He^+ Plasma Cleaning of Epiready InSb(112)B Surfaces for Compound Semiconductor Heteroepitaxy

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Abstract

Cleaning of InSb(112)B substrate to prepare this semiconductor for heteroepitaxy by molecular beam epitaxy (MBE) is presented. The InSb(112)B surface has been prepared by 2-step process consisting of a wet etched step followed by a brief low energy exposure of He^+ plasma with an Inductevely Couple Plasma (ICP) system. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and reflection high energy electron diffraction (RHEED) analysis show that this 2-step process lead to a uniformed "epi-ready" InSb(112) surface that is nearly stoichiometric, and free of oxides and residual contamination.

INTRODUCTION

High quality molecular beam epitaxy (MBE) on compound semiconductor substrates such as InSb required the removal of oxides and residual contamination left after chemo-mechanical polishing. The preparation of a clean InSb(112)B wafer prior to epitaxy would be a major step forward in the search of lattice matched alternative substrates for epitaxy of HgCdTe for infrared detectors. The physical properties of InSb suggest a nearly ideal, alternative substrate for HgCdTe heteroepitaxy. InSb substrates are nearly matched to HgCdTe in both lattice constant and thermal expansion coefficient. Bulk InSb is now available in sizes up to 4 inches in diameter.[1,2] Although InSb substrates cost is greater than that of Si, Ge and GaAs, the cost is still far less than CdZnTe substrates.

A variety of cleaning procedures including; thermal desorption in the absence and in the presence of Sb overpressures,[3-7] atomic and molecular hydrogen treatments,[6-9] ion bombardment and annealing,[3,10-12] and wet etches[13-17] have been reported to prepare InSb (111), (100) and (110) orientations. These studies address the problems associated with invacuo thermal cleaning, since the InSb oxide desorption temperature is close to the melting point of InSb (~527 °C). In addition, the InSb oxide desorption temperature is far in excess of the congruent evaporation temperature (~325 °C) resulting in significant desorption of Sb in thermally cleaned material. Several authors show that the loss of Sb in thermally cleaned InSb can be prevented with Sb overpressures, however, this process leads to a roughened surface. In addition, annealing above 400°C after ion bombardment strongly influence the surface morphology and stoichiometry of InSb, since In droplets are formed. Similarly, chemical etches produce non-stoichiometric, rough, and non-unifom surfaces.

The cleaning of the InSb(112)B surface has only been recently reported.[18] The InSb (112)B orientation has been selected in this work because it is the ideal orientation for HgCdTe. Here, we present a new cleaning process that addresses the uniform removal of the tenacious oxide from the surface of InSb while minimizing surface damage prior to MBE. Specifically, we explore the use of a He^+ plasma generated by an inductively coupled plasma (ICP) system to clean the InSb(112)B substrates. The sample material orientation and analysis techniques were chosen both for technological reasons and to accentuate the near surface effect of the helium plasma. Insitu x-ray photoelectron spectroscopy (XPS), and reflection-high energy electron diffraction (RHEED) were used to determined the characteristics of the ICP etched InSb(112)B, including: near surface stoichiometry, chemical binding (elemental, compound, and oxide), residual contaminants, and crystallinity.

EXPERIMETAL

InSb(112)B three-inch diameter wafers were exposed to He^+ plasma. The duration of the plasma exposures were 15 seconds using He^+ in an ICP system. The ICP systems have been previously described.[19] XPS data were collected using a 16 channel detector, with a spherical capacitor analyzer at a take off angle of 25° with respect to the sample surface plane. The emission from incident 1486.6 eV monochromatic Al K_α x-rays was collected using a high resolution energy analyzer with pass energy of 2.95 eV. The binding energies reported have been shifted such that adventitious carbon yielded 284.6 eV. Base pressure was $5x10^{-10}$ torr during XPS analysis. In-situ RHEED characterization was performed with a 10 kV beam with a ~1° glancing angle of incidence.

RESULTS AND DISCUSSION

Uniform removal of the surface oxides and residual contamination of InSb wafers is required for MBE HgCdTe. As mentioned wet chemical and dry etchants have previously lead to incomplete oxide removal, as well as non-stoichiometric and roughened InSb surfaces. In this work, a plasma cleaning process that produces an epi-ready InSb(112)B surface has been developed. The He^+ plasma process described here would eliminate or minimize the Ar^+ heavy ion damage providing a more ideal "epi-ready" InSb(112)B surface for MBE. The process consists of cleaning the InSb(112)B with a wet etch (lactic acid:HNO_3:HF at 25:4:1) followed by a brief (15 second) low energy exposure of He^+ plasma in an ICP system. This 2-step process yields oxide and contaminant free, nearly stoichiometric surfaces. Low energy (slightly above sputter threshold), inert He^+ light-ion exposure reduces sputter rates[20-22] and minimizes chemical effects, (such as hydrogen plasma depletion of Sb[22-24]) and structural damage associated with H^+/Ar^+ plasmas and Ar^+ ion beam sputtering.[22-26]The He^+ plasma is particularly beneficial because of its shallow penetration depth.[27] Figure 5 shows an XPS spectra of a survey and an insert of the C 1s region of before and after plasma-etch of a three-inch InSb(112)B substrate.

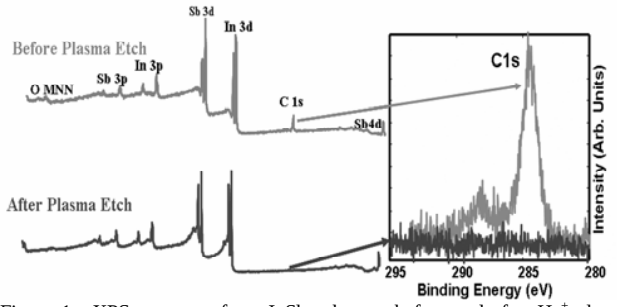

Figure 1. XPS spectrum from InSb substrate before and after He^+ plasma etch. XPS performed using a 25° shallow take-off angle. InSb is nearly stoichiometric and free of C and O contamination after the 15 second He^+ plasma etch. The C 1s region insert shows the complete removal of C contamination.

Figure 1 is a wide spectrum of before and after etched InSb surface, clearly demonstrating the absence of residual carbon and oxygen contamination after the plasma-etch. Due to the high neutralization probabilities and scattering cross sections of low energy ions, ISS enables the selective analysis of the outermost atomic layer. The elastic binary collisions of He^+ ions provide an energy spectrum that is characteristic of the distribution of the masses of the surface atoms. Figure 2 indicates a strong presence of low mass ions or contaminants on the oxidized InSb surface. However, after the InSb surface is cleaned with a wet etched followed by a brief He^+ plasma etched, the ISS signal from the low mass ions on the top layer of the InSb surface is almost vanished. This is a clear indication of a contaminant free InSb(112) b Surface.

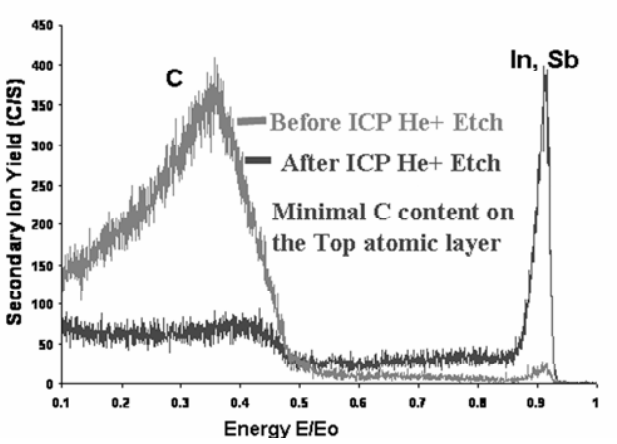

Figure 2. Backscatter geometry $3He^+$ ISS spectra from before and after the cleaning of InSb surfaces.

More details of the surface oxide removal can be observed by examining the spin-orbit doublet 3d energy level XPS spectra of Sb and In as shown in figure 3. The before plasma-etched InSb(112)B surface shows the presence of Sb_2O_5 and/or Sb_2O_3 at about 530.3 eV ($3d_{5/2}$) and 539.7 eV ($3d_{3/2}$). Unlike Sb oxides still showing a small intensity of Sb binding for InSb, the presence of In-based oxides such as In_2O_3 broadened the In $3d_{5/2}$ and $3d_{3/2}$ peaks at binding energies of 444.8 eV and 452.3 eV, (as labeled in figure 2A and 2B) respectively.

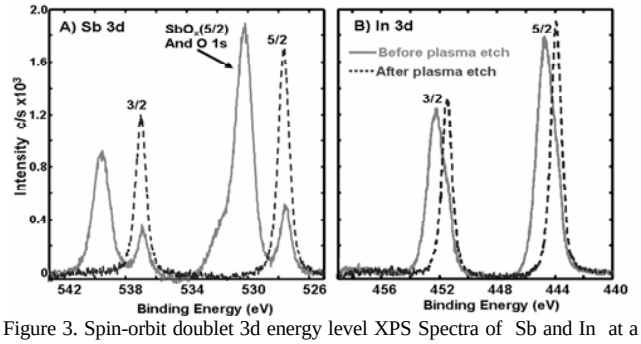

Figure 3. Spin-orbit doublet 3d energy level XPS Spectra of Sb and In at a shallow take-off angle (25°); (A) and (B), respectively. InSb is free of In and Sb oxides.

Cleaning with the 2-step procedure removes the surface oxides and contamination from the InSb(112)B substrate. For InSb surfaces Sb $3d_{5/2}$ and $3d_{3/2}$, peaks in the form of InSb appear at about 527.6 eV and 537.0 eV, respectively, with the spin-orbit splitting of 9.4 eV. The post-treatment In $3d_{5/2}$ and $3d_{3/2}$ peaks are narrower and appear at 444.0 eV and 451.5 eV, respectively, with a splitting of 7.5 eV. These binding energies represent the measured energy positions of In and Sb in a stoichiometric InSb material system. The spin-orbit separation and biding energies are in close agreement with those by W.K. Liu et.al.,[28] where they

presented detailed XPS, with binding energies, chemical shifts and Auger spectra obtained from InSb after chemical preparation and during thermal desorption. The composition of the of the plasma-cleaned InSb(112)B surface was calculated using a standard procedure where in each case a Shirley background subtraction and a 5 point smoothing was applied, then the line areas were divided by the respective sensitivity factors and normalized to total 100%. This procedure yielded a nearly stoichiometric (46at%Sb and 56at%In) plasma-etched InSb(112)B surface. From these results, it is clear that any oxide or elemental species would be evident in our high resolution data, none is observed. We take these observations as evidence of a uniform, stoichiometric surface free of oxides and residual contamination.

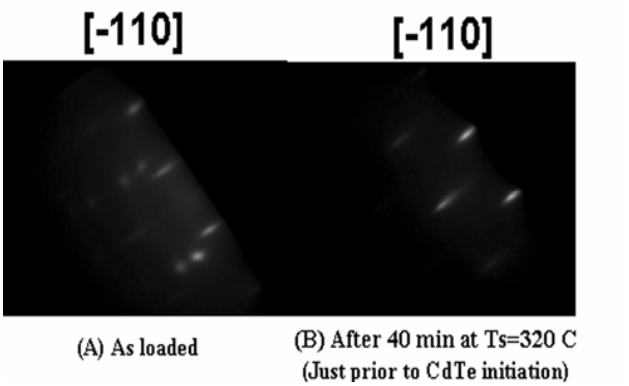

Figure 4. RHEED Patterns of an InSb(112)B substrate after the 2-step He^+ plasma etch for the as-loaded sample (A) and after 40 minutes of reaching the growth temperature (B), just prior to CdTe growth initiation.

In addition to having a stochiometric, oxide and residual contamination free surface, the InSb substrate needs to maintain its crystallinity to be suitable for MBE deposition. Due to its extreme surface sensitivity (top ~10Å probed), RHEED was used to assess the crystal damage on the 2-step He^+ plasma-cleaned InSb(112)B surface. Figure 4 shows the evolution of RHEED patterns at different stages of the preparation process prior to growth initiation. Figure 4A is the RHEED pattern obtained from the 2-step He^+ plasma etched InSb(112)B substrate. A spotty pattern is observed with undesirable surface faceting or of island-like morphology (quite probably In). However, there is indication of an undelying crystalline (streaky) diffraction pattern. These observations indicate minimal damage to the InSb surface crystallinity. In addition, XPS narrow scans of the Sb 4d splitting (data not shown) are resolvable, indicating minimal damage. This assessment is based on the fact that induced amorphization causes loss of resolution in the XPS Sb $4d_{3/2}$ and $4d_{5/2}$ orbital splitting.[21] Figure 4B is for the 2-step He^+ plasma etched InSb after 40 minutes at 320 °C (thermocouple reference MBE CdTe deposition temperature). The RHEED pattern observed in figure 4B displays a staircase step structure which is more defined and brighter than the pattern in figure 4A, suggesting a more ordered crystallographic structure; thus, providing the InSb(112)B pristine surface desired for an appropriate MBE heteroepitaxy growth.[29]

As mentioned previously, currrent technology development envisions that the next generation of infrared sensors will be based on large-format (megapixel) arrays of photovoltaic detectors with multi-spectral capabilities. Therefore, the lateral and uniform oxide removal from the InSb surface must be accomplished for it to be used as a large-area, low cost alternative substrate, as these factors influence the final quality of the HgCdTe heterostructure. This result verifies the large area InSb substrates are a viable alternative to CdZnTe substrates, which limit the affordability and ultimate array size of future sensor systems.

CONCLUSIONS

Plasma cleaned InSb(112)B wafers are free of native oxides and other contaminants with a restored undamaged surface for subsequent MBE growth. The ICP He^+ plasma clean of a wet etched InSb(112)B surface demonstrates a large-area, smooth, and mirror-like surface which is indicative of a uniform oxide and contamination removal across the wafer. Optimization of clean processes for the ICP He^+ plasma-cleaned, wet-etched InSb substrate are expected to yield high quality heteroepitaxy HgCdTe.

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ACRONYMS

InSb: Indium Antimonide
MBE: Molecular Beam Epitaxy
RHEED: Reflection High Energy Electron Diffraction
XPS: X-ray Photoelectron Spectroscopy
AES: Auger Electron Spectrosco