

# Atomic Hydrogen Cleaning of Epiready InSb (100), (111)B, and GCIB Processed InSb (111)B Surfaces

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## Abstract

**X-Ray photoelectron spectrometry (XPS) performed on the surfaces of atomic hydrogen (H\*) cleaned chemical mechanical polished (CMP) "epi-ready" InSb (100), (111)B, and a gas cluster ion beam (GCIB) processed InSb (111)B substrates indicates the removal of native oxides from the substrate surfaces. All the processed surfaces showed strong elemental XPS peaks with no oxide side-lobes after H-atom (H\*) treatments of 20 min at substrate temperatures of 200 °C. Ex-situ atomic force microscopy measurements showed no change in the surface roughness of the CMP (100) and (111)B surfaces after H\* treatment. The GCIB surfaces, however, showed an increase in surface roughness after treatment, indicating that a rough oxide/substrate interface may be formed in the GCIB process used here.**

## INTRODUCTION

Chemical mechanical polishing of compound semiconductor substrates forms an oxide over-layer on the substrate surface and this undesirable oxide layer must be removed before initiating molecular beam epitaxy (MBE) growth. Although thermal desorption of the surface oxides in the MBE growth chamber can be used with most III-V's just prior to growth, oxide desorption on the low-temperature antimonides is problematic. The antimonides are able to form, depending on the polishing or processing technique, a variety of surface oxides that desorb at a variety of temperatures.

Surface oxide desorption properties of CMP InSb (100) and (111)B surfaces as a function of substrate temperature have been recently reported [1]. In that work thermal x-ray photoelectron spectroscopy (TXPS) was used to study the desorption of the InSb surface oxides as a function of temperature and the lowest temperature that appeared to remove all of the oxides was used in the MBE growth process to grow homoepitaxial layers over the surface. However,

cross-sectional transmission electron microscopy (XTEM) micrographs of the MBE grown epitaxial structures showed defects indicative of the presence of residual oxides at the InSb (100) substrate-epilayer interface, implying further desorption of surface oxides is necessary. To make matters worse, the indium oxides desorb at temperatures that are only a few degrees below the melting point of the InSb wafer. This suggests the need for other methods to remove the surface oxides for epitaxial growth and device processing.

Atomic hydrogen cleaning of the antimonide surface at a moderate substrate temperature has been found to remove the surface oxides while retaining an ordered crystalline surface structure on which to commence MBE growth. Atomic hydrogen cleaning [2, 3] and molecular hydrogen cleaning [4] of (100) surfaces have been reported in the literature. Haworth *et al* [2] used a radio frequency (r.f.) plasma source to generate high flux atomic H to remove the Sb based oxides from (100) surface at room temperature, while In based oxides were not affected at this temperature. However, atomic H cleaning at elevated temperatures followed by annealing resulted in a complete oxide removal with identical roughness to the starting surface, exhibiting an Indium rich 4x2 reconstruction. Though this paper reports the preparation of clean and flat InSb surfaces by H cleaning, crucial x-ray photoelectron spectroscopy (XPS) data is not furnished. In a very recent report, Tessler *et al* [4] showed the complete removal of oxide over layer from a 8x8 mm<sup>2</sup> sized InSb (100) surface using molecular hydrogen cleaning. In this paper, we present the results obtained using atomic H (H\*) treatment on CMP processed InSb (100) and (111)B surfaces, and a GCIB (gas cluster ion beam) processed InSb (111)B surface at moderate temperatures. The device important InSb (111)B surfaces are included in our experiments along with a GCIB processed (111)B surfaces so as to compare the effectiveness of H\* treatment with ion beam processing.

## EXPERIMENT

Smooth and defect free InSb substrates with average roughness ( $R_a$ ) of  $\sim 0.5$  nm were used for this work. These substrates are n-type with carrier concentrations of  $2 \times 10^{18}$  and  $7 \times 10^{14}$   $\text{cm}^{-3}$  for (100) and (111)B wafers respectively. GCIB process of InSb (111)B substrate used gas species of  $5\% \text{NF}_3/\text{O}_2$ . This GCIB process was chosen based on our experience with GCIB's ability to produce smooth, epitaxial GaSb substrates for MBE growth (processing details are found in [5]).

$\text{H}^*$  treatment was carried out in a MBE style growth chamber equipped with a reflection high energy diffraction (RHEED) system, joined under ultra high vacuum to a conventional ESCALAB system. The instrument is located at Hanscom AFRL/SNHC. All the  $\text{H}^*$  treatments were lasted for 20 minutes at a substrate temperature of  $200$  °C. The filament of the VEECO atomic hydrogen cleaning gun was maintained at high temperatures  $\sim 2300$  °C (9.8 amps), while hydrogen was being supplied through a leak valve. The background pressure during  $\text{H}^*$  treatment was maintained at  $1 \times 10^{-6}$  Torr by adjusting the hydrogen flow in to the system. These  $\text{H}^*$  treated samples were tested for RHEED reconstruction patterns and then transferred in to X-ray photoelectron spectroscopy (XPS) chamber (background pressure of  $2 \times 10^{-10}$  Torr) for analytical measurements. An Al  $K\alpha$  (1486.6 eV) source for photoelectron measurements was employed with hemispherical electron analyzer. Samples were then taken out for follow up surface morphology measurements using a Digital Instruments AFM under non-contact mode. The investigated samples size was about  $15 \times 15$   $\text{mm}^2$ .

## RESULTS AND DISCUSSION

X-ray photoelectron spectra of the as received "epitaxial" InSb (100) surfaces showed strong presence of Sb based oxides in the form of  $\text{Sb}_2\text{O}_5$  and/or  $\text{Sb}_2\text{O}_3$  at 531 eV and 540 eV along with weak In based oxides and carbon contamination. Unlike Sb oxide peaks with modest intensity, the presence of In based oxide in the form of  $\text{In}_2\text{O}_3$  broadened the In  $3d_{5/2}$  and  $3d_{3/2}$  peaks at BE's of 445.25 eV and 452.75 eV, respectively [6]. This result is supported by the fact that native Sb oxides contribute 55%, while native In oxides 27% of the elemental composition on the surface [7].

Thermal desorption of the surface oxides from (100) and (111) B surfaces used in this work suggested that by  $400$  °C (well above the congruent temperature of  $325$  °C) all of the Sb based oxides are desorbed giving rise to strong  $1 \times 1$  RHEED patterns. Though the complete desorption of In based oxides is inconclusive, narrowing FWHM of the In  $3d$  peaks as a function of temperature (up to  $450$  °C) suggests partial removal of  $\text{In}_2\text{O}_3$ . Liu *et al* presented a detailed study

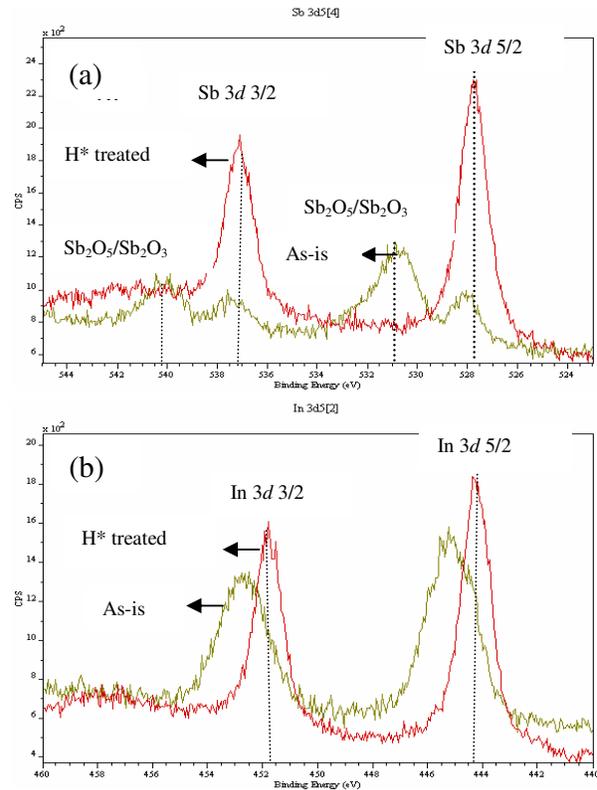


Fig. 1: XPS peaks confirming (a) the desorption of Sb based oxides (b) narrowing the In peaks suggestive of removal of  $\text{In}_2\text{O}_3$  after  $\text{H}^*$  treatment off the InSb (100) surface.

of thermal desorption properties of oxides of chemically treated InSb (100) substrates under Sb flux and used the narrowing FWHM feature of In  $3d$  peaks as an indirect measure to judge the desorption of  $\text{In}_2\text{O}_3$  [8].

The InSb (100) homoepitaxial structures grown based on these thermal desorption properties of the surface oxides showed a weak residual oxide layer at the interface which is attributed to incomplete desorption of the oxides, while InSb (111)B homoepitaxial structures lack any interface defects. This suggests that surface oxides desorption is incomplete on InSb (100) substrate while all the oxides may be fully desorbed in InSb (111)B surface. The Sb overpressure during the desorption process, which is different for these two orientations, may have a role on the desorption properties of oxides. After being treated with  $\text{H}^*$  for 20 minutes at a substrate temperature of  $200$  °C all the surface oxides from the InSb (100) substrate appear to be removed as confirmed by the XPS results shown in Fig. 1. For InSb (100) surfaces Sb  $3d_{3/2}$  and  $3d_{5/2}$  elemental peaks in the form of InSb appear at 537 eV and 527 eV, respectively, with the spin-orbit splitting of 10 eV. Sharp In  $3d_{3/2}$  and  $3d_{5/2}$  appear at 451.5 and 444 eV, respectively, with a splitting of 7 eV coherently representing elemental composition of InSb material system.

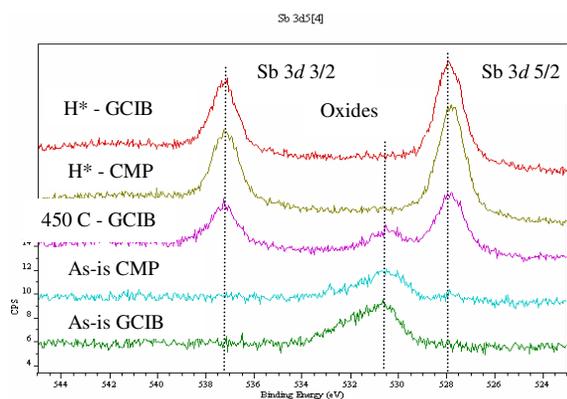


Fig. 2: Evolution of Sb 3d peaks from (111) B surfaces under different conditions. As-is surfaces showed only the presence of the oxide over-layer, while those treated with H\* showed sharp Sb 3d elemental peaks.

H\* treated (111)B and GCIB processed (111)B surfaces also showed the removal of surface oxides leaving strong elemental peaks in the form of InSb as shown in Fig. 2. Both the as-is surfaces showed strong presence of oxides with a single peak positioned at 530.5 eV due to O 1s element and broadened In 3d peaks due to In based oxides mainly in the form of In<sub>2</sub>O<sub>3</sub>. XP spectra of a GCIB processed substrate, that was heated to 450 °C for 30 minutes, showed the presence of persistent oxide peaks suggesting that higher desorption temperatures are required when using this final polishing recipe. All of our earlier work on InSb homoepitaxial growth on GCIB processed surfaces yielded much rougher epifurfaces which we now attribute to residual oxides. In those runs an oxide desorption temperature of 450 °C was used.

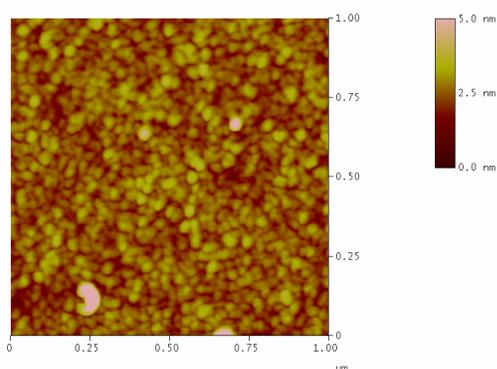


Fig. 3: AFM image of H\* treated InSb (100) surface after exposure to air.

After treating the (111) surfaces with H\* for 20 minutes, the Sb based oxides are completely removed as Sb oxide peaks disappeared. The evolution of sharp In 3d 5/2 and 3/2 peaks with narrowing FWHM at 44.5 eV and 452 eV (orbital splitting of 7.5 eV) respectively, suggest the elimination of

the surface In oxides. Over all, these results suggest that H\* processing of InSb surfaces is effective and well suited for producing InSb (111) oxide free surfaces on both CMP and GCIB polished surfaces.

AFM measurements showed that the surface roughness metrics are not affected by H\* treatment for CMP InSb (100) and (111)B surfaces. The GCIB processed InSb (111)B surface, however, became rougher after H\* processing with an Rms roughness about 1.20 nm. The Rms roughness of H\* treated CMP (100) (shown in Fig. 3) and (111)B surfaces were found to be 0.50 nm and 0.85 nm respectively with z-range values around 6-7 nm. In addition, all the H\* treated surfaces produced RHEED reconstruction patterns, while none of the CMP substrates produced any RHEED patterns before H\* treatment even when their temperatures were raised to 450 °C.

## CONCLUSIONS

In this study, the H\* treatment of InSb surfaces showed the removal of both Sb and In based surface oxides without damaging the original surfaces. Both (100) and (111)B surfaces produced similar elemental peaks after H\* cleaning. Work is underway to install a hydrogen cleaning system in the transfer module of our Riber 3200 MBE system in order to determine by XTEM that the homoepitaxy/substrate interfaces on H\* treated (100) surfaces are indeed free of oxide residues. This cleaning method may also be implemented during ohmic contact formation and may lower the contact resistances of antimonide based devices.

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#### ACRONYMS

InSb: Indium Antimonide

MBE: Molecular Beam Epitaxy

RHEED: Reflection High Energy Electron Diffraction

XPS: X-ray Photoelectron Spectroscopy