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Post-etching mesa surface composition investigation of InAs/GaSb type-II strained layer superlattices using XPS characterization

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HIGHLIGHTS

- InAs/GaSb superlattice p-i-n and bulk samples were fabricated to compare H_3PO_4-based and HCl-based treatments.
- Spectral and imaging X-ray photoelectron spectroscopy (XPS) analysis were performed on the bulk sample.
- Dark current measurements were performed on the p-i-n sample.
- XPS and electrical characterization results were compared.

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ABSTRACT

XPS characterization was used to determine the surface chemistry of a mid-wave infrared T2SL treated by both an HCl-based and an H_3PO_4-based etching solution. This analysis, performed over both the etched and unetched portions of the sample, revealed that the HCl-based etch removed Ga and Sb oxides while the H_3PO_4-based etch removed In and As oxides. XPS imaging was also done on 200 μm × 200 μm areas of the sample, and showed that HCl solution (Ga, and O) produced surfaces that were less stoichiometric than the H_3PO_4 solution (Ga_2O_3, Sb_2O_5, Sb in GaSb). Single-pixel, p-i-n test structures were fabricated using either etching solution, and an electrical comparison revealed over an order of magnitude improvement in dark current for the sample treated with the H_3PO_4 solution, compared to the HCl sample.

1. Introduction

There are many advantages to using InAs/GaSb type-II superlattices (T2SL) as infrared detectors. They are shown to have low tunneling currents [1], as well as suppressed Auger recombination [2], and can be designed to suppress dark currents through heterostructure engineering using such structures as nBn [3], CBIRD [4], M-structure [5], or pBiBn [6]. However, one of the main challenges still facing this technology is the lack of a widely-accepted surface passivation technique [7]. Surface leakage paths are formed during mesa etching [8]; unsatisfied bonds on the newly etched surface react with the atmosphere [9], forming oxides such as Ga_2O_3, Sb_2O_3 [9], In_2O_3, As_2O_3 [10]. These oxides and their elemental components can facilitate higher surface leakage, surface recombination velocity, and Fermi level pinning. For example, elemental antimony and antimony oxides were shown to be a major contribution to diode leakage current [11].

Many passivation methods and materials for T2SL have been explored in an attempt to alleviate this problem, including dielectric coatings [12], organic solutions [13], chalcogenides [14], electro-chemical passivation [15], epitaxial overgrowth [16], and atomic layer deposition [8]. Generally, these techniques are performed by first removing the oxides, and then applying a material that satisfies the dangling bonds, prevents re-oxidation, and/or encapsulates the device. Thus, oxide removal is crucial step in the passivation process, and one of the common ways to do oxide removal is by chemical etching. However, while much effort has gone into finding materials for passivation, not as much effort has gone into studying the effects of a chemical etchant on surface chemistry. For successful pre-passivation oxide removal on T2SL, it is unclear what oxides must be removed. Also, it is important that the etching solution maintains surface stoichiometry, otherwise surface state density will be increased [17].

We report on our study of the surface chemistry before and after etching T2SL. Two etching solutions were tested, an HCl- and an H_3PO_4-based solution. HCl was selected because it has been shown to remove surface oxides on GaSb while maintaining

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stoichiometry [17], and H_3PO_4 was selected because it had been used previously in pre-passivation oxide removal [13]. First, X-ray photoelectron spectroscopy (XPS) was used to determine the surface chemistries of T2SL etched by the HCl and H_3PO_4 solutions. Then, to correlate this information with device performance, a set of single-pixel p-i-n devices was fabricated using either solution, dark current data were collected, and device performance was compared between the etching treatments.

2. Experiment

Both the XPS and p-i-n dark current samples (see Fig. 1) were grown using a solid source molecular beam epitaxy (MBE) VG-80 system equipped with valved cracker sources for the group V Sb_2 and As_2 fluxes, and Ga/In SUMO® cells. The two XPS samples were grown on Te-doped (n-type) GaSb epi-ready substrates and consisted of a non-intentionally doped layer 0.6 μm thick of superlattice of 10 monolayers (MLs) InAs/10 MLs GaSb. These samples were grown consecutively and on pieces from the same substrate, in order to minimize variation in growth. The p-i-n detector structure was grown on nominally undoped GaSb (100) epi-ready substrate and was composed of the 8 monolayers (MLs) InAs/8 MLs GaSb T2SL non-intentionally doped (n.i.d.) absorber layer with thickness of ~3.6 μm (700 periods) grown on top of the 200 nm thick p-type GaSb layer serving as a bottom contact. The structure was finished by a 144 nm thick n-type top contact layer formed by the T2SL with the same thickness and composition as the absorber layer. Doping concentrations were 2×10^{18} cm^{-3} for n-type top and p-type bottom contact layers. To improve the transport of photo-generated carriers, the doping of top 50 periods and bottom 10 periods of T2SL absorber region was graded. This sample was cleaved into two pieces after growth, with one half used in the H_3PO_4-based solution, and the other for the HCl-based solution.

After growth, half of each of the two XPS samples were covered in photoresist and the other half was left exposed (defining an unetched area, an edge, and an etched area), and then each was etched in either an HCl-based solution ($HCl:H_2O_2:H_2O = 1:1:4$) or an H_3PO_4-based solution ($H_3PO_4:H_2O_2:H_2O = 2:1:20$). After etching, the photoresist was removed with acetone, isopropyl alcohol, and dried with nitrogen.

For the electrical performance study, device fabrication was initiated with a standard optical photolithography to define 410 μm × 410 μm square mesa devices with apertures ranging from 25 to 300 μm. With the same mask variable area diode (VADA) arrays were defined with mesa side size varied from 30 μm to 400 μm. Detector mesa delineation was performed using inductively coupled plasma (ICP) reactor with BCl_3 gas. Next, ohmic contacts were evaporated on the bottom and top contact layers using Ti (500 Å)/Pt (500 Å)/Au (3000 Å) in both cases. Finally, devices were passivated by SU-8 2007 photoresist. Prior to passivation, the devices were immersed into phosphoric acid based ($H_3PO_4:H_2O_2:H_2O = 1:2:20$) or hydrochloric acid based ($HCl:H_2O = 1:10$) solutions for 30 s to remove any native oxide film formed on the etched mesa sidewalls. Note that the recipes for these acid solutions have changed compared to the ones used for the XPS samples. The spectral response of the samples was taken to confirm device operation; a representative plot of the spectral response (from the H_3PO_4 sample) is presented in Fig. 2.

The XPS characterization was performed with a Kratos Ultra DLD spectrometer using two different analytical methods, spectral XPS and imaging XPS analyses. Small area XPS spectra were collected in 55 μm areas, analyzing areas in increments of 50 μm from the edge on both the etched and unetched sides. High resolution 200 by 200 μm photoelectron images with the edge in the center were acquired. These images were acquired within As, Ga, In and Sb/O spectral regions with 0.5 eV increments. All the images were combined into multispectral data sets and principal component analysis (PCA) was applied. The output of multivariate analysis are images that show spatial distribution of different phase. The type of chemical bonds or elements that have similar spatial distribution are combined into one chemical map showing this particular spatial distribution. Spectral XPS analysis provides percentages of elements and a quantitative comparison, while photoelectron imaging indicates which elements are present on a surface and allows for a qualitative comparison.

3. Results and discussion

First, we studied the surface chemistries of T2SL samples before and after H_3PO_4- and HCl-based treatments. The results of XPS spectroscopic analysis are plotted in Fig. 3. Plots a and b are the H_3PO_4 results and c and d are the HCl results. Each plot has a vertical line running down the center, representing the edge between the etched (right) and unetched (left) sides of the sample. Legends for all data are shown in plots c and d. Plots a and c are for the Ga and Sb components, while b and d are for the In and As components. Comparing the surface chemistries before and after etching for both solutions reveals that the etched surfaces are very similar in composition, while the unetched sides are not. This may indicate that there was variation in growth or sample handling prior to etching. Plot a shows little change in Ga and Sb before and after etching with H_3PO_4, while the plot c shows a large reduction in Ga and Sb oxides after etching with HCl (Sb–GaSb and GaSb both

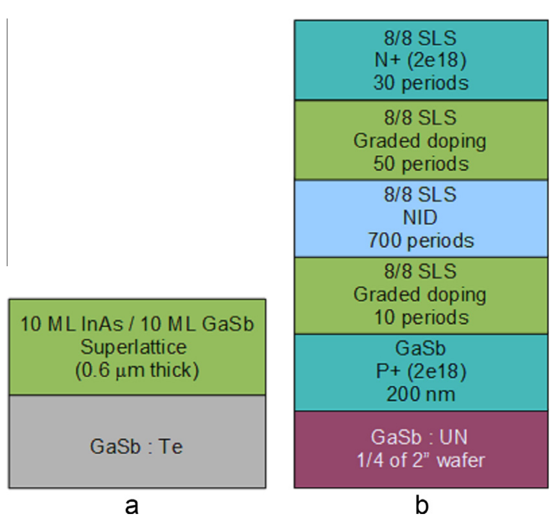

Fig. 1. MBE-grown structures used for this study.

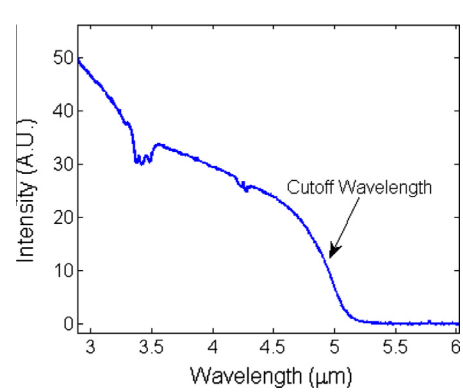

Fig. 2. Representative plot of spectral response from fabricated devices at 77 K.