivate InAs/GaSb mesas [13]. While these techniques have met with varying degrees of success, many of them are expensive and require additional processing [7].

Sulfur based passivation techniques have also received a great deal of interest recently. Fundamentally, these techniques seek to exploit the ability of sulfur to covalently bond to atoms in III-V materials [14,15]. Among these strategies it is most common to use a sulfiding agent such as ammonium sulfide [16], zinc sulfide [4], and sodium sulfide [17], generally dissolved in an organic alcohol. These techniques have been shown to reduce surface conductivity and improve device performance. Thiols, including alkane thiols [18,19], have been deposited on InAs and have been shown to be stable against degradation in air and when exposed to various solutions. An amine functionalized thiol, cysteamine, has also been investigated for use on III-V surfaces [8,20]. Thioacetamide has been suggested as an alternative sulfidizing agent to the commonly used ammonium sulfide [21] due to its ability to form bonds directly with III-V metals (e.g., Ga—S), rather than bonds with an intermediate oxide (e.g., Ga—O—S) [5]. Electrochemical sulfur deposition from a Na_2S solution in ethylene glycol [5] also showed the potential to improve performance of InAs/GaSb SLS detectors. Again, while these techniques have proved promising, there is evidence that suggests they may not protect long-term against surface oxidation and that passivation chemistry may differ for different III-V elements [21].

A final category of passivation techniques employs polymeric materials to provide a protective coating on the III-V surface to prevent further oxidation due to air exposure. Specifically, this has involved the use of SU-8 photoresist, which showed a one order of magnitude reduction in dark current [1]. Further, surface resistivity for the SU-8 passivated SLS detector was higher than an SiO_2 passivated device, but lower than that of a ZnS passivated device. Polyimide, a polymer commonly used for surface capping in conventional silicon based technologies, has also been employed for III-V materials [9,22,23]. Therein, polyimide was found to greatly reduce surface current leakage [22], and provide surface stability [23]. The advantages of using polyimide are that it is inexpensive, readily available, and often used in conventional technology.

While the use of polyimide is attractive, there is no evidence to suggest that polyimide itself would covalently bond with the III-V material. In addition, it is well established that water will adsorb at polyimide-silicon oxide surfaces. If similar water adsorption effects also occur with polyimide-III/V interfaces, then surface leakage current and device performance could gradually change with time due to slow oxidation and eventual polyimide delamination. Adhesion promoters like those commonly used in silicon-based electronic materials might therefore be useful for III/V materials. For example, 3-aminopropyl triethoxysilane (APTES), is commonly used to modify silicon surfaces [24] in preparation for the application of a polyimide coating. However, little is known about their structure on III/V surfaces.

In this paper, we explore the use of APTES on InAs and GaSb surfaces using atomic force microscopy (AFM), variable angle spectroscopic ellipsometry (VASE), X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS). We further employ density functional theory to explore adsorption energies of APTES on gallium oxide surfaces to elucidate the possible mechanisms of deposition. We particularly focus on the ability to process APTES from aqueous solutions, eliminating the need for organic solvents that are more commonly described in the literature [25]. We demonstrate that APTES films can successfully be deposited on III-V substrates and directly compare these films to those deposited on silicon substrates.

2. Materials and methods

2.1. Materials

Citric acid (≥ 99.5%, ACS reagent, Sigma–Aldrich), hydrochloric acid (37%, Semiconductor Grade, Sigma–Aldrich), hydrofluoric acid (49%, OmniTrace Ultra, EMD Millipore), 3-aminopropyltriethoxysilane (>95% APTES, VM651, HD Microsystems), acetone (Spectroscopy grade, Sigma–Aldrich), and isopropanol (99.9%, Chromasolv, Sigma–Aldrich) were used as received. Undoped, 3 μm thick, InAs and GaSb substrate layers used in this study were deposited on 3 inch diameter GaAs substrates with a (1 0 0) molecular orientation via molecular beam epitaxy by IQE, Inc. (Bethlehem, PA). The bulk InAs and GaSb layers were deposited immediately preceding SLS device growth in the same molecular beam epitaxy reactor to ensure they were representative of the InAs and GaSb found in SLS device layers.

2.2. Sample preparation

2.2.1. Silicon wafer oxide preparation

The native oxide of the silicon wafer samples was removed and regrown using the procedure described herein. First, silicon wafers (Rogue Valley Microdevices, <100>, p-type, boron doped) were cleaned in a UV/ozone cleaner (Novascan PSD Pro) for 30 min. This was followed by sonication in fresh toluene and ethanol for 30 min each. After sonication, the wafers were rinsed with ultrapure DI water (18.1 MΩ cm) and were then blown dry with ultrapure nitrogen. To remove the native oxide, the wafers were then placed in a 1 wt% solution of HF in ultrapure DI water for 2 min. Wafers were then removed and rinsed three times with ultrapure DI water before being blown dry with ultrapure nitrogen. To regrow the oxide layer, the wafers were placed in the UV/ozone cleaner for 2 min. Ellipsometry measurements showed that the regrown oxide had a thickness of 2.0 nm.

2.2.2. Surface preparation

First, organic contaminants were removed from all substrate surfaces by rinsing with acetone followed by isopropanol for 5 s each. To remove oxides from the surfaces of III-V materials in preparation for APTES deposition, two treatment steps were used; first, exposure to 10% HCl [26] followed by exposure to 1 M citric acid [27], both in ultrapure water. For HCl treatment, the substrates were gently swirled in 10% HCl for 30 s, then placed in ultrapure DI water for 60 s, and then rinsed again with ultrapure DI water. Then,